OMCOS18

Organometallic Chemistry Directed Towards Organic Synthesis

IUPAC International Symposium

Sitges - Barcelona **2015**

From June 28th to July 2nd

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IUPAC INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

EXCELENCIA SEVERO OCHOA

Abstract book

ORAL PRESENTATIONS

O-001

Investigating the mechanism of ru(ii)-catalysed direct arylation with dft

Dr Claire L. McMullin[1], Mr Kevin J. T. Carr[1], Prof. Stuart A. Macgregor[1]
[1]*Heriot-Watt University, Edinburgh, UK*

Monday Morning, junio 29, 2015, 11:20 - 12:35

C-C bond formation via cross-coupling based on initial C-H activation is termed “direct” aryl- or alkylation and Ru(II) catalysts have been shown to be particularly effective in mediating such transformations.[sup]1,2[/sup] An example is the coupling of 2-phenylpyridine with phenyl iodide to give the direct arylation product shown in Scheme 1a.

Despite these synthetic advances, kinetic and mechanistic data are sparse on these catalytic systems, leading to speculation as to the precise order of the reaction steps. For example, is the C-H activation followed or preceded by oxidative addition of the aryl halide[sup]3,4[/sup] and what is the nature of the oxidative addition step? We have used DFT calculations to study these processes, using a model catalyst, $[(C_6H_6)Ru(OAc)_2]$, for the reaction of 2-phenylpyridine with phenyl iodide in o-xylene.

Our results suggest that C-H activation occurs prior to C-I activation. Moreover, the low polarity of the o-xylene solvent indicated that incorporating ion-pairs into the model was essential to produce viable energetics for the key bond activation steps. The presence of acetate in the outer coordination sphere also led us to propose a novel acetate-assisted process for C-I bond activation (Scheme 1b).

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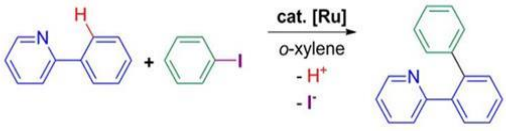
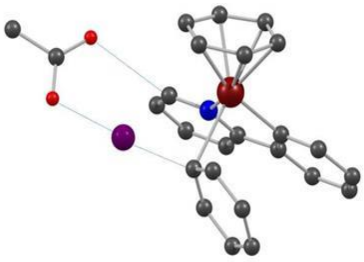


Scheme 1; a) direct arylation reaction of 2-phenylpyridine and PhI with a Ru(II) catalyst



b) Acetate assisted C-I bond cleavage transition state

O-002

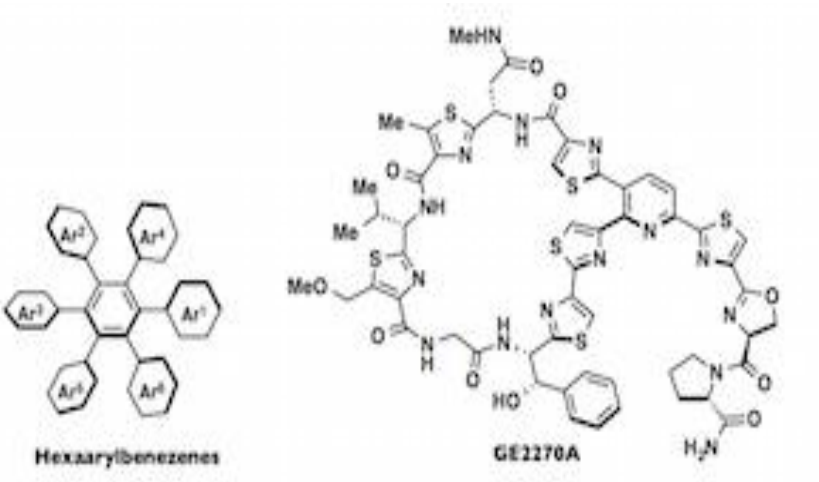
A C–H Coupling/Ring Transformation Approach: Synthesis of Polyarylated Arenes and Natural Products

Prof. Dr. Junichiro Yamaguchi[1]
[1]*Nagoya University, Japan*

Monday Morning, junio 29, 2015, 11:20 - 12:35

Polyarylated arenes are privileged structures with many interesting functions and fascinating optoelectronic or biological properties, and therefore, the construction of these scaffolds has been a topic of great importance in chemistry. Recently, the C–H arylation method of arenes has garnered much attention from the synthetic chemistry community as a next-generation coupling method to construct such motifs. The development of C–H arylation of five-membered heteroarenes with controlled regioselectivity has been well established. However, the C–H arylation of six-membered aromatics such as benzenes and pyridines has considerable room for further investigations in terms of overcoming challenges in reactivity and regioselectivity. To address these issues and to synthesize polyarylated arenes, the regioselective C–H arylation of five-membered heteroarenes, followed by a ring transformation approach, has been developed.

To this end, the synthesis and characterization of hexaarylbenzenes with five or six different aryl groups was achieved by first a C–H arylation of thiophenes, followed by thiophene oxidation, then a [4+2] cycloaddition of the resulting tetraarylthiophene S-oxide. Furthermore, a formal synthesis of GE2270A, a thiopeptide antibiotic, has been accomplished by using this approach



O-003

Gold-, Platinum- and Silver-Catalyzed Activation of Alkynes – A Journey in Molecular Diversity

Dr. Veronique Michelet[1], Dr. Alexandre Pradal[1], Dr. Chung-Meng Chao[1], Prof. Serafino Gladiali[4], Dr. Patrick Toullec[1], Prof. Jean-Pierre Genet[1], Dr. Gaelle Mariaule[2], Gregory Newsome[1], Prof. Philippe Belmont[2], Dr. Emanuela Pietropaolo[3], Prof. Antonio Arcadi[3]

[1]PSL Research University, Chimie ParisTech-CNRS, Institut de Recherche de Chimie Paris, Paris, France [2]Université Paris Descartes, Faculté de Pharmacie de Paris, Paris, France [3]Dipartimento di Scienze Fisiche e Chimiche, Università di L'Aquila, L'Aquila, Italy, [4]Dipartimento di Chimica e Farmacia, Universita di Sassari , Sassari, Italy

Monday Morning, junio 29, 2015, 11:20 - 12:35

Over the past few years, significant research has been directed toward the development of new methodologies for synthetic efficiency and atom economy processes. Among them, the potential of transition-metal catalyzed cycloisomerization and domino processes reactions have been steadily demonstrated (Pd, Ru, Rh, Ir, Cu and more recently Au, Pt and Ag), as they give a direct and selective way toward the synthesis of highly valuable products.[1] We have been engaged in a wide project dedicated to the development of catalytic methodologies for the synthesis of original and functionalized carbo- and heterocycles. Our interest has been focused on the cyclization and/or functionalization of alkynes including enynes,[2] aniline-[3] and formyl-[4] functionalized alkynes. This presentation will show an overview of the latest results implying achiral and chiral platinum, gold and silver complexes.

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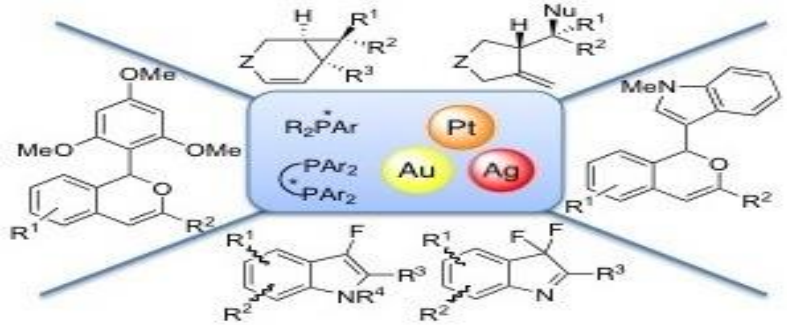

O-004

Titanium-Catalyzed Reductive Umpolung Reactions and their Application in Organic Synthesis

Dr Jan Streuff[1]
[1]*Albert-Ludwigs-Universität Freiburg, Freiburg, Germany*

Monday Morning, junio 29, 2015, 11:20 - 12:35

Reductive umpolung reactions such as the pinacol coupling give access to 1,2-, 1,4-, or 1,6-difunctionalized compounds that are difficult to access otherwise.[1] It is our goal to expand this concept towards cross-coupling reactions by means of titanium(III) catalysis using titanocene dichloride precursors and a stoichio-metric reductant. Using this approach, we successfully established intra- and intermolecular couplings between ketones or imines and nitriles, giving rise to various α-hydroxyketones, α-aminoketones or pyrrolidinones (Scheme 1).[2] In presence of a chiral ansa-titanocene, even an enantioselective ketone-nitrile radical coupling was achieved.[2c] We further transferred this concept towards reductive cross-couplings between activated olefins such as enones and acrylo-nitriles that afforded 1,6-difunctionalized building blocks.[3] The reactions were scalable, simple to carry out and did not require chromatographic purification in many cases. To demonstrate the power of our reductive umpolung reactions, we developed a straight-forward access to functionalized bridged benzazocines and -oxocines as well as a high-yielding erythrina alkaloid synthesis with such umpolung reactions as key steps.[4]

O-005

Sustainable Gold Catalysis: Synthesis of New Spiroacetals

Prof. Norbert Krause[1]
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Monday Morning, junio 29, 2015, 11:20 - 12:35

Spiroacetals appear in a wide range of natural products and biologically active molecules. Consequently, there is a high demand for efficient methods to synthesize these privileged scaffolds. Among these, transition metal-catalyzed cyclizations of suitable unsatured substrates are gaining importance. In particular, several examples for the gold-catalyzed spiroacetalization of acetylenic diols and related substrates have been disclosed recently.[1] Here, we describe the application of recyclable gold catalysts to spiroacetalizations in water as bulk reaction medium. For example, treatment of acetylenic diols with ammonium-salt-tagged NHC-gold complexes of the type A affords saturated [O,O]-spiroacetals of the type 1,[2] whereas the use of gold catalysts in nanomicelles (B) provides unsaturated spiroacetals 2 from acetylenic triols by dehydrative spirocyclization.[3] Recently, we have extended the spirocyclization to new types of [O,O]- and [N,O]-spiroacetals (e.g., 3-5), which are of interest as new molecular scaffolds in medicinal chemistry.[4]

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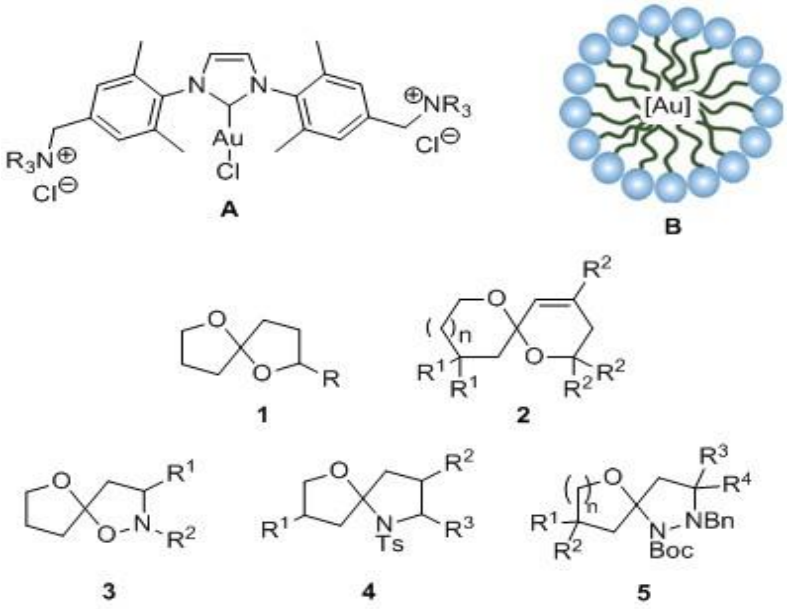

O-006

Borenium cations: versatile reagents for the formation of aryl and vinyl boronate esters

Dr. Michael Ingleson[1]
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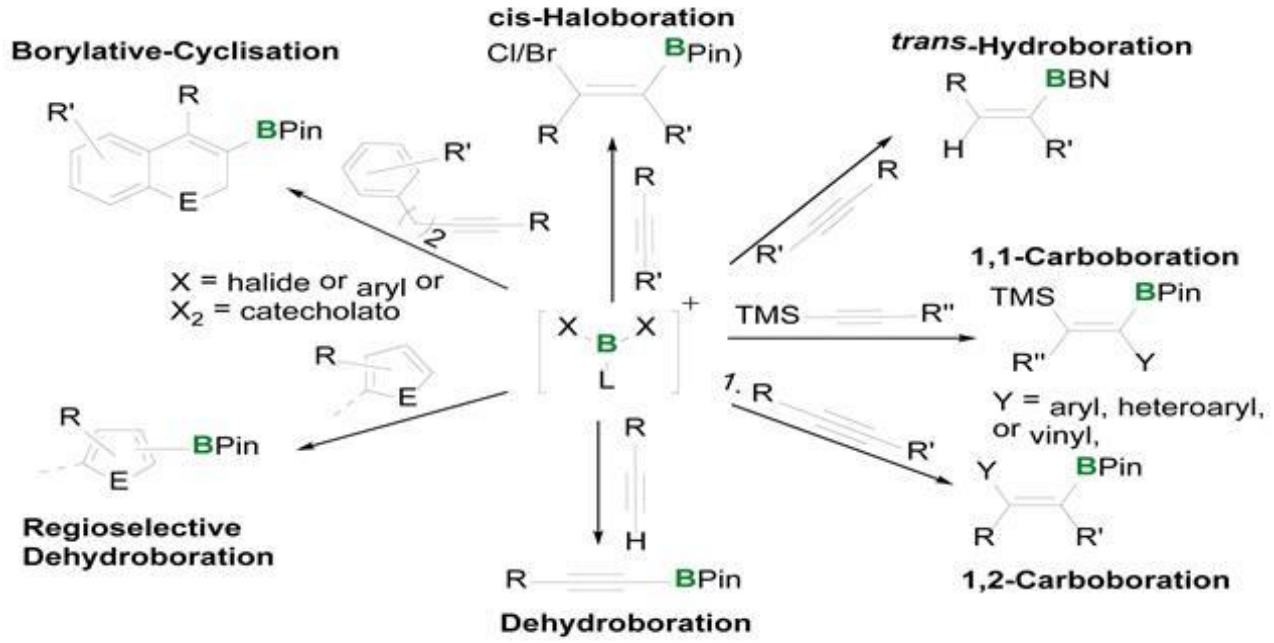
Monday Afternoon, junio 29, 2015, 16:00 - 17:00

After decades of principally 'academic' interest there has been a recent surge in the use of borenium cations (three coordinate borocations) in synthesis and catalysis. In the past five years borenium cations have been developed that are effective for hydrogenation, aliphatic C-H activation, direct arene borylation, hydroboration and hydrosilylation. We will present our recent work studying the reactivity of a range of borenium cations towards pi nucleophiles. Rational modification of borenium cation structure has proved key to expanding their synthetic versatility. This will be emphasised using specific examples including direct C-H borylation, the carboboration and haloboration of alkynes, the trans-hydroboration of alkynes and borylative cyclisations. These new synthetic methodologies represent simple routes to highly versatile aryl and vinyl boronate esters that are ubiquitous intermediates in chemical synthesis.



O-007

Ligand and mechanistic studies on the iridium-catalyzed, substrate-directed C–H borylation of benzylic amines

Associate Prof. Timothy Clark[1], Kathryn A. McGarry[1], Lillian V. A. Hale[1], Marissa A Ringgold[1], Clay M. Oliver[1]
[1]*University of San Diego, San Diego, USA*

Monday Afternoon, junio 29, 2015, 16:00 - 17:00

C–H borylation reactions have become a selective and reliable method to access aryl boronate esters from simple starting materials with the selectivity controlled by steric congestion, avoiding borylation adjacent to substituents in most cases. Recently, a number of examples of substrate-directed C–H borylation have been reported that overcome the steric sensitivity of the catalyst and directs the activation to the adjacent C–H bond. Our research group has focused on the use of hemilabile diamine ligands that can partially dissociate from the iridium trisboryl complex to provide two open coordination spheres for a benzylic amine to coordinate to the catalyst and undergo C–H activation. The focus of this presentation will be on studies regarding the role of each nitrogen of the diamine ligand in the catalytic cycle, resulting in an optimized ligand, N-benzylaminopyridine, for catalyst efficiency and selectivity to obtain monoborylation in the ortho position of benzylic amines. Early mechanistic studies will also be presented, including kinetic isotope effect studies, synthesis of stable pre-catalysts, and observations of catalytic intermediates.

O-008

Development of a Complementary Metalation Strategy to Directed ortho-Metalation

Dr. Charles O'Hara[1]
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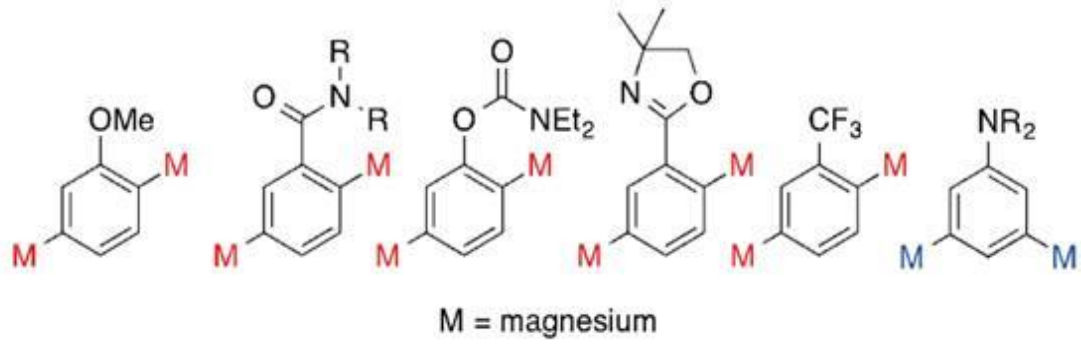
Monday Afternoon, junio 29, 2015, 16:00 - 17:00

To date the seminal metalation strategy employed in synthesis has been Directed ortho-Metalation (DoM). The first example of DoM was reported as long ago as 1938/9,1,2 and this discovery propelled organometallic compounds from being 'exotic rarities' to 'indispensible tools in modern synthesis'.3 While there have been a number of reports of metalation at more remote sites, in general these reactions operate in the same way as "DoM", namely that the position of metalation is controlled by the substituent attached to the aromatic ring. In our new template approach, it is primarily the positions of the metal centers within the template ring that control the positional metalation reactions. In this presentation, our recent results using sodium magnesiate chemistry to perform metalations will be discussed, culminating in Directed ortho-metaʹ- and meta-metaʹ-Dimetalations.4 Other examples of the versatility of the template base approach to metalation will also be revealed. (1) H. Gilman, R. L. Bebb, J. Am. Chem. Soc. 61, 109-112 (1939). (2) G. Wittig, U. Pockels, H. Droge, Ber. Deutsch. Chem. Gesel. 71, 1903-1912 (1938). (3)M. Schlosser, Organometallics in Synthesis Third Manual. M. Schlosser, Ed., (JohnWiley & Sons, Inc., Hoboken, New Jersey, 2013). (4) A. J. Martinez-Martinez, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, Science, 346, 834-837 (2014).



O-009

Reactivity and Structure-Building Principles of LiCKOR Base Mixtures in THF

Prof. Carsten Strohmann[1], Ulrike Kroesen[1], Stephan G. Koller[1], Kathrin Louven[1]
[1]*TU Dortmund, Dortmund, Germany*

Monday Afternoon, junio 29, 2015, 16:00 - 17:00

The LiCKOR superbase or “Schlosser’s base” constitutes an important component in the tool kit of organometallic chemists.[1] It is comprised of a mix of an alkyllithium reagent, usually n-butyllithium (“LiC”), and a bulky alkoxide of a heavier alkaline metal, typically potassium tert-butoxide (“KOR”). Their metalating power exceeds that of their single components by far. This synthetically well exploited synergic increase in reactivity has recently attracted our interest as the successful structural elucidation of species arising from LiCKOR mixtures, especially in the commonly used polar solvent THF, remains a challenge.[2] Herein, we present the structures of the species formed from reaction mixtures containing LiCKOR components and substrates which undergo metalation by this base mix even at –78 °C in THF. Furthermore, the synthetic value of a Schlosser’s base-mediated metalation under mild conditions was demonstrated using dimethylphenethylamine.[3] This pharmaceutically attractive synthetic building block can be selectively metalated in the benzylic position by LiCKOR mixtures at low temperatures. Thus, decomposition of the ß-metalated intermediate via elimination is efficiently avoided and its conversion with electrophiles can be achieved.

References:
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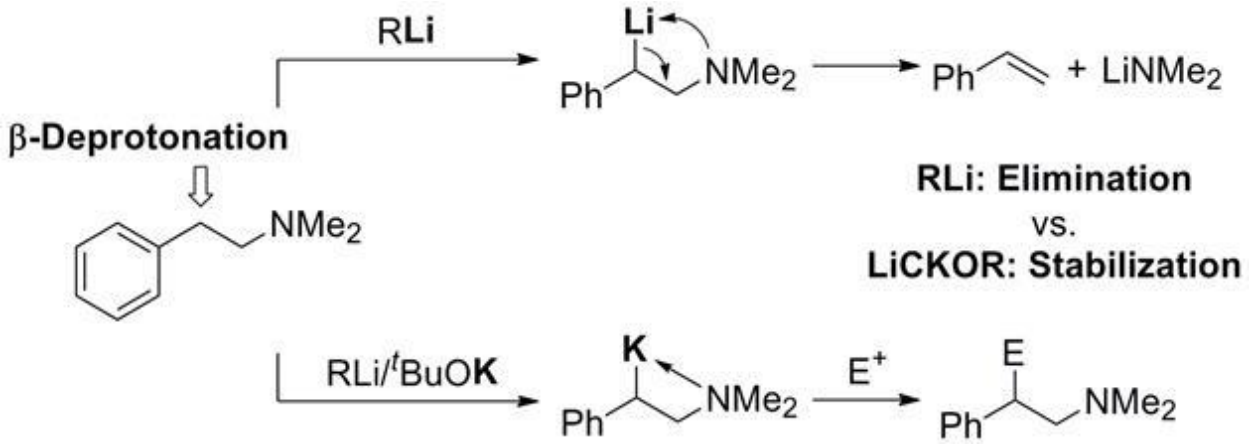
[3] a) C. Unkelbach; H. S. Rosenbaum; C. Strohmann, Chem. Commun. 2012, 48, 10612–10614; b) C. Unkelbach, D. F. O'Shea, C. Strohmann, Angew. Chem. Int. Ed. 2014, 53, 553–556.



O-010

Catalytic Chemoselective Conjugate Addition of

Alcohol over Amine

Dr. Takashi Ohshima[1], Mr. Shuhei Uesugi[1], Mr. Zhao Li[1], Mr. Masamichi Tamura[1], Dr. Ryo Yazaki[1]
[1]*Kyushu University, Fukuoka, Japan*

Tuesday Morning, junio 30, 2015, 11:20 - 12:35

Catalyst-controlled chemoselective reaction offers new opportunities for minimal reliance on protecting groups even in the presence of innately more reactive functionalities. Despite the prospects for contribution to both atom and step economy, progress of this area especially reversing innate reactivity of amino and hydroxyl group has been limited. Recently a few examples of catalyst-controlled chemoselective reaction of hydroxyl group in the presence of amino group were reported including our chemoselective acylation.[1] However, the patterns of reaction were highly limited and inevitable formation of the stoichiometric amount of chemical waste reduced the reaction efficiency. Herein, we report a cooperative catalyst-controlled chemoselective conjugate addition of hydroxyl group (oxa-Michael reaction) in the presence of innately more nucleophilic amino group.[2] Combined use of soft Lewis acidic copper(I) with hard Brønsted base allowed for chemoselective activation of alcohol and subsequent conjugate addition to soft Lewis basic electrophile. Conjugate addition of hydroxyl group is under proton-transfer conditions without generation of any waste and well applicable to the natural product synthesis. To the best of our knowledge, there is no example of catalyst-controlled chemoselective conjugate addition of hydroxyl group over amino group.
Recently, we also suceeded in expansion of substrate generality of electrophiles by using optimized reaction conditions, where very unique β-aminoalcohol selective reactions were achieved.

References:
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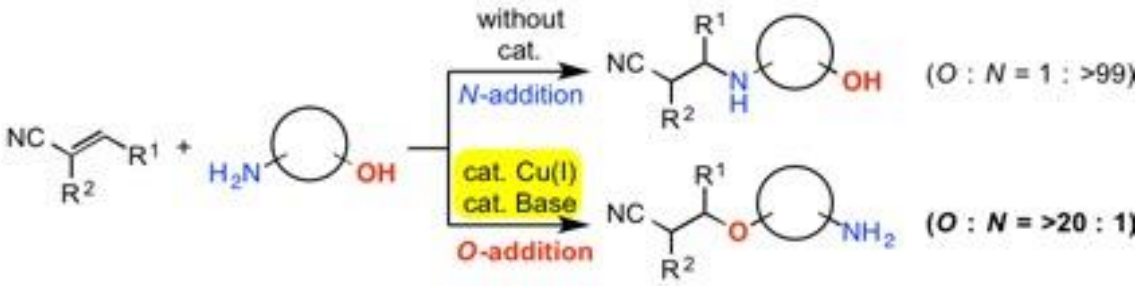

O-011

Cooperative Effects in Catalysis of cycloisomerization reactions with 2-Indendiide Pincer Complexes

Dr. Noelangel Espinosa[1], Mr. Diandian Ke[1], Mr. Paul Brunel[1], Dr. Julien Monot[1], Prof . Blanca Martin Vaca[1], Dr. Didier Bourissou[1]

[1]*Toulouse University - CNRS, Toulouse, France*

Tuesday Morning, junio 30, 2015, 11:20 - 12:35

Pincer complexes have attracted an upsurge of interest in the last few years as a result of their particular balance between stability and reactivity. Those promoting original catalytic transformations involving metal / ligand cooperativity can be particularly highlighted.[1] In this context, our group has reported a novel family of pincer ligands, based on indene skeletons.[2] The non-innocent character, conferred by the electron-rich π-delocalized backbone, was first evidenced by the involvement of the ligand back-bone in the reaction with organic and metallic electrophiles,[3] and then applied in metal/ligand cooperative catalysis. The cycloisomerization of alkynoic acids and alkynylamides takes place in the presence of palladium and platinum indenediide complexes without involvement of an external base.[4] An important breakthrough has been achieved for the formation of 5-, 6- and even 7-membered ring lactones and lactams including the first efficient preparation of alpha-methylene caprolactone/lactame.[4]
The tune of the catalysts structure and the scope of the reactions will be presented. In addition, a particular attention will be paid to the mechanistic experimental and theoretical investigations that strongly supports metal/ligand cooperation. Finally, the spectacular improvement of the activity achieved thanks to the association with an H-bonding agent will be disclosed.

References:

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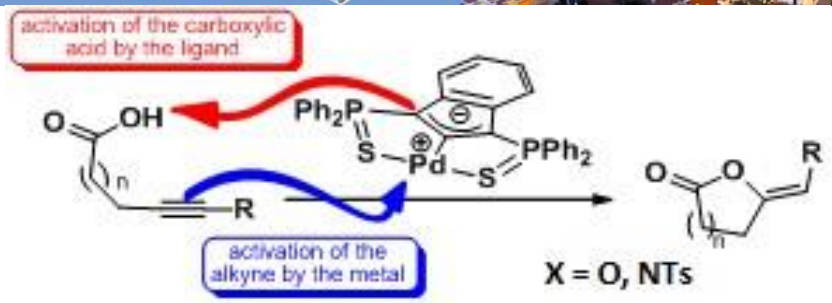

- ✓ High thermal robustness
- ✓ Broad substrate scope
- ✓ 5-7 membered lactones and lactames

O-012

Reactivity of a nickel(II) bis-amide complex with HmCPBA: formation of a formally nickel(IV) oxidizing species

Dr. Anna Company[1], Ms. Teresa Corona[1], Mr. Florian Pfaff[2], Mr. Ferran Acuña-Parñes[1], Dr. Apparao Draksharapu[3], Dr. Julio Lloret-Fillol[1], Dr. Wesley R. Browne[3], Dr. Kallol Ray[2]

[1]Universitat de Girona, Girona, Spain [2]Technische Universität Berlin, Berlin, Germany, [3]University of Groningen, Groningen, The Netherlands

Tuesday Morning, junio 30, 2015, 11:20 - 12:35

The study of high-valent nickel complexes, in particular, and the redox chemistry of nickel, in general, has attracted the attention of the bioinorganic chemistry community to provide models of nickel-containing enzymes that catalyze redox processes [1]. In synthetic systems, high-valent nickel species have been frequently postulated as key reaction intermediates both in the catalytic cycle of oxidation reactions and in coupling reactions [2].

Focusing in oxidation reactions, there are very few nickel-oxygen species that have been trapped and spectroscopically characterized. These species are specially interesting because they are presumably the active species responsible to elicit the oxidation event. Most proposals agree that these nickel(III)-oxygen and nickel(IV)-oxygen adducts are formed after homolytic or heterolytic O-O bond cleavage upon coordination of the nickel(II) precursor with the oxidant (HmCPBA, peracetic acid, H_2O_2, ...).

Herein, we report the formation of a highly reactive nickel(IV)-oxygen/nickel(III)-oxyl species (2) that has been spectroscopically trapped by reaction of a nickel(II) precursor (1) with HmCPBA (see Scheme). Compound 2 is only detectable at low temperatures and it is much more reactive towards organic substrates (C-H bonds, C-C double bonds and sulfides) than the previously reported well-defined Ni-oxygen species. Remarkably, this species is formed by heterolytic O-O bond cleavage as supported by experimental and computational methods.

References:

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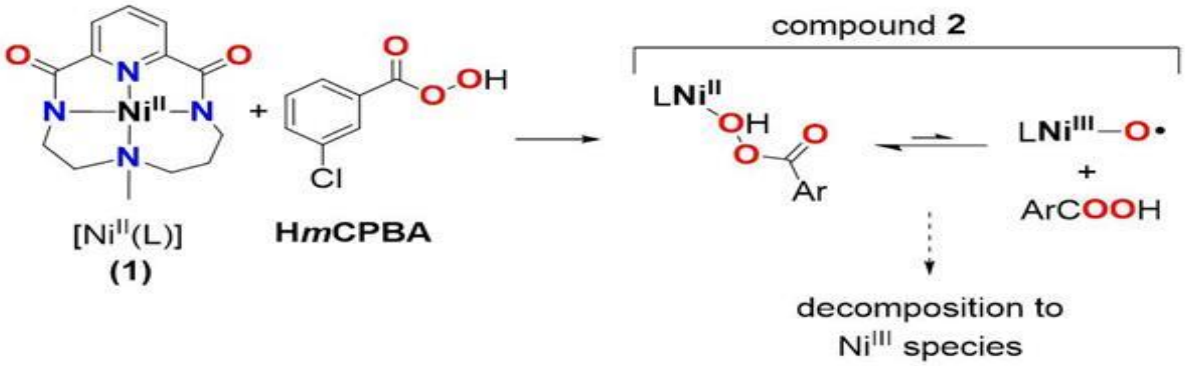
[Ni^{II}(L)]
(1)
HmCPBA
compound 2
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+
ArCOOH
Ar
decomposition to
Ni^{III} species

O-013

Enantioselective Construction of 3-Hydroxypiperidine Skeletons by Sequential Actions of Light and Rhodium upon N-Allylglyoxylamides

Dr. Naoki Ishida[1], Dr. David Nečas[1], Mr. Yusuke Masuda[1], Dr. Masahiro Murakami[1]
[1]*Kyoto University, Kyoto, Japan*

Tuesday Morning, junio 30, 2015, 11:20 - 12:35

A piperidine skeleton is a structural motif prevalent among biologically active compounds. Although a wide variety of methods developed for construction of piperidine skeletons, it is still desired to develop catalytic asymmetric methods starting from readily available substances. Herein, we report enantioselective construction of 3-hydroxypiperidine skeletons from N-allylglyoxylamides by sequential actions of light and rhodium. Initially, an acetonitrile solution of N-allylglyoxylamide 1 was irradiated with a LED lamp (365 nm) for 10 h. The Norrish-Yang type photocyclization[1] took place to furnish β-lactam 2 as a diastereomer mixture (80% yield, cis:trans = 77:23). Next, the diastereomeric mixture of 2 was treated with a chiral rhodium catalyst prepared in situ from $[Rh(OH)(cod)]_2$ (5 mol %) and (R)-(S)-JOSIPHOS (12 mol %) in dioxane at 100 °C. Enantioselective restructuring of the β-lactam skeleton took place to afford 3,4-dihydropyridone 3 in 69% isolated yield with 98% ee. In a formal sense, the whole process is an enantioselective addition reaction of allylic C–H bond across the ketonic carbonyl group with migration of the double bond (carbonyl-ene type reaction), forming the six-membered ring with a chiral quaternary carbon center in an atom-economical way.

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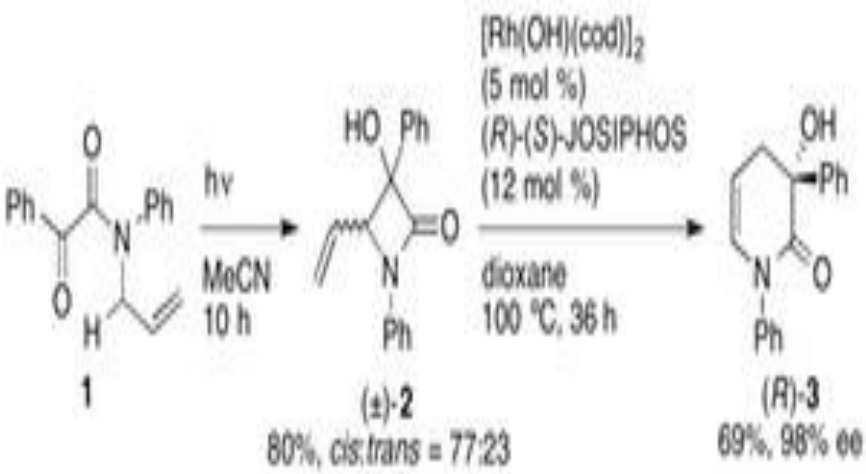

O-014

C-C and C-H Functionalizations of Carboxylic Acids

Prof. Dr. Lukas Gooßen[1]
[1]*TU Kaiserslautern, Kaiserslautern, Germany*

Tuesday Morning, junio 30, 2015, 11:20 - 12:35

Decarboxylative coupling reactions in which C–C bonds to carboxylate groups are cleaved with formation of new C–C bonds, have evolved into a powerful synthetic strategy.[1] Their key benefit is that they draw on easily available carboxylic acids rather than organometallic reagents as sources of carbon nucleophiles. They have been utilized e.g. in syntheses of biaryls, vinyl arenes, aryl ketones and azomethines. C-Heteroatom bonds can be formed via decarboxylative Chan-Evans-Lam reactions.[2] In recent variations of this reaction type,[3] the carboxylate groups are first utilized as directing groups for ortho-C–H functionalizations and then either cleaved tracelessly or used as leaving groups in subsequent ipso-substitution reactions. In such transformations, the arene substitution pattern of the benzoate substrates is altered in a defined way, so that they ideally complement the preceding protocols.
Besides decarboxylative couplings, other sustainable C–C and C–heteratom bond-forming concepts will be discussed including isomerizing olefin metatheses.[4]

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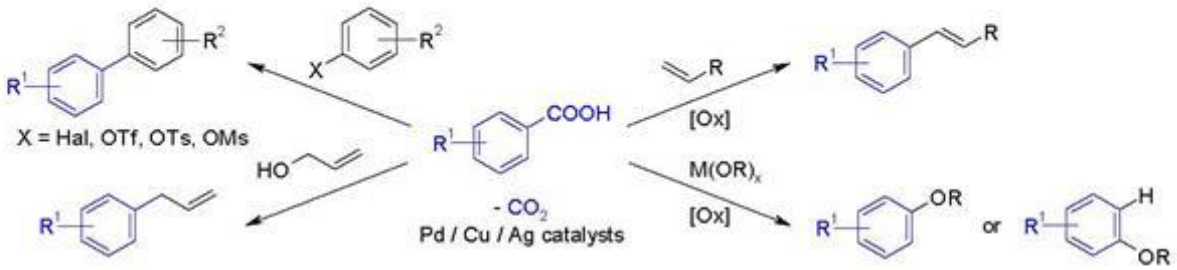
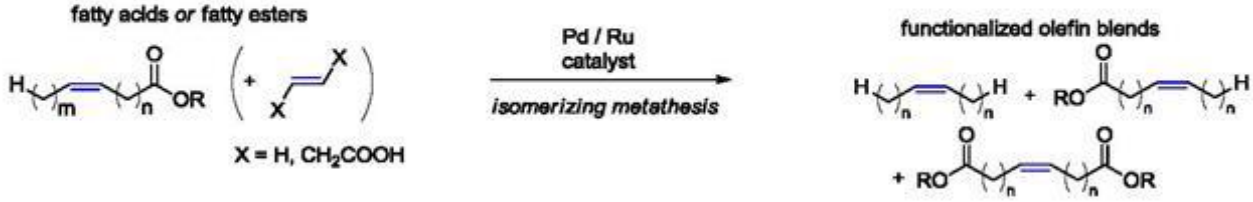
[1] a) Gooßen, L. J., Deng, G., Levy, L. M., Science 2006, 313, 662. b) Rodríguez, N., Gooßen, L. J., Chem. Soc. Rev. 2011, 40, 5030. c) Fromm, A., van Wüllen, C., Hackenberger, D., Gooßen, L. J., J. Am. Chem. Soc. 2014, 136, 10007. [2] Bhadra, S., Dzik, W. I., Gooßen, L. J., J. Am. Chem. Soc. 2012, 134, 9938. [3] Bhadra, S., Dzik, W. I., Gooßen, L. J., Angew. Chem. Int. Ed. 2013, 52, 2959. [4] Ohlmann, D. M., Tschauder, N., Stockis, J.-P., Gooßen, K., Dierker, M., Gooßen, L. J., J. Am. Chem. Soc. 2012, 134, 13716. b) S. Baader, P. E. Podsiadly, D. J. Cole-Hamilton, L. J. Gooßen, Green Chem. 2014, 16, 4885

Decarboxylative Couplings



Isomerising Metatheses



O-015

Nickel(0)-Catalyzed Transformation Reactions via Aza-Nickelacycle Intermediates

Prof. Sensuke Ogoshi[1]
[1]*Osaka University, Suita, Yamadaoka2-1, Japan*

Wednesday Morning, julio 1, 2015, 11:20 - 12:35

Oxidative cyclization with low-valent transition metals has received considerable attention because the reaction enables the construction of a C–C bond between a variety of unsaturated compounds, and, indeed, the resultant five-membered metallacycles are assumed to be a key reaction intermediate in transition-metal-catalyzed cycloaddition as well as multicomponent coupling reactions.
This presentation focuses on the preparation of a five-membered aza-nickelacycle generated via the oxidative cyclization of an imine and an alkyne with nickel(0). Such aza-nickelacycles are much rarer than the related oxa-nickelacycles because imines are generally weaker electrophiles than aldehydes. Therefore, it is logical to assume that electron-withdrawing substituents are required for oxidative cyclization by promoting a back donation from nickel(0) to imines; the generation of a five-membered aza-nickelacycle is efficiently promoted by a chelate coordination of a donor atom on the N-substituent group to a vacant coordination site on the nickel center. In 2007, we reported the first isolation of a corresponding aza-nickelacycle via the oxidative cyclization of N-sulfonylimine and an alkyne.[1] Herein, two different types of nickel-catalyzed transformation reactions will be discussed: (a) [2+2+2] cycloaddition reaction leading to 1,2-dihydropyridines;[2] (b) [2+2+1] carbonylative cycloaddition to give γ-lactams.[3] These nitrogen-containing products are ubiquitous structural motifs for natural products in small molecules that have biomedical relevance and are among the most versatile synthetic intermediates for use in the synthesis of a wide range of other valuable molecules.

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2. Hoshimoto, Y.; Ohata, T.; Ohashi, M.; Ogoshi, S., Chem. Eur. J., 2014, 20, 4105-4110.
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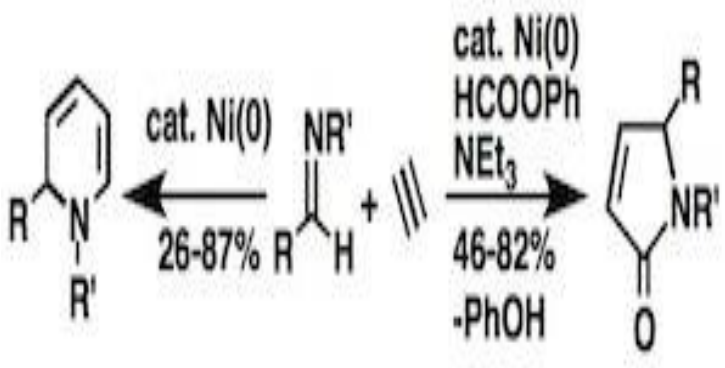

O-016

Catalytic C–H Bond Functionalizations: Advantages of Benzenesulfonyl Chlorides as Arylating Agents

Dr Jean-Francois Soule[1], M. Kedong Yuan[1], Dr. Henri Doucet[1]
[1]*Institut des Sciences Chimiques de Rennes, Université de Rennes, Rennes, France*

Wednesday Morning, julio 1, 2015, 11:20 - 12:35

The development of new chemical transformations –based on metal-catalyzed functionalizations of C–H bonds– has the potential to develop novel efficient synthesis of complex molecules.[1] Among the diverse cross-coupling partners, aryl bromides remain as one of the most useful arylating agents. We plan to show the advantages of benzenesulfonyl chlorides as suitable alternative to aryl halides in direct arylations of several electron rich heteroarenes.[2] Such desulfitative arylations were performed using a simple catalytic system based on phosphine-free palladium catalyst. Among the several advantages of such desulfitative arylations, we can highlight:

i)High regioselectivity: thiophenes were arylated at unexpected β-position,[3] while furans and pyrroles were arylated at α-positions in high yields.[4]

ii)High chemoselectivity: the reaction tolerates substrates bearing C-halogen (X = F, Cl, Br, I) bonds without their cleavages.

iii)Allow iterative C–H bonds arylations: as example, we will present an efficient two steps synthesis of heterocycles with a bridgehead nitrogen such as pyrrolo[1,2-a]azepine and Ullazine derivatives.[5]

iv)Desulfitative conjugate additions of benzenesulfonyl chlorides to enones will be also presented,[6] as well applications in synthesis of tetrahydroquinolines.[5]

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[5] Unpublished Results

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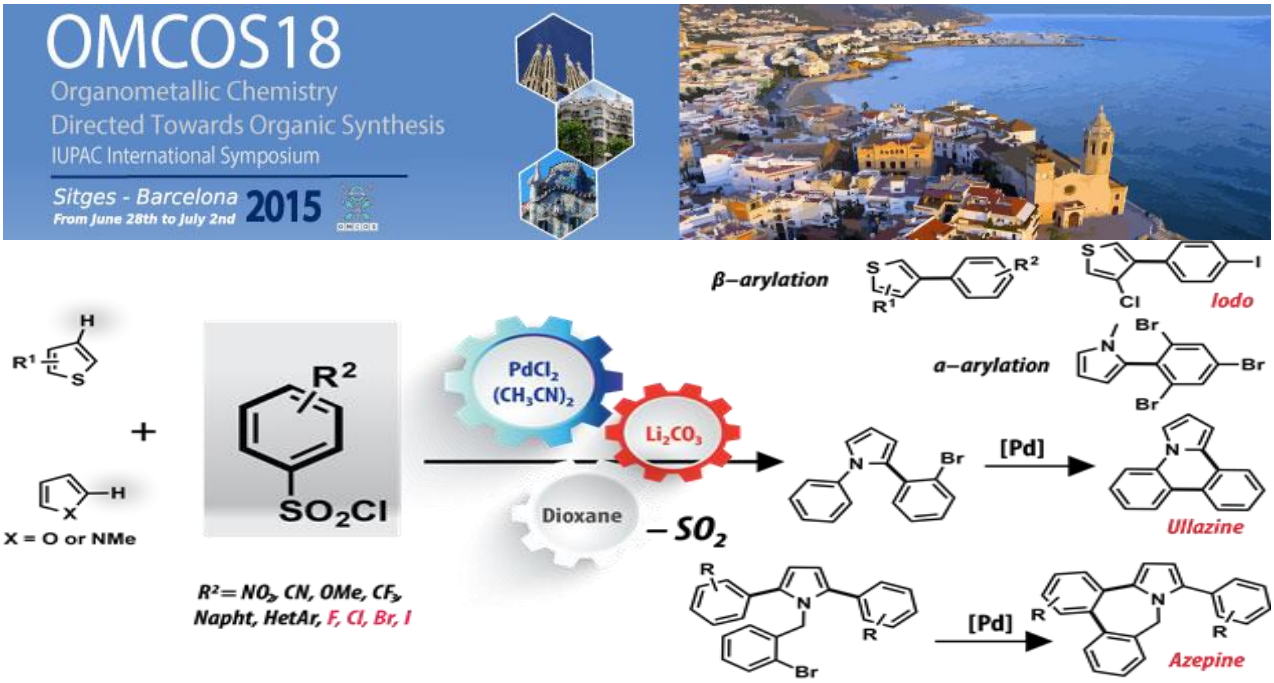
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β–arylation
Iodo
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X = O or NMe
R²= NO₂, CN, OMe, CF₃,
Napht, HetAr, F, Cl, Br, I
PdCl₂(CH₃CN)₂
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[Pd]
Ullazine
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Azepine

O-017

Rhodium-catalyzed Regioselective alpha-Acylalkylation of Aromatic C–H Bonds with Cyclic Alkenyl Carbonates

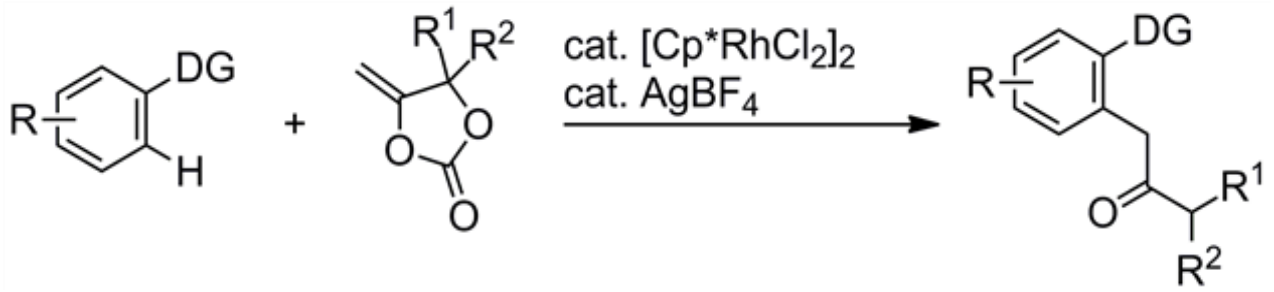
Prof. Fumitoshi Kakiuchi[1]

[1]*Keio University, Department of Chemistry, Faculty of Science and Technology, Yokohama, Japan*

Wednesday Morning, julio 1, 2015, 11:20 - 12:35

Catalytic C–C bond formations via C–H bond cleavages have widely been studied. We have developed a variety of strategies concerning catalytic conversion of C-H bonds to C-C bonds. We recently found a new entry of C-H alkylation that a reaction of arylpyridines, aromatic amides, and related compounds with cyclic alkenyl carbonates using a cationic rhodium catalyst took place via C–H bond cleavage to give ortho α-acylalkylation products.

When a reaction of 2-phenylpyridine with 4-methylene-1,3-dioxaspiro[4.4]nonan- 2-one was carried out using 5 mol % $[Cp^*RhCl_2]_2$ and 20 mol % $AgBF_4$ as catalysts at 80 °C for 48 h, C-C bond formation took place at an ortho position to give 1-cyclo- pentyl-2-(2-(pyridin-2-yl)phenyl)ethanone in 57% yield. Various arylpyridines and related compounds can be used for this C–H α-acylalkylation. Instead of sp^2 nitrogen as a directing group, an amide carbonyl oxygen is applicable as a coordinating functionality. The reaction of benzpyrrolidides with the cyclic alkenylcarbonates was performed under similar reaction conditions employed for the reaction of arylpyridines, the corresponding ortho α-acylalkylation products were obtained in good to high yields. Functional group compatibility of this C–C bond formation reaction is wide. Various electron-donating and -withdrawing groups are tolerated.



O-018

Recent advances in the regioselective palladium-catalyzed functionalization of imidazoles

Prof. Fabio Bellina[1], Dr Marco Lessi[1], Dr Laura Lodone[1], Dr Chiara Manzini[1], Dr Giulia Marianetti[2], Dr Alessandro Panattoni[1], Dr Luca Alessandro Perego[1,2], Dr Cristofer Pezzetta[1,2]

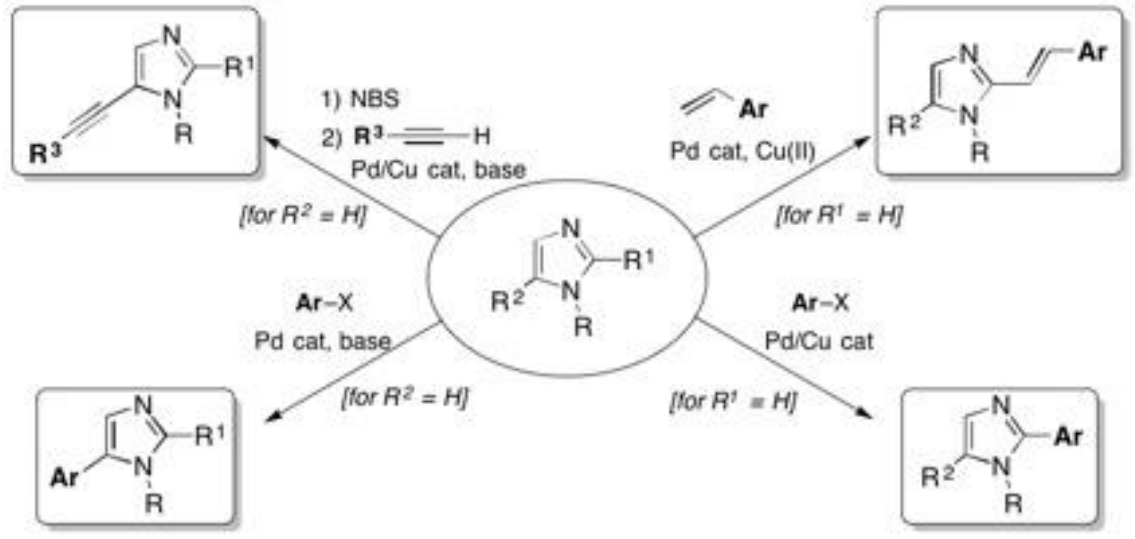
[1]Dipartimento Di Chimica E Chimica Ind.le Universita' Di Pisa, Pisa, Italy, [2]Scuola Normale Superiore, Pisa, Italy

Wednesday Morning, julio 1, 2015, 11:20 - 12:35

Imidazole scaffolds are frequently found in natural bioactive products, market drugs, agrochemicals, and organic functional materials such as liquid crystals and fluorescent dyes. Thus, considerable attention has been turned to the synthesis and selective functionalization of imidazoles in the past.

Over the last years, we were interested in studies aimed at broadening the scope of regioselective functionalizations of the imidazole core by palladium-catalyzed carbon-carbon bond forming reactions. In particular, we devoted our efforts to the development of efficient and robust procedures for the regioselective direct C5-H and C2-H arylation of N-substituted and NH-free imidazoles with (hetero)aryl halides. More recently, we prepared a variety of 2-substituted 5-alkynylimidazoles by an unprecedented one-pot C5-bromination followed by a Sonogashira coupling. Furthermore, 5-alkenylimidazoles were obtained by a new cross-dehydrogenative alkenylation involving 2-substituted imidazoles and styrenes.

In this communication we will report the results of these studies, along with the application of these protocols to the preparation of bioactive products and synthetic dyes.



O-019

Ruthenium-catalyzed synthesis of biologically relevant heterocycles through carbon-heteroatom bond formation

Dr Martín Fañanás Mastral[1], Rodrigo Bernárdez[1], Damián Padín Santos[1], Dr Jaime Suárez[1], Borja Pérez Saavedra[1], Prof Jesús Varela[1], Prof Carlos Saá[1]

[1]*CIQUS. University of Santiago De Compostela, Santiago De Compostela, Spain*

Wednesday Morning, julio 1, 2015, 11:20 - 12:35

The synthesis of chiral heterocycles through carbon–heteroatom bond formation is at the heart of organic chemistry. The ability to build, through chemical synthesis, a wide range of heterocyclic structures is critical for natural product chemistry and biological studies, as well as for future developments in medical science. The discovery of novel catalytic carbon–heteroatom bond forming processes for the construction of chiral hetrocycles continues to be an especially challenging goal.

In this contribution different ruthenium-catalyzed synthesis of several chiral heterocycles are presented. Here we report the synthesis of epoxypyrrolidines and dihydropyrans through catalytic formation of vinyl ruthenium carbene intermediates which are easily formed from [Cp*RuCl(cod)] and TMSCHN2.[1] The synthetic utility of these protocols is illustrated with the synthesis of the anticancer agent Tubulexin B.[2] Furthermore we present a dual ruthenium hydride / Brønsted acid catalyzed dihydro-1,3-benzoxazines preparation.

References:

[1] a) F. Cambeiro, S. López, J. A. Varela, C. Saá, Angew. Chem. Int. Ed. 2012, 51, 723. b) F. Cambeiro, S. López, J. A. Varela, C. Saá, Angew. Chem. Int. Ed. 2014, 53, 5959.

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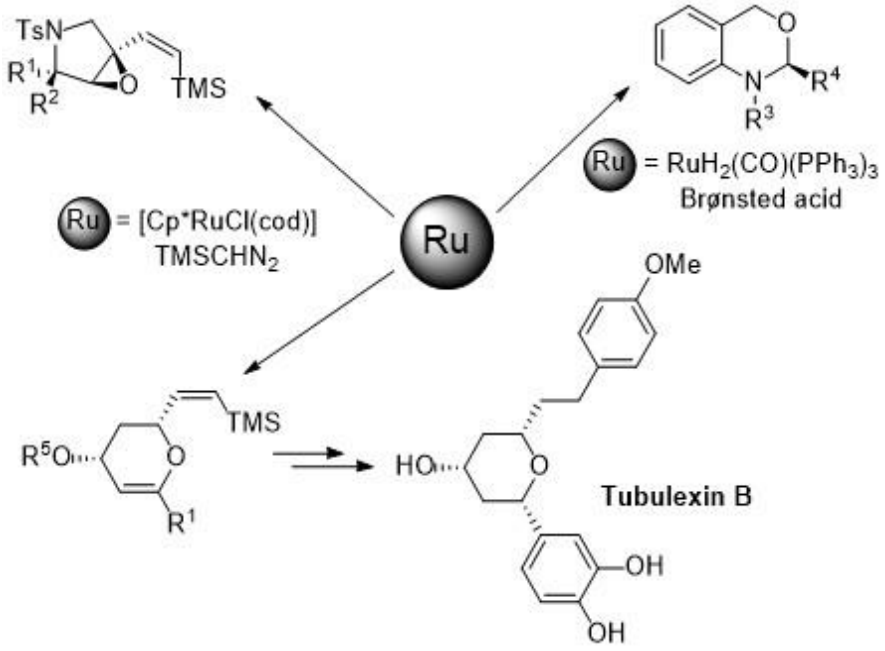
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Ru = RuH2(CO)(PPh3)3
Brønsted acid
Ru = [Cp*RuCl(cod)]
TMSCHN2
Ru
OMe
TMS
R5O
O
R1
HO
O
Tubulexin B
OH
OH

O-020

p-Block Organometallic Catalysis: Considering Phosphorus as a 'Metal'

Assistant Prof. Alexander Radosevich[1]
[1]*Pennsylvania State University, University Park, USA*

Wednesday Afternoon, julio 1, 2015, 16:00 - 17:00

Tricoordinate P(III) compounds play an important but largely peripheral role as supporting ancillary ligands in conventional organotransition metal catalysis. By way of complement, we have demonstrated a new and essentially organometallic role for phosphorus in catalysis, wherein the phosphorus center itself is the locus of bond making and breaking events. Under this circumstance, phosphorus experiences two-electron cycling of formal oxidation state in analogy to well-known catalytic reactivity of the transition metals. The guiding notion is that by enforcing nontrigonal geometries on tricoordinate P(III) compounds, the structural and electronic conditions necessary to facilitate catalytic cycling in the P(III)⇌P(V) redox couple are accessible. This approach has resulted in the development of diverse catalytic atom transfer and bond activation methods based on inexpensive, nonmetal phosphorus catalysts. First, we will describe C–O, C–N, and C–C bond forming synthetic methods gated by O-atom transfer to and from trivalent phosphorus. Mechanistic aspects of these reactions and their connection to other P-catalyzed methods will be discussed. In a second thrust, we will describe efforts to design tricoordinate phosphorus compounds suitable for activation of enthalpically strong bonds (i.e. N–H, O–H) by oxidative addition to phosphorus. A rationale based on an electronic structure argument will be presented, and specific attention will be devoted to a discussion of potential future synthetic directions.

O-021

Iron-Catalyzed Directed C-H Bond Activation

Dr. Laurean Ilies[1], Prof. Eiichi Nakamura[1]
[1]*The University of Tokyo, Tokyo, Japan*

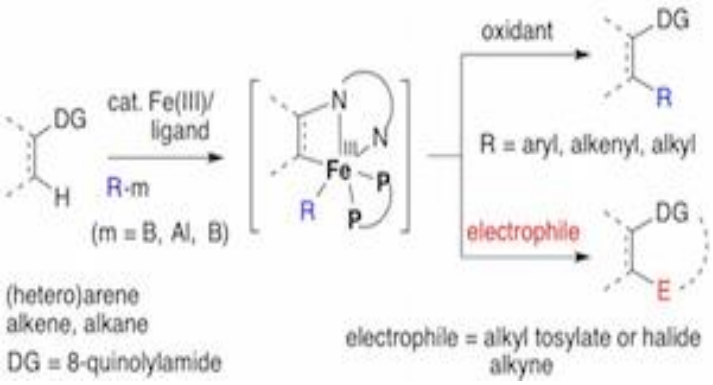
Wednesday Afternoon, julio 1, 2015, 16:00 - 17:00

Iron-catalyzed C-H bond activation is of interest because iron is abundant, inexpensive, and non-toxic, and direct functionalization of simple substrates streamlines the synthetic strategy. However, the reactivity of catalytic organoiron species is difficult to control, hampering the development of efficient and selective reactions.

This presentation will describe our journey to the development of an organoiron(III) catalyst for C-H bond activation that shows versatility comparable with and even surpassing precious metal catalysis. Thus, we found that the C-H bond of a (hetero)arene-, alkene, or alkane amide bearing an 8-aminoquinolyl group can be activated by an iron(III) catalyst, a diphosphine ligand, and an organometallic base to generate a ferracycle(III) intermediate, which can then undergo reductive elimination in the presence of an oxidant, or can be reacted with an electrophile.

Several reactions using this catalyst manifold will be presented: 1) Oxidative reaction of carboxamides with organoboronates, where the same iron catalyst can be used for stereospecific synthesis of dienes and trienes, and arylation, alkenylation, and alkylation of (hetero)arene-, alkene-, and alkaneamides (1); 2) Oxidative methylation of various carboxamides, naphthylamines, and benzylamines with trimethylaluminium at catalyst loading as low as 0.01 mol% (TON up to 6500); 3) Alkylation of alkene- and (hetero)arene-amides with primary and secondary alkyl tosylates or halides (2); 4) Reaction of alkene- and (hetero)arene-amides with alkynes to give pyridones or isoquinolones, indenones, or alkenylated amides selectively, depending on the fine tuning of the reaction conditions.

References:
(1) Shang R.; Ilies, L.; Asako, S.; Nakamura, E.; J. Am. Chem. Soc. 2014, 136, 14349.
(2) Ilies, L.; Matsubara, T.; Ichikawa, S.; Asako, S.; Nakamura, E.; J. Am. Chem. Soc. 2014, 136, 13126.



O-022

A new mode of long-range metal ligand cooperation in novel iron PCP-pincer complexes – synthesis and reactivity

Dr Alexander Dauth[1], Prof David Milstein[1]
[1]*The Weizmann Institute of Science, Rehovot, Israel*

Wednesday Afternoon, julio 1, 2015, 16:00 - 17:00

Activation of small molecules and subsequent transfer to organic substrates e.g. in the form of hydrogenation or de-hydrogenation are fundamental transformations in organometallic chemistry and catalysis research. In recent years, transition metal complexes which employ metal-ligand cooperation have emerged as a versatile and powerful alternative to classic bond activation system.[1,2]

Herein, we report the development of unprecedented iron PCP-pincer complexes which exhibit remarkable long-range metal ligand cooperation. The resulting complexes could be utilized in the activation of small molecules like H_2, O_2 and S_8 and are active in the dehydrogenation of alcohols as well as the semi-hydrogenation of alkynes.

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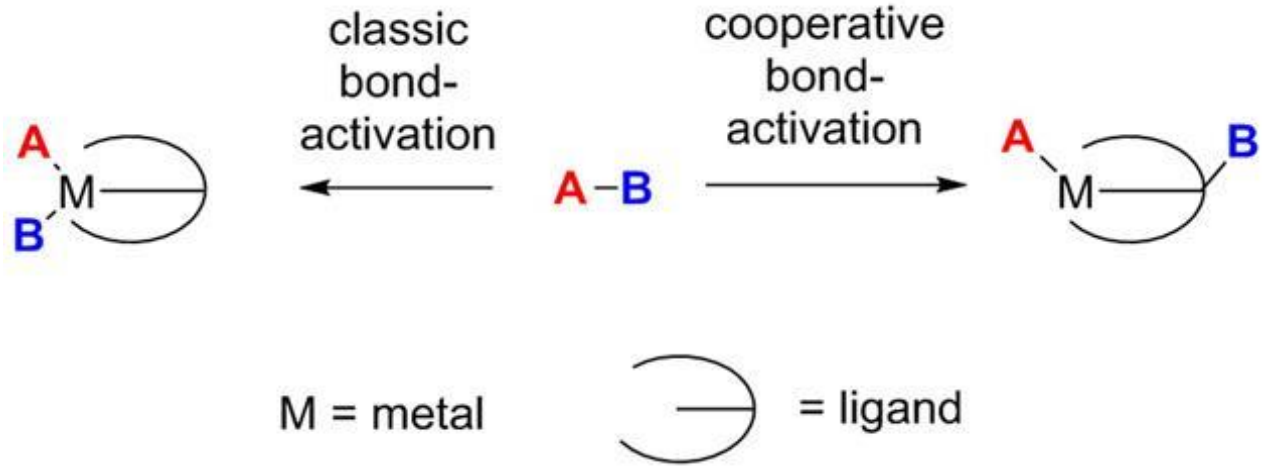


O-023

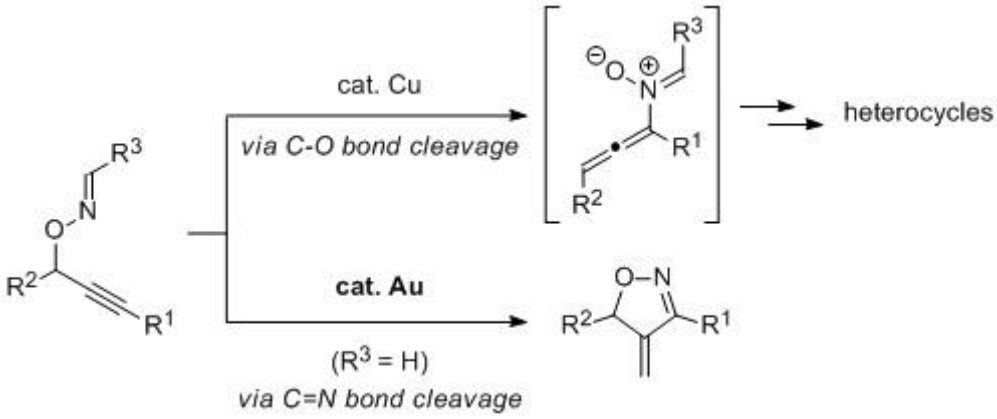
Gold and copper-catalyzed skeletal rearrangement of O-propargylic oximes

Prof. Itaru Nakamura[1], Shinya Gima[1], Yu Kudo[1], Prof. Masahiro Terada[1]
[1]*Tohoku University, Sendai, Japan*

Wednesday Afternoon, julio 1, 2015, 16:00 - 17:00

We have recently demonstrated that O-propargylic oximes serve as an intriguing substrate in π-acidic metal-catalyzed skeletal rearrangement reactions, leading to multisubstituted heterocyclic compounds. The reaction mainly proceeds via 2,3-rearrangement involving C-O bond cleavage, which is promoted by copper catalyst. Herein, we report that gold catalysts promote skeletal rearrangement of O-propargylic oximes in a totally different manner; the reaction proceeds through cyclization-intermolecular methylene group transfer via C=N bond cleavage, producing 4-methylenated 2-isoxazolines in good to excellent yields [1]. In addition, we demonstrated that the reaction pathway of cascade reaction between O-propargylic oxime and electron-deficient olefin can be perfectly controlled by the choice of metal catalyst.

References:
[1] I. Nakamura, S. Gima, Y. Kudo, M. Terada, Angew. Chem. Int. Ed. accepted DOI: 10.1002/anie.201501856R2



O-024

Transition Metal Catalyzed Functionalization of

Prof. Zuowei Xie[1]
[1]*Department of Chemistry, The Chinese University of Hong Kong, Shatin NT*

Thursday Morning, julio 2, 2015, 11:20 - 12:35

Carboranes are a class of polyhedral boron hydride clusters in which one or more of the BH vertices are replaced by CH units. They constitute a class of structurally unique molecules with exceptionally thermal and chemical stabilities and the ability to hold various substituents. These properties have made them useful basic units in supramolecular design, medicine, catalysts and materials. However, their unique structures make derivatization difficult, resulting in a limited application scope. Thus, it is important and necessary to develop new methodologies for the functionalization of carboranes. Inspired by transition metal catalyzed C-C/C-B bond forming reactions via benzene C-H activation and our earlier work on transition metal mediated multicomponent cross-cycloaddition for the preparation of benzocarboranes,[1] we have developed transition metal catalyzed regioselective cage B functionalization of o-carboranes. These results will be discussed in this presentation.[2,3]

References:
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2. Y. Quan, Z. Xie, J. Am. Chem. Soc. 2014, 136, 15513.
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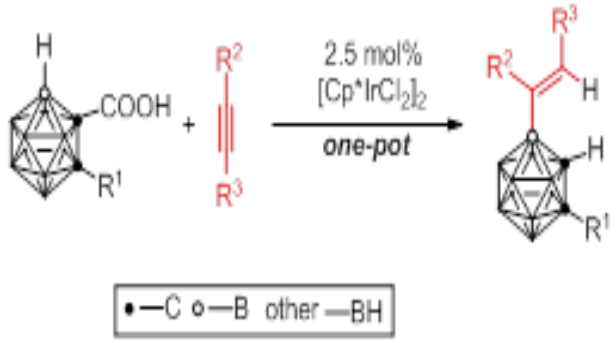


O-025

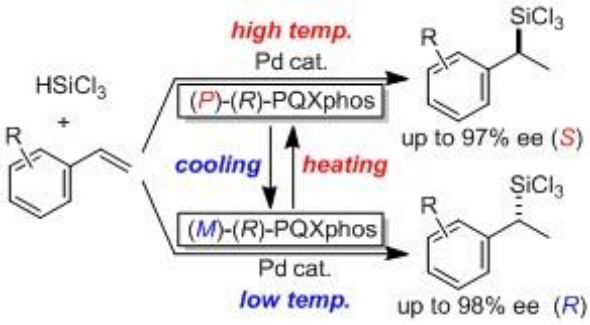
Temperature-Dependent Switching of Enantioselection in Palladium-Catalyzed Asymmetric Reactions

Dr Takeshi Yamamoto[1], Mr Yuto Akai[1], Prof. Michinori Suginome[1]
[1]*Kyoto University, Kyoto, Japan*

Thursday Morning, julio 2, 2015, 11:20 - 12:35

We have recently developed poly(quinoxaline-2,3-diyl)-based helically chiral phosphine ligands PQXphos, which have chiral side chains and achiral phosphine pendants. Since the enantioselectivity of PQXphos relies on the helical chirality induced by chiral side chains, solvent–dependent inversion of the helical chirality of PQXphos has enabled us to obtain highly enantioenriched both enantiomeric products from a single chiral catalyst. Herein, we report temperature-dependent switching of enantioselection in palladium-catalyzed asymmetric reactions using PQXphos.

(R)-PQXphos bearing (R)-2-octyloxymethyl chiral side chains adopted a pure (M)-helical structure at 0 °C in THF/1,1,2-trichloroethane (5/2). On heating the solution to 30 °C, the (M)-helical structure was completely inverted to a (P)-helical structure. In palladium-catalyzed asymmetric hydrosilylation of styrenes, (M)-(R)-PQXphos/Pd prepared at 0 °C in THF/1,1,2-trichloroethane (5/2) afforded (R)-products with up to 98% ee at 0 °C. Under the same reaction conditions expect for the temperature, (P)-(R)-PQXphos/Pd afforded (S)-products with up to 97% ee at 30 °C. The generality of temperature-dependent switching of enantioselection was also demonstrated in asymmetric Suzuki-Miyaura cross-coupling.



O-026

SYNPHOS and DIFLUORPHOS in Asymmetric Catalysis : Synthetic Applications

Dr Virginie VIDAL[1], Dr Zi WU[1], Dr Damien CARTIGNY[1], Dr Farouk BERHAL[1], Dr Olivier JACKOWSKI[1], Pr Zhaoguo ZHANG[2], Dr Tahar AYAD[1], Pr Jean Pierre GENET[1]

[1]CNRS - ChimieParisTech, Paris, France, [2]School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China

Thursday Morning, julio 2, 2015, 11:20 - 12:35

Over the past few years, significant research has been directed toward the development of new methods for synthetic efficiency and atom economical processes. Among them, the potential of transition-metal catalyzed reactions has been steadily demonstrated. We have been engaged in a project dedicated to the development of catalytic methods for the synthesis of biorelevant targets using C-H [1] and C-C bond forming processes, which provide important catalytic approaches to fine chemicals. There is no doubt that chiral ligands are at the heart of any enantioselective homogeneous process. Catalytic applications of SYNPHOS [2] and DIFLUORPHOS [3] are presented. [4]

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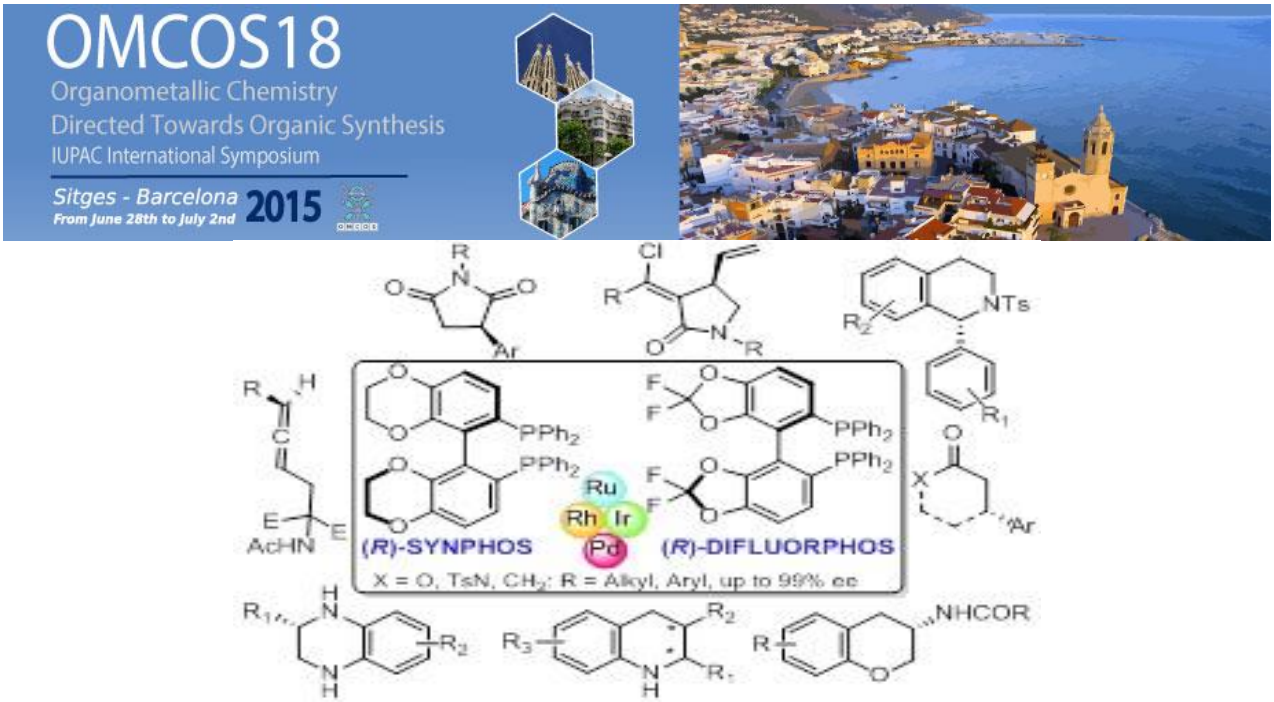
OMCOS18
Organometallic Chemistry
Directed Towards Organic Synthesis
IUPAC International Symposium
Sitges - Barcelona
From June 28th to July 2nd 2015
(R)-SYNPHOS
(R)-DIFLUORPHOS
X = O, TsN, CH2; R = Alkyl, Aryl, up to 99% ee
Ru
Rh
Ir
Pd
AcHN
NHCOR

O-027

Nickel-catalyzed asymmetric hydrogenation reactions using formic acid

Prof. Jianrong (Steve) Zhou
[1]*Nanyang Technological University*

Thursday Morning, julio 2, 2015, 11:20 - 12:35

Asymmetric hydrogenation is being practiced in pharmaceutical industry to prepared chiral drugs on large scales. Often metal catalysts based on expensive, toxic noble metals such as Rh, Ir and Ru are used. Recently, we found that nickel complexes supported by electron-rich bisphosphines such as Binapine and Duphos can promote transfer hydrogenation of prochiral enamides, olefins, imines and ketones in high enantioselectivity. The use of formic acid as a hydrogen surrogate avoided pressure reactors for hydrogenation and associated safety hazard. Our mechanistic studies revealed that hydride insertion into a,b-unsaturated esters formed nickel enolates which were then protonated in the reaction media.

O-028

Iron-Catalyzed C–H Amination of Aniline Derivatives

Dr Masaharu Nakamura[1,2], Mr Yuma Aoki[1,2], Mr Ryuji Imayoshi[1,2], Dr Takuji Hatakeyama[1,2,3], Dr Hikaru Takaya[1,2,4]

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Thursday Morning, julio 2, 2015, 11:20 - 12:35

Aromatic amines are widely used for functional organic compounds such as organic electronic materials, agrochemicals and pharmaceuticals.[1] Transition-metal-catalyzed C–H amination reaction is one of the most efficient and attractive approaches for the synthesis of aromatic amines due to no need for pre-functionalization of the aromatic core.[2] We have developed novel iron-catalyzed inter- and intramolecular ortho-C–H aminations of aniline derivatives.[3] These reactions proceed smoothly by the use of in situ-generated magnesium amides and 1,2-dibromoethane as an oxidant in the presence of catalytic amounts of an iron salt. The intramolecular ring closing C–H amination of o-phenylenediamines, prepared by the intermolecular amination, gives a variety of 5,10-diaryl-5,10-dihydrophenazines,[4] which are potential hole injection materials.[5]

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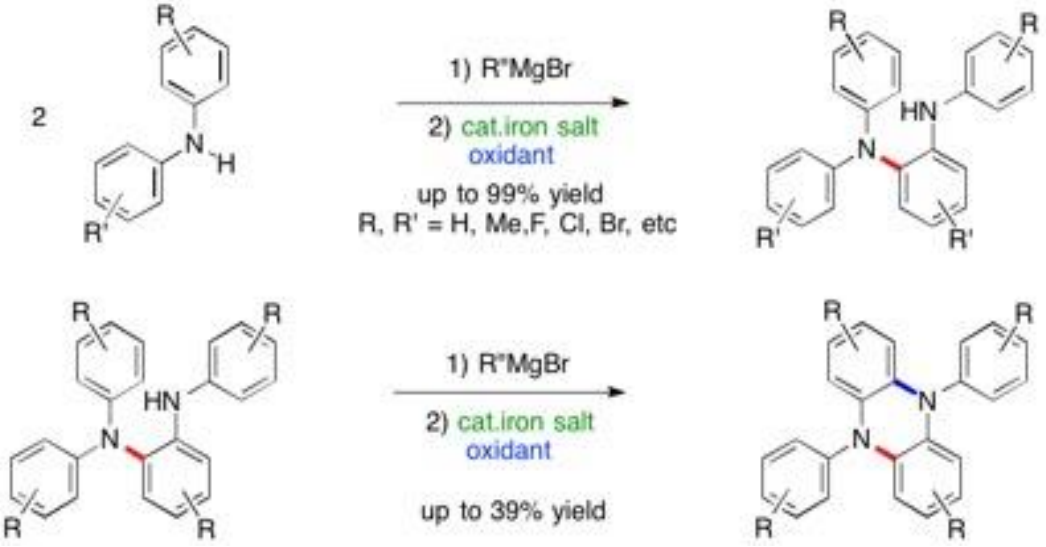
Scheme 1. Iron-catalyzed inter- and intramolecular C–H aminations of aniline derivatives



POSTER PRESENTATIONS

P-001

Palladium-Mediated Cascades: a Powerful Tool to Access Complex Polycycles

Dr. Gaelle Blond[1], Dr, Jean Suffert[1], Dr. Catherine Hulot[1], Dr. Mélanie Charpenay[1], Dr. Julien Petrignet[1]
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Poster Session 1

The elaboration of complex molecules from simple starting material in the minimum of operations is a challenging goal in modern organic synthesis. Towards this end, the use of transition metal-catalyzed processes has become a powerful tool for the construction of functionalized molecules. In particular, cyclocarbopalladation has emerged as a potentially general and versatile synthetic method for the one-pot preparation of complex polycyclic systems. Palladium-catalyzed cascades are especially noteworthy in terms of atom economy, stereocontrol and overall efficiency.
In this context, we develop new methodologies for the formation of carbon-carbon bond leading to unique types of polycyclic compounds. Recent results will be presented for the synthesis of fenestranes 1, cyclooctatrienes 2 and taxol analogs 3.

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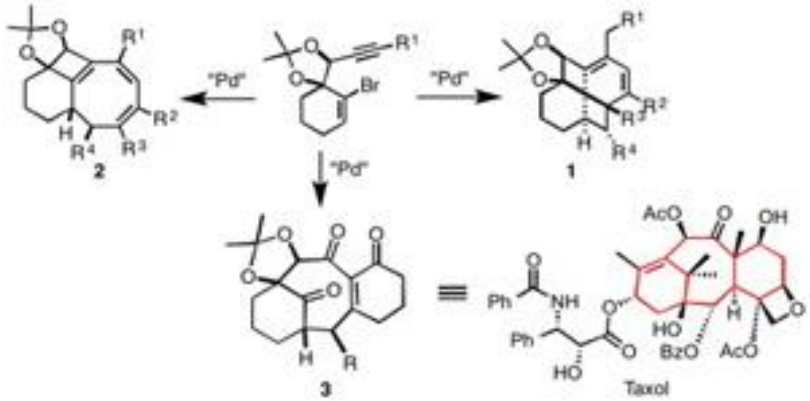

P-002

Development of new catalytic systems for asymmetric hydrogenation of exotic substrates

Dr. Oscar Pamies[1], Prof. Montserrat Diéguez[1]
[1]*Universitat Rovira i Virgili, Tarragona, Spain*

Poster Session 1

The asymmetric hydrogenation of olefins is one of the most sustainable and reliable catalytic methods for preparing chiral compounds.[1] Most of the research has been focussed in the reduction of olefins containing an adjacent polar group, which takes advantage of the substrate chelation to achieve high levels of enantiocontrol, whereas the hydrogenation of minimally functionalized olefins is less developed. For this latter class of substrates, the early success of phosphine-oxazoline ligands has focussed the research in the development of new P,N-ligands.[1] Our group has demonstrated that the introduction of phosphite groups into the ligand is advantageous.[2] Mixed phosphite-N have therefore emerged as extremely effective ligands. Despite the advances with Ir-P,N catalysts, their selectivity for reducing some significant olefins still needs to be improved. In this respect, our research has more recently progressed to mixed ligands bearing more robust N-donor groups than oxazolines (pyridines, thiazolines, oxazoles, etc.).[3] We have recently described the first successful use of non-N-donor mixed ligand (P,S), with similar substrate scope than P,N-ligands.[4] The catalyst design has been aided by DFT studies. In this communication I will present our latest developments in this field.

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P-004

Nickel-catalyzed synthesis of dialkyl ethers by C–C bond formation between acetals and aryl iodides

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Poster Session 1

Alkyl ether linkages are prevalent in pharmaceuticals and natural products as well as several classes of agrochemicals. Installation of the carbon–oxygen bond is commonly constructed using chemistry that requires quite reactive organometallic reagents and harsh conditions. We have developed a program aimed at generating these types of products through carbon–carbon, rather than carbon¬–oxygen, bond formation. Acetals serve as non-traditional electrophiles in a variety of nickel-catalyzed cross couplings. Specially, I will discuss the application of this strategy to the reductive coupling of acetals and aryl halides to generate dialkyl ethers. Kinetic, structural, and physical organic studies probing the mechanism of the reaction will be presented.

P-006

Mechanistic Elucidation of Amine Directed Aliphatic C–H Bond Aziridination of Highly Substituted Morpholinones

Mr. Adam Smalley[1]
[1]*University of Cambridge, Cambridge, UK*

Poster Session 1

One of the major challenges in the field of C-H activation is the predictable, selective functionalisation of C-H bonds. As such, any information that can be gleaned to explain existing transformations is of vital importance in the rational design of future reaction pathways. Herein we describe the mechanistic elucidation of a palladium catalysed aziridination through intermediate characterisation and physical chemistry techniques. Previous work in our group (1) showcased the aziridination of morpholinones through a direct N-H/C-H coupling between a secondary amine and an unactivated alkane using palladium catalysis. The utility of this method was realised by the creation of fully functionalised quaternary amino acids by nucleophilic ring opening of the aziridine products and subsequent cleavage of the heterocycle. Density functional theory based calculations were performed to explain the C-H insertion regioselectivity as well as the chemoselectivity responsible for the C-N bond formation. Mechanistic comprehension led to improvements in the synthetic procedure and has fuelled further investigations into ways of additionally controlling this reaction and expansion to more diverse chemical frameworks.

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P-007

PREPARATION, CHARACTERIZATION AND CATALYTIC PROPERTIES OF SIZE SELECTED PLATINUM NANOCLUSTERS

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Poster Session 1

Noble metal nanoparticles have attracted significant interest in recent years due to their importance in both fundamental science and technological applications such as asymmetric catalysis, sensing, medicine, drug or DNA delivery, optics, photonics and nanotechnology. In this work i present platinum nanoclusters (PtNCs) protected by different ligands like L-glutathione (L-GSH) reduced, N-acetyl-L-cysteine (NALC), L-penicillamine (L-pen), D-penicillamine (D-pen) and racemic mixture Rac-penicillamine (Rac-pen) ligands, which have been successfully synthesized. The clusters are characterized by various methods to deduce their size and optical properties. To obtain the exact number of platinum atoms and thiolate ligands in the cluster, the Pt/S ratio has to be determined by thermogravimetric analysis (TGA) and elemental analysis. The particles sizes of these clusters are ~1 nm, which were assessed by transmission electron microscopy (TEM). The optical properties of platinum nanoclusters are studied by UV-vis spectroscopy. To elucidate the structural properties of ligand binding to the platinum nanoclusters, FTIR was measured the absorption spectra of pure ligand and protected platinum nanoclusters and confirmed the disappearance of the S-H vibrational band (2535-2570 cm-1) in the platinum nanoclusters due to the anchoring of ligand to the cluster surface through the sulfur atom. The unique atom-packing structure and electronic properties of platinum nanoclusters (~1 nm) are rationalized to be responsible for their extraordinary catalytic activity observed in oxidation of benzyl alcohol in acetonitrile solution. A complete (~100%) stereoselectivity is obtained.

P-008

Synthesis of new η5-(cyclopentadienyl)-tricarbonylmanganese complexes of isoxazolidines

Ms. Nataliya Zarovkina[1]

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Poster Session 1

The one of the priority area in the chemistry of isoxazolidines is the increase of the selectivity of 1,3-dipolar cycloaddition between C,N-disubstituted nitrones and unsymmetrical alkenes, because this process generally leads to a mixture of isomers (Scheme 1). The use of substances with Mn(CO)3-moiety is attractive for this purpose. It's related with the accepting properties and a large size of Mn(CO)3-group. In order to obtain a number of new individual tricarbonyl-manganese complexes of isoxazolidines by 1,3-dipolar cycloaddition and to establish the selectivity of the process, we carried out a series of reactions between free (1a-c) and coordinated (1d-f) nitrones with styrene (2a) and η5-(vinylcyclopentadienyl)tri-carbonylmanganese (2b) that occurred in toluene in sealed glass tubes at a temperature of 80 °C in accordance with the Scheme 1. The all formed derivatives – isoxazolidines (3a-i) were isolated, purified and characterized by HPLC, UV, IR, 1H NMR – spectroscopy, mass spectrometry and X-ray diffraction. It is found out that the all reactions proceed with full regioselectivity and high stereoselectivity with the formation of C(5)-substituted isoxazolidines having predominantly cis-configuration.

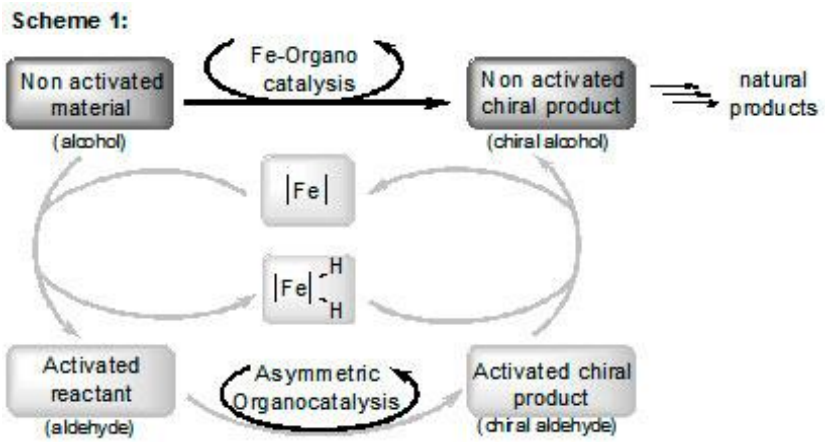
P-009

Combination of iron and organo-catalysis in enantioselective synthesis

Dr. Quintard Adrien[1]
[1]*Aix-Marseille University, Marseille, France*

Poster Session 1

In the context of our continuous efforts towards the development of innovative eco-compatible transformations, we recently designed a multicatalytic borrowing hydrogen-iminium catalysis process allowing to bypass the three distinct classical oxidation / Michael addition / reduction steps usually required for the enantioselective functionalisation of allylic alcohols.This reaction proceeds through an iron catalyzed reversible hydrogen transfer from alcohols to aldehydes. In combination with an iminium catalytic activation, it enables the addition of various nucleophiles to allylic alcohols in a globally redox-neutral process (scheme 1). Extension of this process to unprecedented transformations and applications in natural products synthesis have highlighted its great potential.



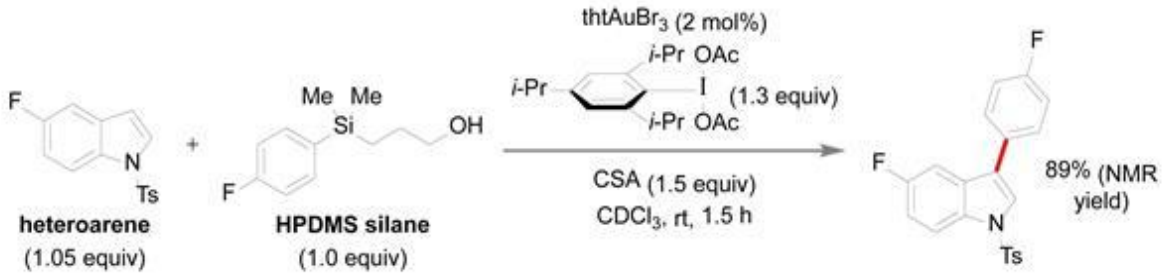
P-010

Gold-Catalysed C–H Arylation: New Developments and Insights

Prof Guy C Lloyd-Jones[1], Dr. Alex Cresswell[1]
[1]*University of Edinburgh, Edinburgh, UK*

Poster Session 1

We have recently developed a gold-catalysed, oxidative cross-coupling between arenes and aryltrimethylsilanes, employing thtAuBr3 as the precatalyst (tht = tetrahydrothiophene), PhI(OAc)2 as the oxidant, and camphorsulfonic acid (CSA) as an additive. As well as being orthogonal to Pd-catalysed cross-coupling (i.e. aryl halides and aryl boronic esters are untouched), the conditions are extraordinarily mild for a C–H arylation (room temperature) and the reactions can be executed without taking special precautions to exclude air and moisture. In terms of drawbacks, the method suffers from long reaction times (7–80 h) and cannot utilise more electron-rich heteroarenes as coupling partners. The current work seeks to overcome both of these issues. Part of the solution has been the development of a new type of silyl group on the arylsilane coupling partner – the 3-hydroxypropyldimethylsilyl (HPDMS) group. Relative to TMS (trimethylsilyl), aryl silanes bearing a HPDMS group undergo transmetalation at an accelerated rate, and this can circumvent a catalyst deactivation pathway which competes with transmetalation in certain cases. For the C–H arylation of more electron-rich heteroarenes (e.g. indoles, furans, uracils), we have found that a sterically-hindered I(III) oxidant, which is slow to oxidise the arene directly, is highly effective (Scheme 1). This method could soon provide an attractive and mild alternative to existing Pd-catalysed C–H arylations of a variety of pharmacologically important aromatic heterocycles.



P-012

CuI Catalyzed Reactions of Silylboranes: From Catalysis to Mechanistic Insight

Dr. Christian Kleeberg[1]
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Poster Session 1

Copper(I) catalyzed addition reactions of silylboranes with substrates such as carbonyls, imines and -unsaturated carbonyls are synthetically well established reactions.1 However, comprehensive studies on the fundamental reactivity and in particular on the intermediates involved are still scarce. Employing an NHC CuI complex as a catalyst we were able to perform efficient catalytic transformations as well as to isolate and characterize a number of key intermediates. Employing these intermediate CuI complexes individual catalytic cycles for different substrates could be established and were retraced step-by-step in stoichiometric reactions.2 Our recent results towards a thorough understanding of the relevant reactivity leading to experimentally verified catalytic cycles, including possible side-reactions, will be discussed in detail.

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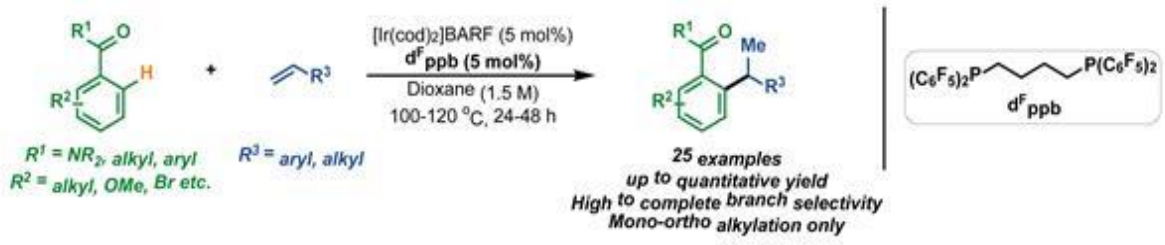
P-013

Branch Selective Ir-Catalyzed Hydroarylation of Monosubstituted Alkenes via a Cooperative Destabilization Strategy

Mr. Giacomo Crisenza[1]
[1]*University of Bristol, Bristol, UK*

Poster Session 1

In the last decades, C-H functionalization has emerged as a straightforward and powerful tool for the development of atom economical methodologies. In particular, Murai and co-workers demonstrated that Ru-catalyzed alkene hydroarylation can be achieved by carbonyl directed aryl C-H activation, providing access to linear hydroarylation products. Following this discovery, a wide range of transition metal catalyzed directed π-bond insertion procedures have been reported. For cases involving mono-substituted alkenes linear selectivity dominates and branched products are not usually accessible. Branch selectivity would provide direct and potentially enantioselective access to products that are difficult to obtain using conventional cross-coupling chemistry. However, to date, a protocol enabling carbonyl-directed branch selective hydroarylation remains elusive. We have developed a highly branch selective carbonyl directed hydroarylations of monosubstituted alkenes. The chemistry relies upon cationic iridium (I)-catalyst modified with a wide bite angle and electron deficient bisphosphine ligand. This methodology provides for the first time a regioisomeric alternative to the Murai hydroarylation protocol.



P-014

Azetidines in Gold-Catalyzed Hydroammoniumation Reactions: Towards a Variety of Azacyclic Derivatives

Ms. Solène Miaskiewicz[1]
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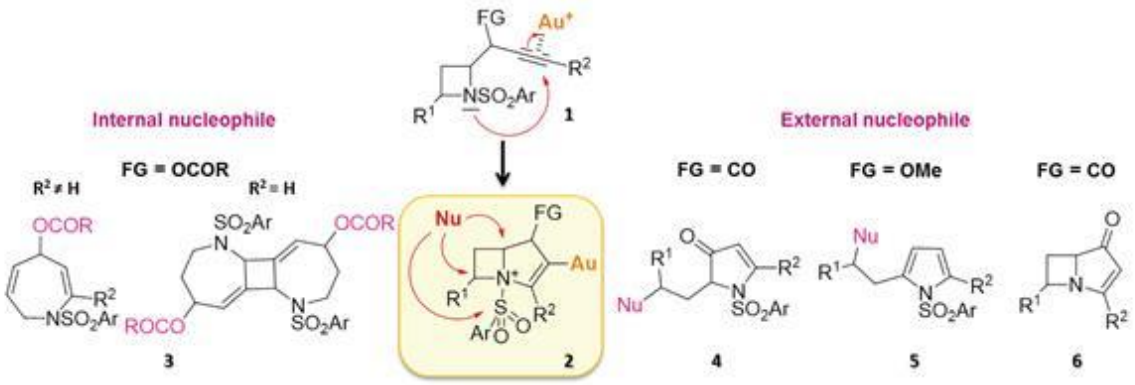
Poster Session 1

Azetidines are four-membered N-heterocycles found in many natural products and bioactive compounds. We have recently developed a straightforward access to carbonylated N-sulfonylazetidines from α-bromo N-sulfonylpyrrolidinones. Surprisingly, azetidines have almost never been used in gold catalysis even though they are potentially very interesting building blocks to develop new methodologies towards various other N-heterocycles. Starting from azetidine derivatives bearing a triple bond and a specific functional group (FG), a gold-catalyzed hydroammoniumation reaction has been studied, leading in each case to a fascinating bicyclic intermediate (Scheme 1). Depending on the type of external or internal nucleophile used, different electrophilic positions can react to form azepine derivatives, pyrrolones, pyrroles, or even compounds containing the carbapenem core. This work opens large perspectives with the scope exploration and mechanistic study of each reaction. Furthermore, we may easily highlight this hydroammoniumation reaction by its direct application to the total synthesis of carbapenem natural products.



Scheme 1 : Gold-catalyzed hydroammoniumation reaction

P-015

Mechanistic and Kinetic Studies of the Direct Alkylation of Benzylic Amines– Surprisingly an sp2 C-H Activation

Prof. Michael Schnürch[1]
[1]*Vienna University Of Technology, Vienna, Austria*

Poster Session 1

Upon carrying out mechanistic investigations of a Rh(I)-catalyzed direct C−H alkylation of benzylic amines with alkenes it was observed that this reaction, even though formally an C(sp3)−H activation, actually proceeds via imine intermediates and, hence, via C(sp2)−H activation. To proof this hypothesis, series of synthetic experiments were carried out which allowed us to show that the substrate is initially dehydrogenated to the corresponding imine, which is then alkylated and reduced back to the amine product. Additionally, to get further insight into the reaction mechanism, kinetic experiments were carried out using the method of initial rates. There, an interesting influence of the base was observed showing that K2CO3 is actually only needed at the beginning of the reaction to form a catalytically active species. However, the reaction rate is dependent on the amount and on the source of base, respectively its specific surface area, to some extent, which will be elaborated in this contribution. Furthermore, the reaction shows a primary kinetic isotope effect of 4.3 at the benzylic C−H position together with a reversible H−D exchange at the same position, which indicates that there are at least two distinct steps in which the corresponding C−H bonds are broken. The presented transformation shows an interesting side product profile as well, indicating that the catalyst is not only capable of activating C-H but also C-C bonds. Based on our results we were able to propose a kinetic model of this direct alkylation which is in agreement with all our experimental findings.

P-016

The Synthesis of Hydrophilic Narrow Sized Au55 Nanoparticles and their Application as Styrene Oxidation Catalysts

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Poster Session 1

In most reports, dendrimer encapsulated nanoparticles (DENs) are prepared in water, since the most commonly used templates such as poly (propylene imine) (PPI) and poly (amido amine) (PAMAM) dendrimers are water soluble [1]. There are however a few reported cases of DENs being prepared in organic solvents [2]. The synthesis of DENs in an organic medium and subsequent extraction into an aqueous medium would result in the formation of hydrophilic nanoparticles. One of the advantages of hydrophilic nanoparticles is its potential use as catalysts in biphasic oxidation reactions. With biphasic catalysis there would be the advantage of easy recovery and subsequent reusability of the catalyst. Here we report the synthesis and catalytic activity of hydrophilic Au55 nanoparticles stabilized by 1,3,5-triaza-7-phosphaadamantane (PTA). After extraction into an aqueous medium and upon stabilization by PTA, Au55 atom cluster nanoparticles were found to have an average particle size of 1.5 nm ± 0.9. This is approximately the size of a single Au55 atom cluster nanoparticle [3]. The reported synthesis method represents a simpler, less laborious manner in which to synthesize single Au55 atom clusters compared to classical methods [4]. The extracted Au55 nanoparticles were subsequently utilized in the bi-phasic catalytic oxidation of styrene. Preliminary catalysis results indicated that the Au55 nanoparticles were active oxidation catalysts and furthermore proved active upon being recycled at least twice after initial use.

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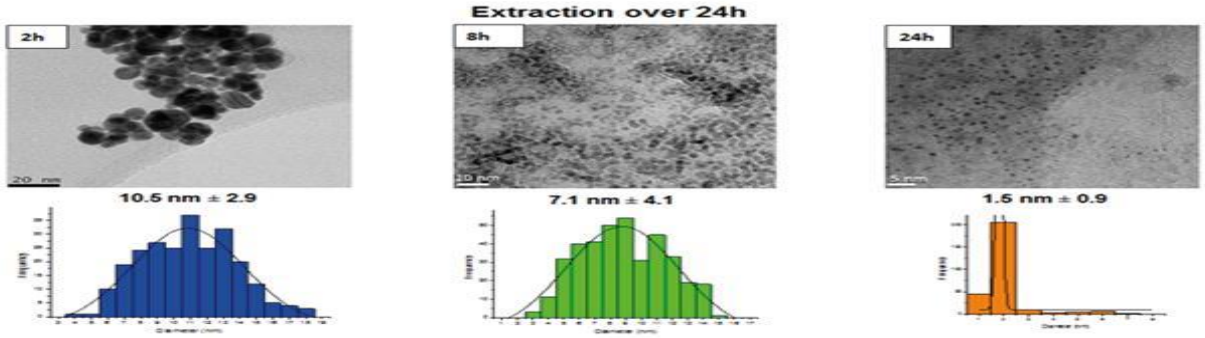

P-018

Direct Arylation of Pyrazolo[1,5-a]pyrimidines with Complete and Switchable Regiocontrol

Ms. Michelle Montgomery[1]
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Poster Session 1

The pyrazolo[1,5-a]pyrimidine scaffold has recently been recognised as a privileged structure in drug discovery and can be found in commercial anxiolytic and sedative agents Zaleplon, Indiplon and Ocinaplon (Figure 1). In addition, compounds bearing the pyrazolo[1,5-a]pyrimidine core have been shown to inhibit key kinases involved in a plethora of therapeutic areas as well as exhibiting antitumor, antinflammatory and antiviral properties. As such, they are of wide pharmaceutical interest. Traditionally, the synthesis of aryl substituted pyrazolo[1,5-a]pyrimidines relies upon the cyclocondensation of a substituted aminopyrazole and a dicarbonyl synthon. Unfortunately such reactions can suffer from poor functional group tolerance and unpredictable regiochemistry as well as requiring the lengthy synthesis of starting materials. We have developed the regiodivergent palladium catalysed C-H arylation of pyrazolo[1,5-a]pyrimidine to yield either the 3-aryl of 7-arylpyrazolo[1,5-a]pyrimidine in one step. The switch in regioselectivity between the 3 and 7 position is under complete catalyst control and a consequence of orthogonal operative mechanisms. Bisaryl phosphine SPhos promotes direct arylation at the most acidic C7 position whereas in the absence of phosphine arylation occurs at the most electron rich position C3.

P-019

The Development of Novel Iridium Complexes for Enantioselective Atom Transfer C-H Functionalization Reactions.

Prof. Simon Blakey[1]
[1]*Emory University, Atlanta, USA*

Poster Session 1

Design principles for the development of new organometallic complexes capable of catalyzing challenging intermolecular atom transfer C-H functionalization reactions will be discussed. An interplay between computational modeling and experiment provides a platform for catalyst evolution. Novel iridium complexes, designed to catalyze highly enantioselective C-H functionalization with classes of diazo compounds and metallonitrene precursors that are typically difficult to control will be presented.

P-025

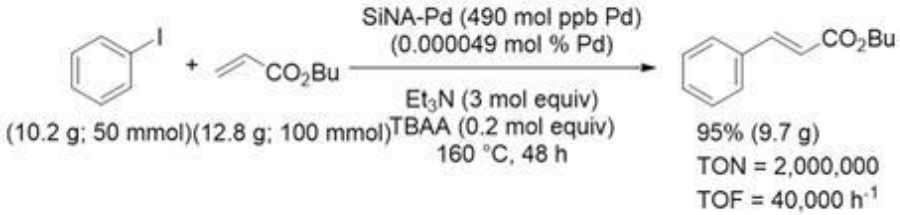
Development of a silicon nanowire array-supported palladium nanoparticle catalyst for organic reactions

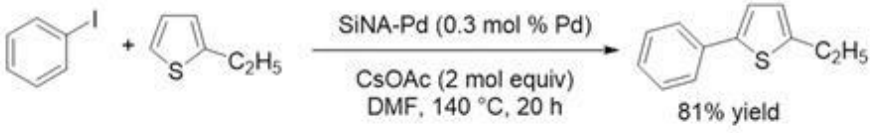
Dr. Yoichi M. A. Yamada[1]

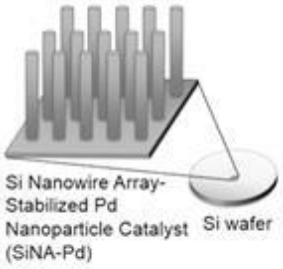
[1]*RIKEN Center for Sustainable Resource Science, Hirosawa, Japan*

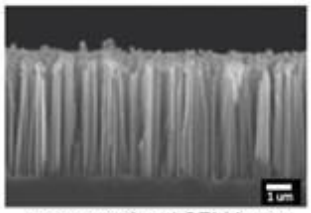
Poster Session 1

We have reported convoluted self-assembled polymeric metal catalysts for organic reactions. For example, we prepared a highly active, reusable, self-assembled catalyst of poly(imidazole-acrylamide) and (NH4)2PdCl4, and its application to coupling reactions. Here, we would like to present the development of a new platform for the catalytic organic reactions, a silicon nanowire array-stabilized palladium nanoparticle catalyst, SiNA-Pd. The novel device was applied to the Mizoroki-Heck reaction, the hydrogenation of an alkene, the hydrogenolysis of nitrobenzene, the hydrosilylation of an alpha,beta-unsaturated ketone, and the C-H bond functionalization reactions of thiophenes and indoles to achieve a quantitative production with high reusability. Especially, SiNA-Pd with 490 mol ppb (0.000049 mol %) Pd promoted the Mizoroki-Heck reaction to give the corresponding products, reaching a TON of 2 000 000.









cross-sectional SEM image

P-027

Synthesis of Versatil Synthetic Intermediates through Copper-Catalyzed Borylations

Dr. Mariola Tortosa[1]
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Poster Session 1

Boronic esters are versatile synthetic intermediates for the preparation of a wide range of organic molecules. The development of new methods to create C-B bonds in an efficient, inexpensive, and environmentally friendly way is therefore an important challenge in organic chemistry. Traditionally, the methods to form C-B bonds have mostly been based on the electrophilic nature of boron. While this classical approach works well for reactions with nucleophilic partners, it naturally limits the types of boron compounds that can be prepared. Recently, copper-catalyzed borylations have emerged as a new source of nucleophilic boron. The lower price and toxicity of copper versus other transition metals and the unique reactivity of the boryl-copper intermediates make these processes particularly attractive. We have used boryl-copper species to synthesize a wide variety of synthetically useful intermediates such as 1,4-diols, alkenes, cyclopropanes and more recently diarylmethanes and cyclobutyl derivatives. Some of the more recent studies ongoing in our group will be presented in this talk.

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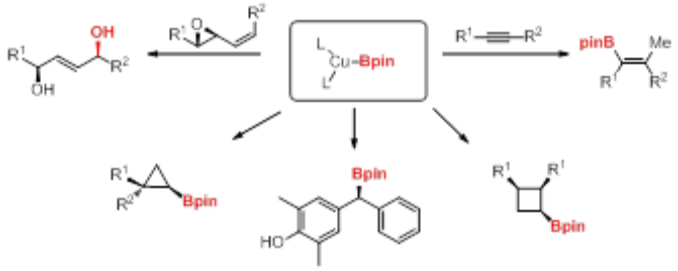

P-028

Novel Iridium(III) cyclopentadienyl complexes: improved understanding of the mechanism of the catalytic asymmetric transfer hydrogenation of imines

Dr. Gemma Sweeney
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Poster Session 1

Enantiomerically pure amines are high value products, intermediates or building blocks for biologically active molecules in medical, pharmaceutical, and agricultural science. A most attractive method for the preparation of chiral amines is the asymmetric transfer hydrogenation of imines. The most significant chiral catalysts for this reaction are ruthenium(II) or iridium and rhodium(III) based, using the optically active N-toluenesulphonyl-1,2-diphenylethylenediamine ligand. Ruthenium complexes typically employ an arene spectator ligand, and iridium and rhodium complexes often contain a pentamethylcyclopentadienyl ligand. The mechanism for the transfer hydrogenation of imines is poorly understood in comparison to the well-documented hydrogenation of ketones to yield alcohols. In this presentation we will discuss our investigations into the mechanism of the asymmetric transfer hydrogenation of imines to yield amines. We have altered the electronic environment around the metal atom by preparing novel complexes with diferent functional groups on the cyclopentadienyl moiety and studied the reaction kinetics of these novel chiral complexes in the transfer hydrogenation of a variety of dihydroisoquinolines. In this way we are working towards further understanding of this vital reaction, in order that catalyst design for maximum efficiency can be realised.

P-029

Density functional theory (DFT) modeling of the transmetalation step in the chiral Rh-catalyzed asymmetric 1,4-arylation

Prof. Eric A. B. Kantchev[1]
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Poster Session 1

The Rh-catalyzed 1,4-arylation reaction has become one of the most important methods for asymmetric C-C bond formation due to its excellent yields and enantioselectivities under mild and environmentally-friendly conditions.1 Whereas the chiral transfer occurs during the carborhodation stage of the catalytic cycle, the overall catalytic activity depends on the rate of transmetalation being the rate limiting step.2 A comparative density functional theory (DFT) study3 of the transmetalation of phenylboronic acid to Rh ligated with chiral diene and diphosphanes will be presented.

P-031

Model systems for unraveling fundamental redox processes of coinage metals

Dr. Xavi Ribas[1]
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Poster Session 1

The mechanistic understanding of transition metal-catalyzed chemical transformations is of fundamental importance to design optimized methodologies for the synthesis of target products. We are interested in coinage metal catalysis, with special focus in unravelling the detailed molecular mechanisms and redox chemistry involved in C-C and C-heteroatom cross-coupling reactions. Here we present the unprecedented isolation of elusive aryl-copper(III)-halide species directly involved in C-heteroatom catalytic reactions using model aryl halide substrates. In situ spectroscopic studies of Cu-catalyzed C-X (X= F, Cl, Br, I), C-N, C-O, C-S, C-Se, C-P and C-C coupling reactions provides definitive evidence for the involvement of an aryl-copper(III)-halide intermediate in a redox Cu(I)/Cu(III) catalytic mechanism. On the other hand, analogous two-electron redox catalytic cycles, which are most common in noble metal organometallic reactivity, have never been considered for silver. Herein, we show that an unprecedented Ag(I)/Ag(III) catalytic cycle is operative in model C-O and C-C cross-coupling reactions. We anticipate our study as the starting point for expanding Ag(I)/Ag(III) redox chemistry into new methodologies for organic synthesis, resembling well-known copper or palladium cross-coupling catalysis. Furthermore, findings described herein dismiss the generally accepted conception that silver redox chemistry can only arise from one electron processes. Finally, we present our latest results in exploring the oxidant-free Au(I)-catalyzed cross coupling reactions. (figure 1)

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Acknowledgements
This work was supported by grants from the European Research Council (Starting Grant
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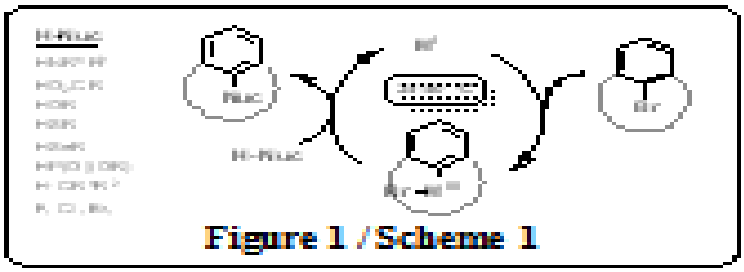

Figure 1 / Scheme 1

P-032

Cp*Rh(III)-Catalyzed C-H Activation Access to Complex Organic Molecules

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Poster Session 1

During the past decade, transition-metal-catalyzed C–H activation has emerged as an attractive strategy to prepare organic building blocks in a step and atom-economical fashion. An impressive number of transformations aimed at directly installing new C-C or C-X bonds have been developed based on this strategy. [1] Herein, we demonstrated the wide application of Cp*Rh(III) catalyst in the synthesis of highly valuable organic compounds as exemplified by arylsultams, polycyclic aromatic hydrocarbons and trans-enol esters via directed C-H activation and non-directed C-H activation.[2, 3, 4]

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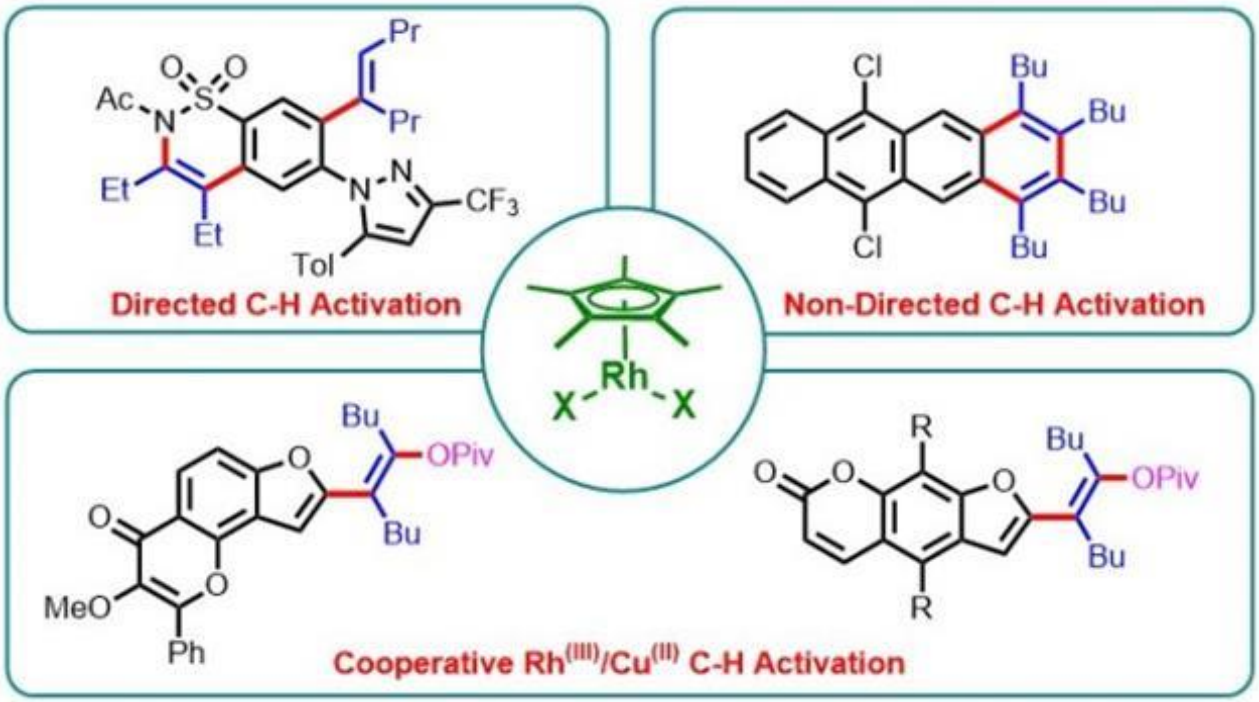

P-033

Air stable pincer (CNC) N-heterocyclic carbene-cobalt complexes and their||application as catalysts for C-N coupling reactions

Prof. Muhammad Bala[1], Halliru Ibrahim[1]
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Poster Session 1

Two new pincer (CNC) NHC-Co complexes: 3,3'-(dimethylimidazolin-2-ylidene)lutidine chlorocobalt(II) hexafluorophosphate, 1 and 3,3'-(dibenzylimidazolin-2-ylidine)lutidine chlorocobalt(II) hexafluorophosphate, 2 were synthesised in good yields via transmetalation of the corresponding Ag-NHC complexes. All ligands and resulting complexes were fully characterised by spectroscopic analyses (1H, 13C, 31P, FT-IR) and analytical techniques (melting point, MS-ES+). The molecular structures of two related ligand precursors determined by single crystal X-ray diffraction analysis are also reported. Both complexes showed excellent activity in catalysing the C-N coupling of aryl halides with primary aryl amines to yield desired secondary aryl amines in good to excellent isolated yields. The catalysts were selective for the production of only the desired 2° amine products with the suppression of 3° amines and biphenyls. A mechanism was proposed to explain the selective action of the NHC-Co complexes in this reaction.

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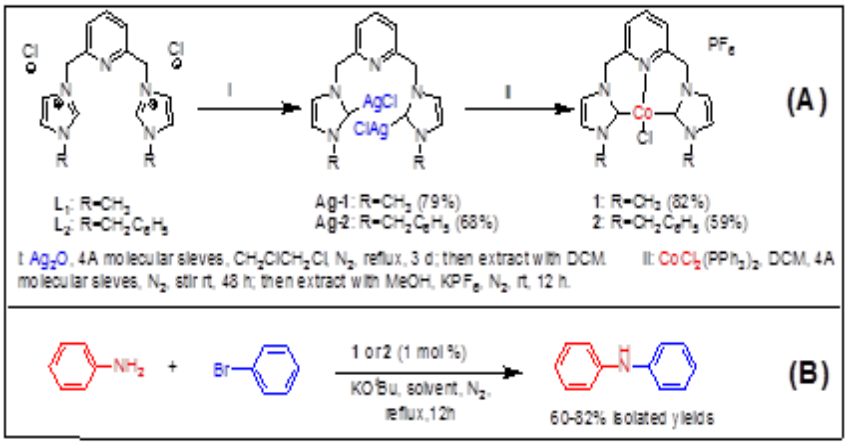

P-034

Air-Stable Cationic Gold(I) Catalyst Featuring Z-Type Ligand and Its Promoting Activity of Enyne Cyclizations

Naoya Maruyama[1], Chiaki Matsumoto[1], Yasuhiko Okada[1], Fuyuhiko Inagaki[1], Chisato Mukai[1]
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Poster Session 1

Based on Green's theory, three types of ligands, the L-, X- and Z-types are categorized depending on the bonding functions for the ligating atom of a ligand.1 The X-ligand provides one electron to the metal to form the covalent bond (M-X) exemplified by a hydride, alkyl, and halogen. The L-ligand (e.g., phosphine, carbon monoxide, and olefin) provides two-electrons for occupying an empty orbital on the metal center. The type of □-accepter (e.g. boron, aluminum, and silicon) is classified as a Z-type ligand. Although the Lewis acidity of Z-type ligand set our expectations for gaining the novel functionalities, the catalytic reaction featuring Z-type ligand has hardly been reported. We have succeeded in the preparation of the novel air-stable [Au→Z]+ complex, [(DPB)Au(□2-cod)Au(DPB)](SbF6)2 (1a: DPB = (o-Ph2PC6H4)2BPh), which features a Z-type ligand as a □-acceptor. The COD ligand of its complex was easily dissociated in solution, which enabled us for investigating the electronic effect of □-acceptor boron atom in the direction of its trans position on gold(I) atom. Our results of the enyne cyclization for comparing the [Au→Z]+ 1a and [Au]+ 1b,c (without Z-type ligand) catalysts provided new experimental evidence that the existence of boron atom dramatically improved the reactivity for the syntheses of 5- and 6-membered rings. In addition, [Au→Z]+ catalyst 1a was also applicable for the efficient construction of larger 7-membered ring systems.2

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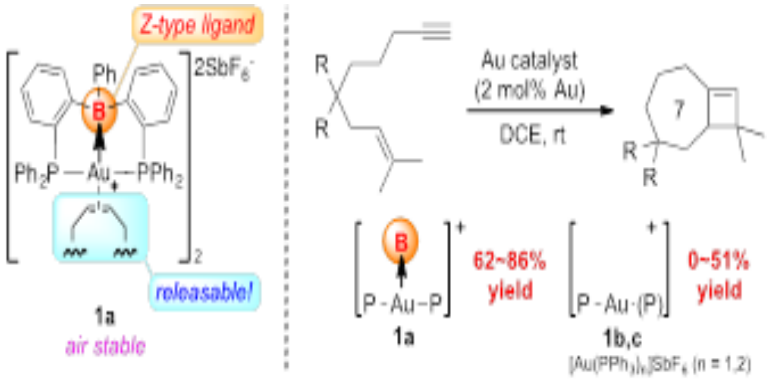

P-035

Iron-catalyzed CDC reactions of azoles with ethers

Dr Arkaitz Correa[1], Bela Fiser[1], Prof. Enrique Gómez-Bengoa[1]
[1]*Universidad del País Vasco-Euskal Herriko Unibertsitatea (UPV-EHU), Vizcaya, Spain*

Poster Session 1

Owing to their low-price, unique reactivity and environmentally friendly character, iron salts constitute potentially ideal catalysts to perform numerous organic transformations of attractive industrial prospect in terms of sustainable chemistry. In particular, such benign metal salts are rarely employed in emerging "Cross-Dehydrogenative Coupling" (CDC) events between two distinct C–H bonds. Notably, the conversion of typically named "inert" C–H bonds holds great promise for reducing the reliance on existing functional groups while improving atom economy and energy efficiency. In this communication, preliminary results dealing with the development of a modular alkylation process applicable to a broad range of azoles featuring the use of iron salts will be presented. Likewise, some insights into the reaction pathway based on computational studies will be discussed.

P-036

Nickel and Copper Co-catalyzed Defluoroborylation of Fluoroarenes for Expeditious Preparation of 18F-Labeled PET Probes

Dr. Takashi Niwa, Takamitsu Hosoya[1], Hidenori Ochiai[1], Yasuyoshi Watanabe[1]
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Poster Session 1

Positron emission tomography (PET) is a less-invasive molecular imaging method that is applied to clinical diagnoses of various diseases, as well as evaluation of drug candidate molecules in vivo at the early stage of drug development. Fluorine-containing compounds, frequently found in commercial pharmaceuticals, are particularly suited for this method because radioactive fluorine-18 with a relatively long lifetime (t1/2 = 110 min) is employable. Although several useful methods for late-stage [18F]fluorination, such as copper-mediated deboryl[18F]fluorination of arylboronic esters,1 have been reported in recent years,2 development of efficient 18F-labeled probes is still impeded due to a paucity of a general method for preparing precursors. We considered that the most straightforward way to address this issue was to prepare the precursors directly from the original non-radioactive 19F-containing compounds.
Here we present an efficient method for converting fluoroarenes directly into arylboronic esters, which are applicable as precursors for [18F]fluoroarenes, via nickel and copper co-catalyzed defluoroborylation. Under optimized conditions, a variety of arylboronic esters were obtained via cleavage of a carbon–fluorine bond in good to excellent yields (up to 97%). Details for optimization of the reaction conditions, substrate scope (>20 entries), and plausible mechanism of this reaction will be also presented. Furthermore, the utility of our method is demonstrated through an expeditious preparation of an 18F-labeled statin derivative from a non-radioactive equivalent molecule in two steps, i.e., sequential defluoroborylation and deboryl[18F]fluorination.

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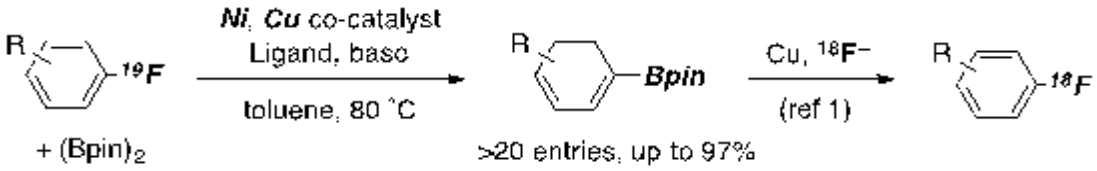

P-037

Palladium-Assisted Aromatic Metamorphosis of Dibenzothiophenes to Triphenylenes

Dr. Hideki Yorimitsu[1], Dr. Dhananjayan Vasu[1], Mr. Yuto Kurata[1], Mr. Shinya Otsuka[1], Mr. Norihito Fukui[1], Dr. Atsuhiro Osuka[1]

[1]*Kyoto University, Kyoto, Japan*

Poster Session 1

Aromatic skeletons are usually considered to be stable and to resist organic transformations. During the course of our research on organosulfur chemistry, we have invented a novel route to triphenylenes from readily available dibenzothiophenes through “aromatic metamorphosis”, which represents a transformation of an aromatic system to another through partial disassembly of the starting aromatic ring.

The aromatic metamorphosis begins with AgBF-mediated S 2 reaction of dibenzothiophene with 1-bromo-4-chlorobutane to form the corresponding sulfonium salt. The sulfonium salt is reactive enough to undergo palladium-catalyzed arylative ring-opening with an arylboron compound for introducing the last benzene ring. The resulting chlorobutyl teraryl sulfide is then converted to the corresponding tetramethylene sulfonium salt by $AgSbF_6$-mediated intramolecular S_n2 reaction. The final step, i.e., ring-closure into triphenylenes, is achieved through unprecedented intramolecular direct C-H arylation with the sulfonium salt.

P-038

Highly Enantioselective Rh(I)-Catalyzed Activation of Cyclobutanones Enantiotopic C-C Bonds

Dr. Laetitia Souillart[1,2], Prof. Nicolai Cramer[1]

[1]*Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland,* [2]*Max Planck Institue für Kohlenforschung, Mülheim an der Ruhr, Germany*

Poster Session 1

Small rings play an important role for C–C bond activation as their inherent ring strain facilitates metal insertion. Our group reported enantioselective β-carbon eliminations from tert-cyclobutanols giving rise to a diverse set of products via different downstream reaction pathways.[1] Strained ketones have proven as well to be highly versatile for reactions involving oxidative addition of transition-metals as C-C cleavage mechanism. We reported the first examples of enantiotopic C-C bond activation of cyclobutanones in which the C-C cleavage step is the enantiodetermining step.[2] This rhodium(I)-catalyzed process allows for an efficient access to the valuable bicycloheptanone scaffold (path A)[2a] or tricyclic lactones (path B)[2b] in exceptionally high enantioselectivities.

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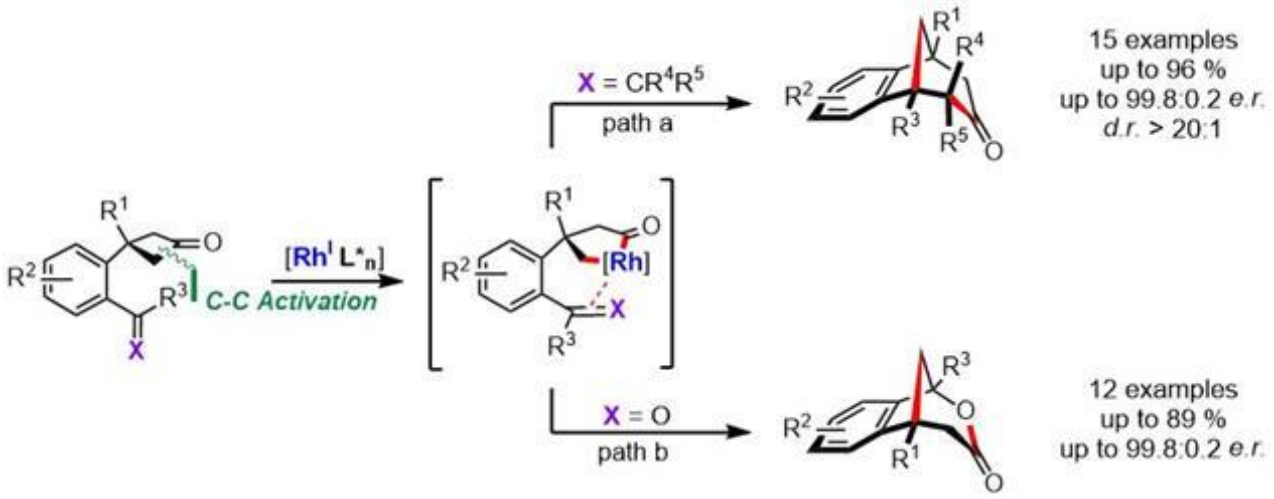

P-039

Catalytic Transformation of 2-Substituted Benzyl Esters by Successive C-O/C-H Bond Activations

Ph.D Masafumi Hirano[1], Mr. Sosuke Kawazu[1], Dr. Nobuyuki Komine[1]
[1]*Tokyo University of A & T, Tokyo, Japan*

Poster Session 1

Catalytic transformation of 2-substituted benzyl esters by successive C-O/C-H bond activations has been achieved by a Pd catalyst.[1] For example, 2-phenylbenzyl trifluoroacetate is converted into fluorene at 100 ˚C by 10 mol% of $Pd(OAc)_2/PPh_3$/MTBD in toluene in 97% yield.[2] This is the first report for the catalytic C-H bond activation without addition of any carboxylate/carbonate salts by IES (or CMD/AMLA) mechanism. The key reaction is the initial C-O bond oxidative addition of benzyl ester to Pd(0) and the resulting carboxylato group in (benzyl)(carboxylato)palladium(II) species acts as the internal base for the subsequent internal C-H bond activation. This is also supported by the DFT calculations.

The stoichiometric reaction of Pd(styrene)(dppe) with 2-phenylbenzyl trifluoroacetate instantly results in the C-O bond oxidative addition to give *cis*-Pd(2-phenylbenzyl)($OCOCF_3$)(dppe) and heating of this product at 70 ˚C quantitatively produces fluorene.

Similar treatments of 2-vinyl- and 2-allylbenzyl trifluoroacetates at 100 ˚C for 1 h produce indene and 2-methyleneindane in 98% and 66% yields, respectively.

References:

(1) M. Hirano, S. Kawazu, N. Komine, *Organometallics*, **2014**, *33*, 1921.
(2) MTBD: 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene


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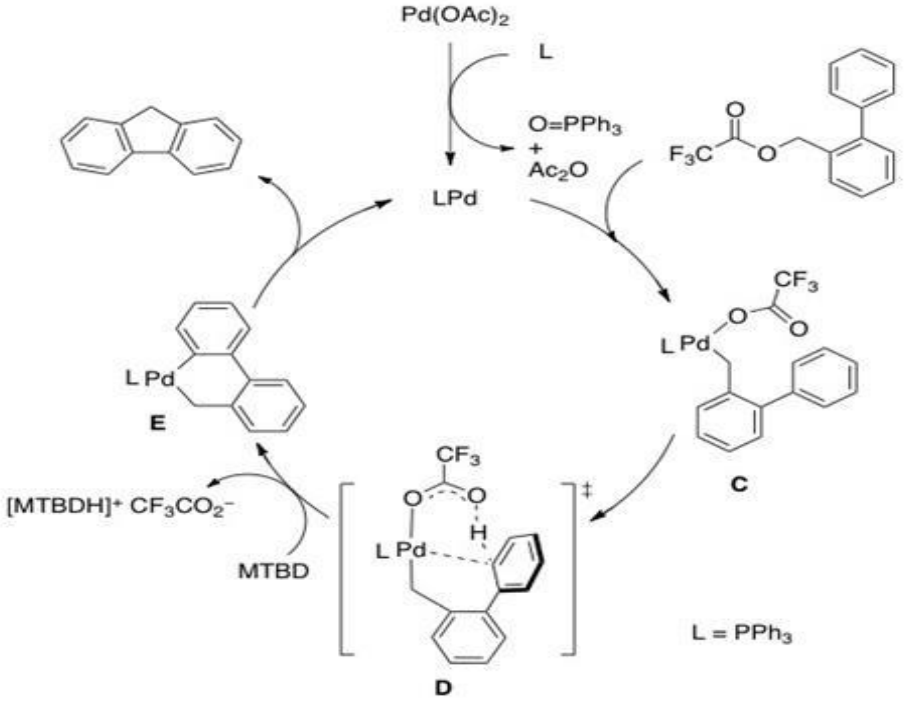

Pd(OAc)2
L
O=PPh3
+
Ac2O
LPd
F3C
O
CF3
L Pd
C
D
E
[MTBDH]+ CF3CO2−
MTBD
L = PPh3

P-040

Nucleophilicity of boron-ate complexes derived from boronic esters

Dr. Guillaume BERIONNI[1], Prof. Paul Knochel[1], Prof. Herbert Mayr[1]
[1]*Ludwig Maximilians University Munich, München, Germany*

Poster Session 1

Chiral organoboron compounds have been recently employed in asymmetric synthesis.[1] In most reactions, a boronic ester R-B(OR)$_2$, which is configurationally stable but weakly nucleophilic, is activated “in-situ” by an organometallic reagent or a Lewis base, to give a more reactive boron-ate complex intermediate (Figure 1), which can react with a wide range of electrophiles.[1]

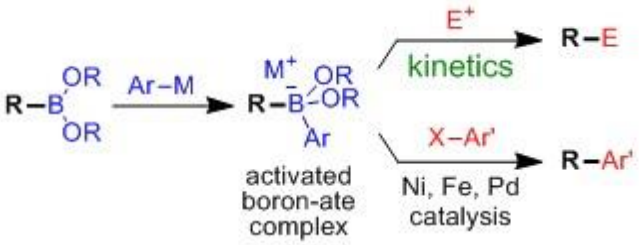
As the knowledge of the structures and of the nucleophilicities of these intermediates is important for their proper use in synthesis, we have now isolated and characterized a series of alkyl, benzyl, aryl, and heteroaryl boron-ate complexes and studied the kinetics of their reactions with carbenium and iminium ions.[2]

On the basis of these kinetic investigations, we have used Eq(1) to determine the nucleophilicity N of numerous organoborates and boronates and we have established a nucleophilicity scale for the most important classes of organoboron compounds.[3] Effects of the diol ligand, the quaternizing group Ar, and the counter-cation M[sup]+[/sup] on the nucleophilic reactivities of several boron-ate complexes have been quantified.

These data allow chemists to rationalize the reactivities of organoboron derivatives in uncatalyzed reactions with electrophiles (Michael additions, halogenations, additions to C=X bonds, ipso-substitutions, Petasis- and Friedel-Crafts reactions…) and to compare the nucleophilicity of organoboron compounds with that of other organometallic reagents

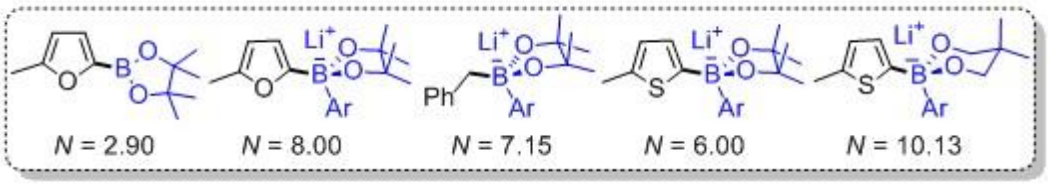
References:

[1] D. Leonori, V. Aggarwal, Angew. Chem. Int. Ed. 2015, 54, 1082.
[2] G. Berionni, A. I. Leonov, P. Mayer, A. R. Ofial, H. Mayr, Angew. Chem. Int. Ed. 2015, 54, 2780.
[3] G. Berionni, B. Maji, P. Knochel, H. Mayr, Chem. Sci. 2012, 3, 878.



$$\log k_2 = s_N (E + N) \quad (1)$$

- k_2 = second-order rate-constant
- E = Electrophilicity parameter
- N = Nucleophilicity parameter
- s_N = Sensitivity parameter



P-041

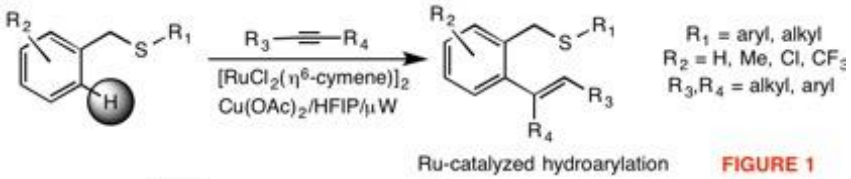
Sulfur as directing group in C-C, C-S and C-O bond forming reactions through CH bond activation: Ru-catalysed hydroarylation and Cu-mediated acetoxythiolation of internal alkynes

Dr. Esteban Urriolabeitia[1], Dr. Pedro Villuendas[1]
[1]*ISQCH (CSIC-Universidad Zaragoza), Zaragoza, Spain*

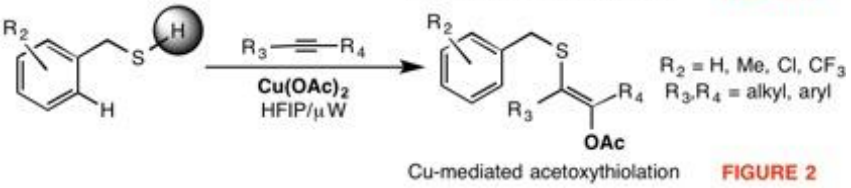
Poster Session 1

The use of directing groups to achieve high selectivities in metal-mediated organic synthesis through C-H bond activation is a well-established methodology.[1] The choice and design of the directing group is not a trivial task since, in order to reach the maximal atom economy, it is usually incorporated to the target molecular skeleton. N- and O-directing groups have been widely used in a variety of processes, being particularly relevants in the synthesis of N- or O-heterocycles. However, the use of S-directing groups in the synthesis of S-heterocycles has been much less studied, in spite of the fact that S-containing molecules are building blocks of a large number of drug compounds, either used in agrochemical applications or with pharmacological activity.[2] Probably the thiophilicity of transition metals, and the unavoidable deactivation of the catalysts, is closely related with this scarce representation; at the same time, however, it is an additional challenge for the in-depth study of these systems.
Aiming to provide new pathways for the synthesis of S-heterocycles we have investigated the reactivity of different S-containing species. We found that benzylthioethers react with internal alkynes, catalysed by [Ru(cymene)Cl2]2, to give the ortho-alkenylated species by hydroarylation using sulfur as the directing group (Figure 1). However, the formation of the S-heterocycle was not observed. The increase of the charge at the S atom changed dramatically the reactivity, instead of promoting the ring closure. Thus, benzylthiolates and thiophenolates react with internal alkynes and stoichiometric amounts of Cu(OAc)2 to give the acetoxy-thiolated cross-coupled species as the only products of double addition to the triple C-C bond (Figure 2).

References:
[1] L. Cuesta, E. P. Urriolabeitia in C-H and C-X Bond Functionalization; X. Ribas Editor; RSC Catalysis Series Nº 11, Cambridge, 2013.
[2] M. D. McReynolds, J. M. Dougherty, P. R. Hanson, Chem. Rev. 2004, 104, 2239.



Ru-catalyzed hydroarylation FIGURE 1



Cu-mediated acetoxythiolation FIGURE 2

P-042

Catalytic Intramolecular Hydroamination with Coordinatively Unsaturated NHC-Iridium(I) Complexes

Mr. Gellert Sipos[1], Mr. Arnold Ou[1], Dr. Brian W. Skelton[1], Dr. Reto Dorta[1]
[1]*The University of Western Australia, Crawley, Australia*

Poster Session 1

Coordinatively highly unsaturated complexes are often assumed to play vital roles in transition metal catalysis, but are rarely stable as such and are normally generated from suitable precatalysts. For example, Wilkinson's catalyst is only active once it liberates an equivalent of triphenylphosphine and generates the active [$RhCl(PPh_3)_2$] fragment.[sup]1,2[/sup] Based on our previous experience in the field of late-transition metal NHC complexes,[3] we set out to explore the feasibility of synthesising such formally 14-electron complexes of group 9 metals. Herein, we present results on the characterisation of iridium complexes with the general formula [(NHC)IrL2]+. These highly unsaturated, nevertheless stable complexes were fully characterised and we will present studies that will explain their unusual stability.
We envisioned that these complexes would be able to facilitate the hydroamination of alkenes, i.e. the addition of an N-H bond across an olefin.[4] This highly atom-economical approach towards nitrogen-containing building blocks is still suffering from relatively low catalytic reactivity profiles.[4] We will present data that show that high turnover frequencies (TOFs up to 3000 1/h) and low catalyst loadings at room temperature are possible in this reaction. Current research focuses on the synthesis of enantiomerically enriched products and catalyst systems where we observe excellent enantioselectivities will be presented.

References:

1. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. J. J. Chem. Soc. A 1966, 1711.
2. Hartwig, J., Ed. Organotransition Metal Chemistry; University Science Books, Sausalito, 2010
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4. Bernoud, E.; Lepori, C.; Mellah, M.; Shulz, E.; Hannedouche, J. Catal. Sci. Technol. 2015, 5, 2017.


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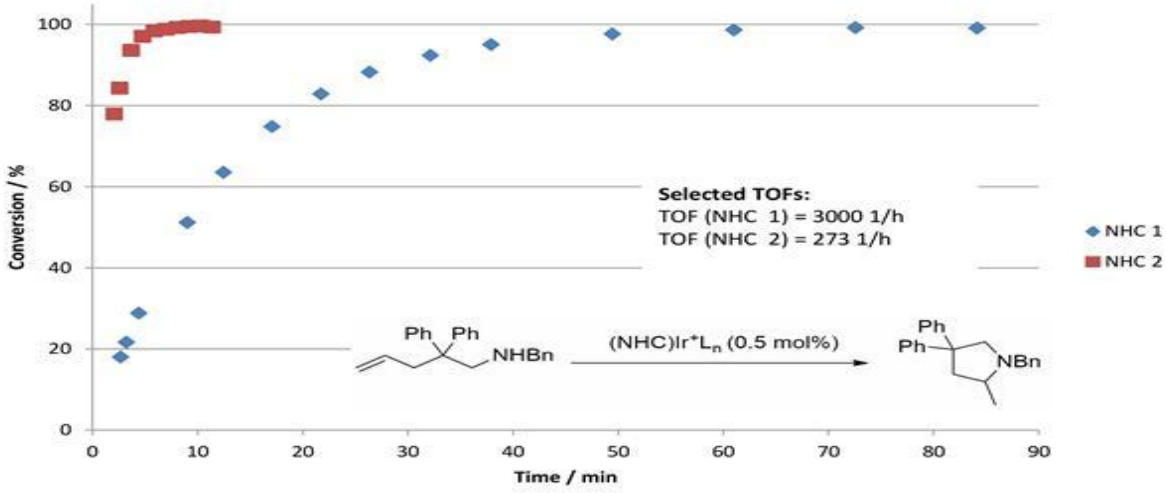
Conversion / %
Time / min
Selected TOFs:
TOF (NHC 1) = 3000 1/h
TOF (NHC 2) = 273 1/h
NHC 1
NHC 2
Ph
Ph
NHBn
(NHC)Ir+Ln (0.5 mol%)
NBn

P-043

Catalytic Generation of α-CF_3 Enolate for Producing Chiral Building Blocks with CF_3-Containing Stereogenicity

Dr. Naoya Kumagai[1], Dr. Lennart Brewitz[1], Dr. Liang Yin[1], Mr. Akinobu Matsuzawa[1], Dr. Kaliyamoorthy Alagiri[1], Dr. Fernando Arteaga[1], Prof. Masakatsu Shibasaki[1]
[1]*Institute of Microbial Chemistry, Shinagawa-Ku, Japan*

Poster Session 1

Nowadays approximately 20% of the newly approved small organic molecule drugs contain at least one fluorine atom.[sup][1][sup] However, the synthesis of fluorine- or CF_3-substituted chiral carbon centers in a catalytic and asymmetric manner remains challenging. To face this challenge, the synthetic community is recently focusing on the development of methods for the asymmetric fluorination of prochiral molecules. Herein a different approach is presented, relying on the asymmetric reaction of an pre-fluorinated molecule via an α-CF_3 enolate. Catalytic asymmetric reactions of α-CF_3 carbonyl compounds with suitable electrophiles have so far largely been neglected as a means to synthesize chiral fluorine containing molecules due to the rapid defluorination.[sup][2][sup] However, the tethering of the α-CF_3 carbonyl moiety to an appropriate Lewis base might suppress the undesired defluorination pathway: the metal ion can chelate with the carbonyl oxygen and the Lewis base which would inhibit its interaction with the fluorine orbitals. The α-CF_3 enolate should thus be stable enough to react with an electrophile. On the basis of this assumption, an α-CF_3 7-azaindoline amide was designed in which the pyridyl nitrogen functions as a Lewis base. The chelated structure was determined in solution by NOE and in the solid state by X-ray analysis. Upon the deprotonation of the α-CF_3 7-azaindoline amide copper(I) complex the corresponding α-CF_3 enolate can be accessed and trapped with N-Boc imines and α-ketoaldehyde hydrates being the ideal electrophiles.[sup][3][sup] The versatility of 7-azaindoline amide is revealed by varying the pendant fluorine containing substituents, which will be discussed in the presentation.

References:
1. S. Fustero, V. A. Soloshonok, H. Liu et al, Chem. Rev. 2014, 114, 2432.
2. Mikami, K.; Itoh, Y. Chem. Rec. 2006, 6, 1.
3. L. Yin, L. Brewitz, N. Kumagai, M. Shibasaki, J. Am. Chem. Soc. 2014, 136, 17958.

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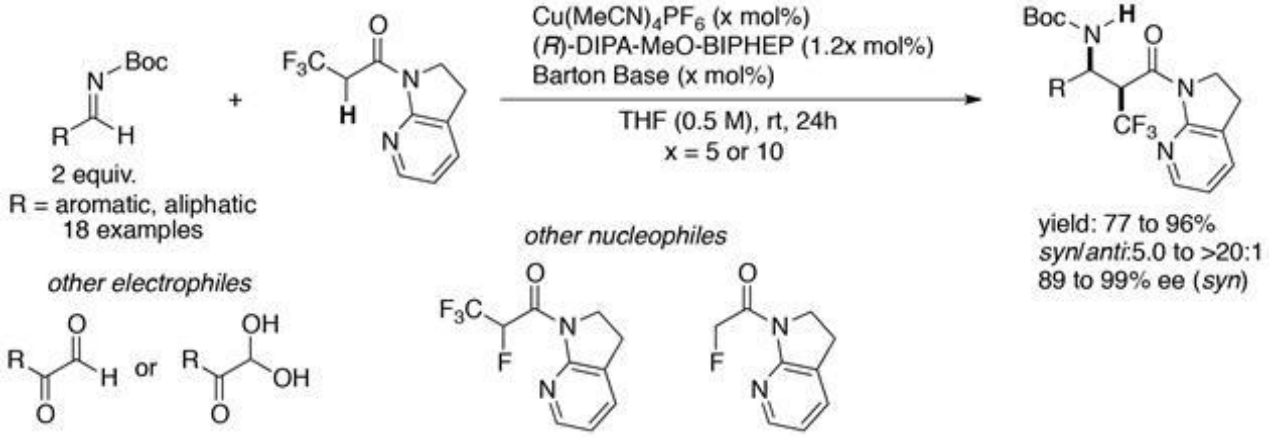

P-044

Direct Catalytic Synthesis of Amides at Room Temperature: A Stride Towards Greener Peptide Synthesis

Mrs. Tharwat Mohy El Dine[1], Dr. Jérôme Blanchet[1], Prof. Jacques Rouden[1]
[1]*Laboratoire De Chimie MoléCulaire Et Thioorganique, ENSICAEN, UNICAEN, Caen, France*

Poster Session 1

Amides are ubiquitous chemical building blocks found in nature as well as in a vast array of synthetic structures (polymers, agrochemicals, pharmaceuticals …). The ideal creation of the amide bond is attained through the direct condensation of readily available carboxylic acids and amines.[1] In order to overcome the barrier of the carboxylate-ammonium salt formation, the activation of the carboxylic acid is generally required. Due to the low atom economy resulting from the use of coupling reagents for such activation, ACS Green Chemistry Institute Pharmaceutical Roundtable has highlighted the need for catalysts which are able to provide a direct and waste-free amide synthesis.[2]

In the last few years, boron-derived reagents and especially boronic acids have acquired a great importance as catalysts and have shown to be effective for direct amide synthesis. To the best of our knowledge, only one couple of catalysts was reported to promote such reaction at room temperature. However, several limitations persist, including low reactivity as well as racemisation during the coupling of chiral α-amino acids and call for further developments.[3]

In this context, we developed an efficient boron-derived catalyst promoting room temperature direct amide synthesis between carboxylic acids and amines.

A wide range of substrates were successfully coupled including α-amino acids with no racemisation observed.[4]

References:
[1] Pattabiraman, V. R.; Bode, J. W. Nature 2011, 480, 471-479.
[2] Constable, D. J. C.; Dunn, P. J.; Hayler, J. D.; Humphrey, G. R.; Leazer, J. L.; Linderman, R. J.; Lorenz, K.; Manley, J.; Pearlman, B. A.; Wells, A.; Zaks, A.; Zhang, T. Y. Green Chem. 2007, 9, 411–420.
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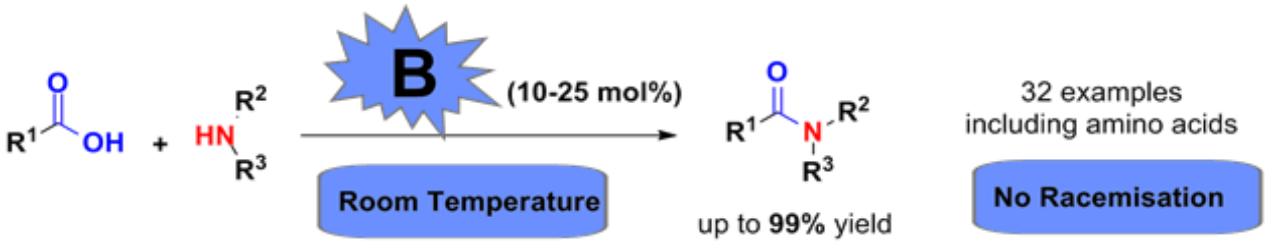
B
(10-25 mol%)
Room Temperature
up to 99% yield
32 examples
including amino acids
No Racemisation

P-045

Chiral $(NH)_2P_2$ Macrocyclic Iron(II) Complexes: Design and Application in the Highly Enantioselective Transfer Hydrogenation of Ketones

M. Sc. Raphael Bigler[1], M. Sc. Raffael Huber[1], Prof. Dr. Antonio Mezzetti[1]
[1]*ETH Zürich, Zürich, Switzerland*

Poster Session 1

In the past decade, great progress has been made to find cheap, environmentally benign 3d metal analogues as alternatives to expensive and often toxic precious metal catalysts, and iron is of central interest.[sup][1][/sup] However, a major problem still is the inherent lower stability of these complexes as the metal-ligand bonds are weaker if compared to their 4d and 5d analogues. To this end, we recently developed chiral tetradentate N_2P_2 macrocyclic ligands that give stable, diamagnetic iron(II) complexes by virtue of the macrocyclic effect.[sup][2,3][/sup] We show here that the corresponding bis(isonitrile) iron(II) complexes bearing a C_2-symmetric diamino $(NH)_2P_2$ macrocyclic ligand efficiently catalyze the asymmetric transfer hydrogenation of polar bonds of a broad scope of substrates (ketones, enones, and imines) in high yield (up to >99.5 %) and with excellent enantioselectivity (up to 99 % ee).[sup][4][/sup] The substrate scope includes challenging ketones like arylalkyl ketones containing bulky alkyl groups, ortho-substituted acetophenones, acetonaphthones, and acyl-substituted heterocycles, i.e. acyl pyridines and acyl thiophenes. Turnover frequencies of up to 1950 h[sup]-1[/sup] were achieved while keeping the catalyst loading low (generally 0.1 mol %). The ancillary isonitrile ligand (C-isonitriles and N-isonitriles were used) have a large and unprecedented influence on the activity and selectivity of the catalyst, which is exploited for the fine-tuning of the catalyst to achieve optimal results for specific substrates. Furthermore, preliminary tests support a homogeneous mechanism.
In sum, this is the first chiral iron(II) catalyst for the transfer hydrogenation of ketones that combines high activity and excellent enantioselectivity for a wide scope of substrates.

References:
[1] R. M. Bullock, Science 2013, 342, 1054.
[2] R. Bigler, E. Otth, A. Mezzetti, Organometallics 2014, 33, 4086.
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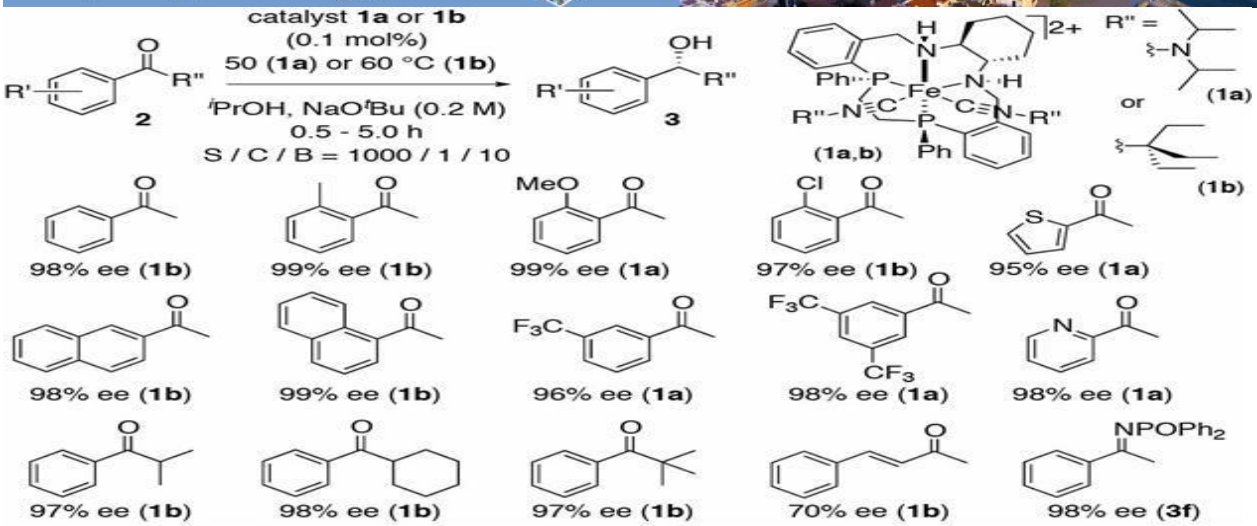
catalyst 1a or 1b
(0.1 mol%)
50 (1a) or 60 °C (1b)
iPrOH, NaOtBu (0.2 M)
0.5 - 5.0 h
S / C / B = 1000 / 1 / 10
2
3
(1a,b)
R" =
(1a)
or
(1b)
98% ee (1b)
99% ee (1b)
99% ee (1a)
97% ee (1b)
95% ee (1a)
98% ee (1b)
99% ee (1b)
96% ee (1a)
98% ee (1a)
98% ee (1a)
97% ee (1b)
98% ee (1b)
97% ee (1b)
70% ee (1b)
98% ee (3f)

P-046

Ruthenium(II)-Catalyzed C–H Activation with Isocyanates: Versatile Route to Phthalimides

Dr. Suman De Sarkar[1], Prof. Dr. Lutz Ackermann[1]
[1]*Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Göttingen, Germany*

Poster Session 1

Over the last few years ruthenium has emerged as a versatile alternative of commonly used expensive transition metals in C–H activation chemistry.[1] Along this line, ruthenium(II)-catalyzed cyclometalation followed by migratory insertion to C–C multiple bonds were well documented in the literature.[2] In contrast, the addition to polar C–Het multiple bonds is extremely rare in ruthenium-catalyzed transformations.[3] In consideration of the practical importance of C–H activations with synthetically-useful auxiliaries,[1b] we explored a convergent method for the imidation of easily accessible benzamides by C–H activation and addition to polar C–N multiple bonds of isocyanates.[4] Thereby, a novel route to synthetically challenging unsymmetrical heteroaromatic diamides was established as well.

References:
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2. S. I. Kozhushkov, L. Ackermann, Chem. Sci. 2013, 4, 886–896.
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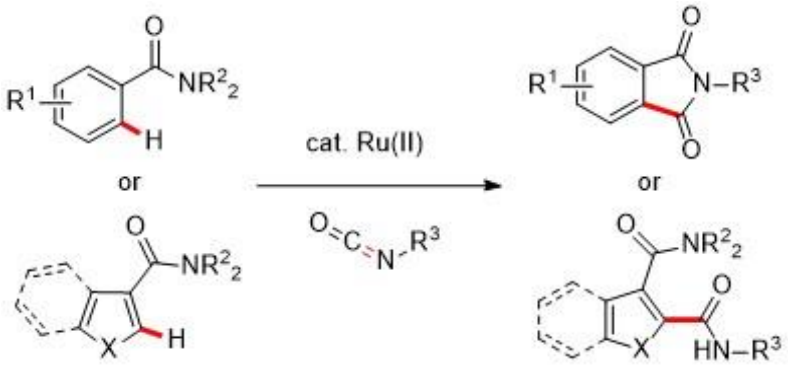

- **Versatile addition to C–N multiple bonds**
- **Neutral reaction conditions**
- **Convergent strategy offers wide substrate scope**
- **Readily functionalizable products**

P-047

Enantioselective Nickel-Catalyzed Hydrocyanation of Vinylarenes using Phosphine-Phosphite Ligands

Dr. Anna Falk[1], Prof. Dieter Vogt[1], Prof. Hans-Günther Schmalz[2]
[1]*University of Edinburgh, School of Chemistry, Edinburgh, UK* , [2]*University of Cologne, Department of Chemistry, Cologne, Germany*

Poster Session 1

The transition metal-catalyzed hydrocyanation of alkenes represents a highly attractive synthetic method from both an industrial and an academic point of view. Starting from olefins and HCN this reaction offers a fully atom economic access to branched (chiral) or linear nitriles, which represent highly versatile intermediates for the preparation of a wide variety of functionalized compounds. We have now succeeded in identifying a superior chiral phosphine-phosphite ligand L* [1] and in developing a practical procedure, which allows performing the Ni-catalyzed hydrocyanation of various vinylarenes, including heterocyclic systems, with unsurpassed enantioselectivities (up to 97% ee) and on a gram scale (Scheme 1).[2]
We further showed that the reaction can be performed using HCN itself or in situ sources like TMS-CN without significant loss of catalyst performance and selectivity. That makes the method attractive for industrial, as well as for smaller scale laboratory applications. The protocol was successfully applied in the multigram synthesis of enantiomerically enriched Ibuprofen and as a key step in the total synthesis of the natural products abiesesquin A and B.

References:
1. M. Dindaroğlu, A. Falk, H.-G. Schmalz, Synthesis 2013, 45, 527–535.
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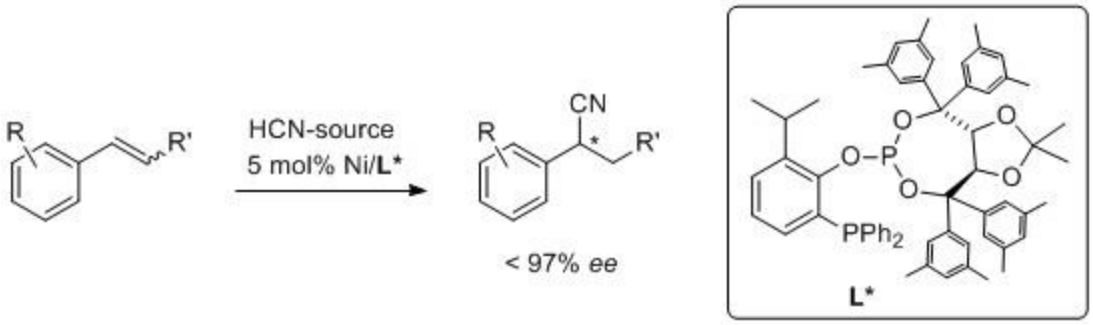

P-048

Molecular iron complex catalyzed amination of alcohol through borrowing hydrogen strategy

Mr. Tao Yan[1], Prof. Ben Feringa[2], Dr. Katalin Barta[3]

[1]Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands, [2]Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands, [3]Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands

Poster Session 1

Selective constructing C-N bond in an efficient way from abundant substrates to produce bulk and fine chemicals is a long-standing task for synthetic chemists. Besides classical organic method such as nucleophilic substitution, lots of catalytic pathways have been established. For example, hydroamination, cross-coupling, reductive amination and so on. Among which amination of alcohol through borrowing hydrogen[1] that starts from simple amines and alcohols and produces water as the only waste, is particular attractive for us. Until now, most works were done with precious transition metals based catalysts like Ru and Ir. A clear challenge emerged which is using alternative abundant metal based catalyst such as iron. Here we reported the first example[2] using molecular iron complex catalyzed amination of alcohol through borrowing hydrogen strategy. In this work, a wide scope has been studied, including monoalkylation of anilines and benzylamines, formation of 5-, 6-, 7-membered N-heterocycles from diols, synthetizing benzylamine derivatives from simple benzylalcohols and extra strategic synthesis cases study. What's more, reaction intermediates like aldehydes and imines have been observed from H NMR study which can prove the borrowing hydrogen pathway. Our future plan could be developing new cheap metal based catalyst which can conduct this reaction in a mild condition.

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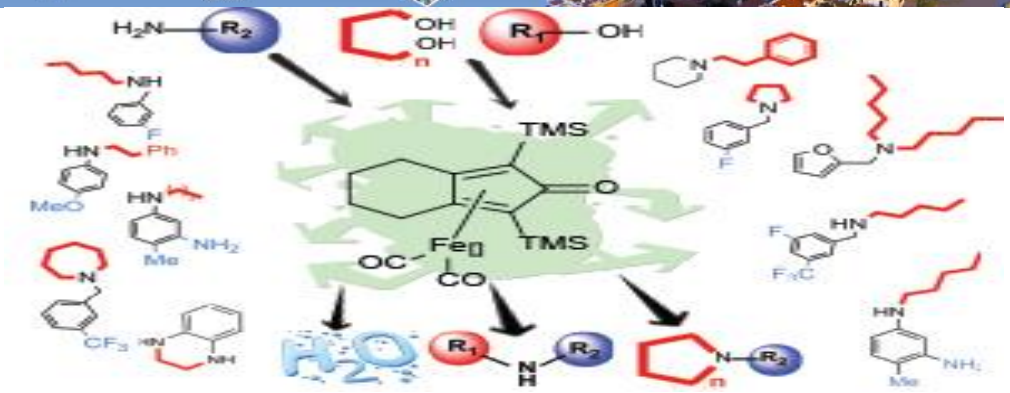
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P-049

Synthesis of Nitrogen Heterocycles by Narasaka-Heck Cyclisation

Miss Adele Faulkner[1], Dr James Scott[2], Dr John Bower[1]
[1]*University of Bristol, Bristol, UK,* [2]*AstraZeneca, Macclesfield, UK*

Poster Session 1

The palladium-catalysed Heck-type reaction of oxime esters can be used intramolecularly to form various heterocyclic compounds (including, pyrroles, pyridines and azaazulenes) and is known as the Narasaka-Heck reaction.[1] The catalytically controlled creation of new N-substituted stereogenic centres is an exciting opportunity for the Narasaka-Heck reaction. Studies within our group have employed oxime esters with pendant cyclic olefins to generated fused bicyclic heterocycles.[2] Initially my research has focused upon the extension of this methodology to the cyclisation of 1,1-disubstituted oxime esters. The scope of the oxime ester and olefin moieties have been examined, and a wide range of sterically and electronically distinct functionalities were tolerated in the cyclisation.[3]

Palladium catalysed 1,2-carboaminations of olefins are valuable but challenging processes and my recent research has focused on investigating new methods for these processes. An attractive strategy has been developed where oxidative initiation at electrophilic nitrogen occurs and cyclisation delivers the key palladium(II) intermediate. Gratifyingly, this intermediate can be directly trapped with a wide range of nucleophiles and a variety of carboamination protocols have been developed, including 1,2 -arylation, -vinylation and -alkynylation. Additionally, the palladium(II) intermediate can also be trapped by CO and then coupling to a nucleophilic partner enables access to a wider range of dihydropyrrole scaffolds. Here, aminoacylation and aminocarboxylation protocols have been developed. [4]

Palladium catalysed Narasaka Heck cyclisations of 1,1-disubstituted olefins and cascade cyclisations have been developed to synthesise a variety of functionalised dihydropyrroles.

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P-051

Synthesis of symmetrical diarylketones by cobalt-catalyzed carbonylation of organozinc compounds

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Poster Session 1

Diarylketones derivatives have attracted considerable interests as they are a common structural motif in natural products and important intermediates in biological, pharmaceutical and material compounds. Conventionally, diarylmethanones are prepared by Friedel-Crafts acylation reactions of aryl derivatives with acid anhydrides or acid halides[1] or by oxidation of diarylmethanols using oxidizing reagents.[2] However, those reactions need hash oxidation conditions or cannot tolerate many functional groups. During the past few decades, new approaches to synthesize these compounds were investigated by transition metals catalysts. Unsymmetrical diarylketones can be obtained by palladium-catalyzed carbonylative reaction of boronic acids and aryl halides in the presence of carbon monoxide[3] or by Heck-type reaction of aryl halides with aromatic aldehydes.[4] However, these methods are generally limited to aryl iodides and aryl boronic acids, whereas precious metal catalysts such as rhodium, palladium and nickel may be substituted by nontoxic and economical metals for sustainable chemistry. In continuation of our previous work on the synthesis of diarylketones from arylzinc reagents and aryl acyl chlorides or carboxylic anhydrides[5] we developed a new cobalt-catalyzed electrophilic carbonylation of arylzinc bromides using ethyl chloroformiate and N-formylsaccharin as the carbonylative sources. Under mild conditions, various diarylmethanones bearing different functional groups such as methoxy, methyl, ester, chlorine, fluorine, trifluoromethyl, thioether and vinyl were synthesized in moderate to excellent yields.

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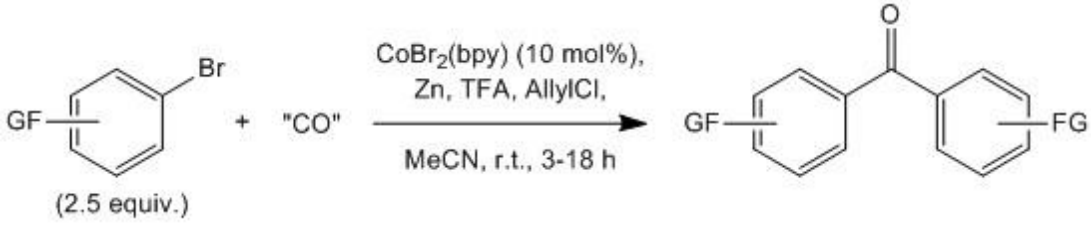

P-052

Cobalt-catalyzed reductive cross-coupling: user friendly method to synthesize functionalized molecules

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[1]*Ecole Polytechnique- CNRS, PALAISEAU, France*

Poster Session 1

Transition metal catalyzed C-C bond formation reactions have profoundly changed the methodologies in organic synthesis. Palladium remains the metal of choice for such transformations; nevertheless its cost has motivated the search for alternatives both in academic and industrial research groups. Several other metals such as nickel, iron, copper, and cobalt have been proposed with success in this research area. In our group, we have privileged the use of cobalt, which is eco-compatible and cheap. CoBr2 was shown to be very efficient even sometimes superior to other metals for carbon-carbon bond formation [1] allowing the synthesis of functionalized molecules under mild conditions.
We have reported several cobalt-catalyzed reductive cross-coupling reactions between two electrophiles [2] during the last past 10 years allowing selective C-C bond formation. This method avoids the pre-formation and handling of organometallic species. A suitable metallic reductant activates in situ the transition metal catalyst.
These methods are very straightforward and environmental friendly. It is efficient for the coupling of a large variety of functionalized organic halides (aryl, primary, secondary, and tertiary alkyls, vinyl) with different substituted compounds. Generally, good to excellent yields are obtained in presence of various functionalities.
In this communication, we will present some selected examples showing the scope, the efficiency and the regioselectivity of these reactions together with possible mechanisms based on experimental observations.

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P-053

Mechanistic Study of Palladium–Catalyzed Isomerization of Highly Substituted Allylic, Homoallylic and Alkenyl Alcohols

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Poster Session 1

Metal-catalyzed directed isomerizations of functionalized olefins are particularly attractive because, upon migration of a C=C bond, the substrates undergo refunctionalization in an overall redox neutral operation with no chemical waste generated. As part of our program directed toward the discovery of well-defined transition metal hydrides for isomerization reactions [1], we have disclosed a readily accessible palladium catalyst that isomerizes a variety of allylic, homoallylic and alkenyl primary and secondary alcohols into the corresponding carbonyl derivatives [2]. To the best of our knowledge, this is the first example of an isomerization catalyst that bridges the gap between allylic and alkenyl alcohols as well as between primary and secondary substrates.

Experimental and computational mechanistic investigations provide complementary and converging evidence for a chain-walking process consisting of repeated migratory insertion/β-H elimination sequences. The irreversible nature of the first migratory insertion across the C=C bond constitutes one of the key features of the proposed mechanism. Interestingly, the catalyst does not dissociate from the substrate in the isomerization of allylic alcohols, whereas it disengages during the isomerization of alkenyl alcohols when additional substituents are present on the alkyl chain. Finally, the effect of the bite angle of the chelating bis-phosphine ligands on the catalyst activity has been rationalized computationally.

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P-055

Formic acid as an alternative hydrogen source in ruthenium catalyzed transfer hydrogenation of olefins.

Mr Grzegorz Zieliński[1], Dr Cezary Samojłowicz[1], Mr Tomasz Wdowik[1], Prof Karol Grela[1]
[1]*Institute of Organic Chemistry PAS, Warsaw, Poland*

Poster Session 1

Catalytic olefin metathesis, as one of the most important methodologies of C-C double bond formation, does not need a particular introduction. Furthermore ruthenium alkylidene complexes were found not only as a great olefin metathesis catalysts[a] but they are well known in literature as active catalysts of numerous non-metathetic reactions.[b]
During our recent study on application of a new nitronate ruthenium complex 1 in olefin metathesis, we have noticed its unexpected non-metathetic activity. Depending on the conditions applied, the same complex promoted efficiently olefin metathesis, cycloisomerization, reduction of a carbonyl group, as well as isomerization of a C-C double bond.[c]
The interesting further results confirmed that complex 1 can also catalyze metathesis and transfer hydrogenation in one-pot sequence without isolation of the metathesis product. Moreover we proved that in this conditions many commercially available ruthenium alkylidene complexes (like Gru-II) can catalyze metathesis and transfer hydrogenation sequence or transfer hydrogenation depending on used substrate (Scheme 1). Methodology was tested on several olefins and more interesting results appeared. The methodology that was developed in our group allows for selective hydrogenation in mild conditions using formic acid instead of dangerous hydrogen gas and does not cleave the benzyl groups.[d]

Figure 1.

References
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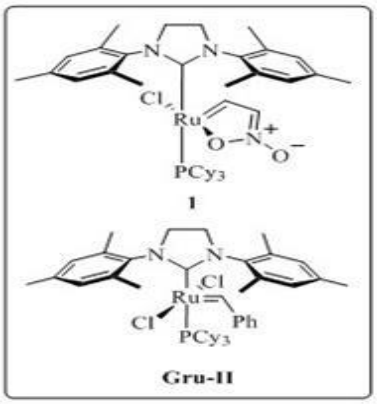
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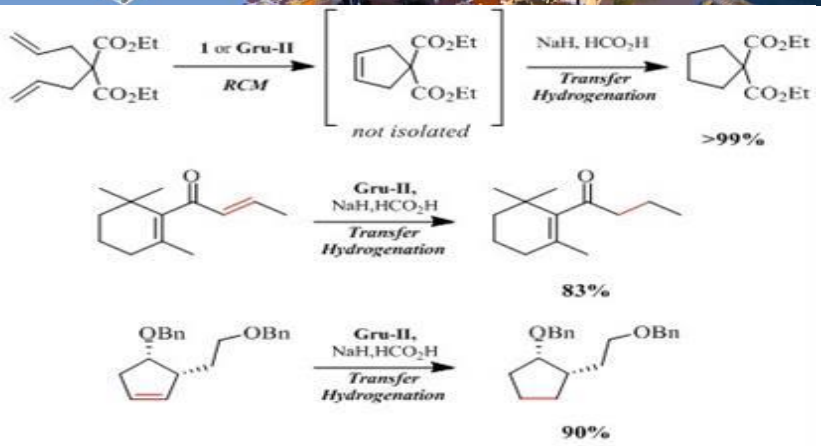
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NaH, HCO2H
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Hydrogenation
CO2Et
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>99%
O
Gru-II,
NaH,HCO2H
Transfer
Hydrogenation
O
83%
QBn
OBn
Gru-II,
NaH,HCO2H
Transfer
Hydrogenation
QBn
OBn
90%

P-056

Recent Advances in the Transition-Metal-Catalyzed C-S Bond Cross-Coupling Reaction

Dr. Chin-Fa Lee[1]

[1]*National Chung Hsing University, Taichung, Taiwan*

Poster Session 1

Sulfur-containing molecules are important skeletons in pharmacetical industry, organic synthesis and materials science. We have developed transition-metal-catalyzed strategy for the synthesis of aryl- and vinyl thioethers by using iron, and other metal sources (Eq. 1).[1] Thioesters are crucial building blocks for organic synthesis, and they have been utilized in acyl transfer reactions as the intermediates. The preparation of such molecules by copper-catalyzed,[2a] iron-catalyzed [2b] and metal-free [2c] conditions in the presence of the oxidants will be discussed (Eq. 2). The synthesis of thioesters through a DTBP-promoted reaction of methyl arenes with disulfides,[3] and more coupling reactions of thiols with heteroatoms will also be introduced.[4]

Faltan las referencias

P-057

An Alternate Approach toward Ferrocenyl Phosphapalladacycle Synthesis and its Application in the Kinetic Resolution of Racemic 5-alkylcyclohexenones

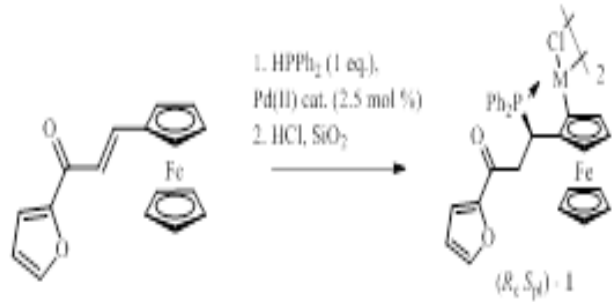
Mr Kennard Gan[1]
[1]*Nanyang Technnological University, Singapore, Singapore*

Poster Session 1

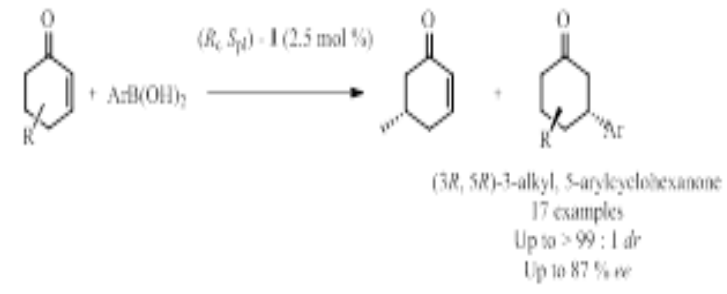
Ferrocenyl phosphines incorporating both central and planar chirality elements are widely acknowledged as dynamic ligands toward asymmetric synthesis. Recent developments in their synthetic strategies have led to the generation of diversified P-N, P-S, P-P and P-C bidendates. However, while these methodologies are highly selective and synthetically relevant, stoichiometric quantities of stereogenic promoter or optically pure starting materials are required.

We have developed an alternate approach toward the synthesis of ferrocenyl phosphapalladacycles (utilising achiral substrates) comprising of a two-step asymmetric hydrophosphination-diastereoselective C-H activation procedure (Scheme 1.1). The catalytic efficacy of the novel ferrocenyl phosphapalladacycle catalyst (Rc Spl) - 1 toward C-C bond formation was subsequently illustrated through the kinetic resolution of racemic 5-substituted alkylcyclohexenones affording trans-3-alkyl-5-arylcyclohexanones in good yields and excellent selectivities (Scheme 1.2). The results obtained suggest a balance between catalyst and substrate control. The basis of the observed synergistic control was further investigated with computational studies.

Scheme 1.1:



Scheme 1.2:



P-058

Computational Ligand Design-guided Enantio- and Diastereoselective Cycloisomerization

Dr Qian Peng[1], Mr. Robert Straker[1], Prof. Edward Anderson[1], Prof. Robert Paton[1]
[1]*University of Oxford, Oxford, UK*

Poster Session 1

Demand for higher efficiency, economy, and selectivity in the synthesis of novel molecular scaffolds drives organic chemistry. Cycloisomerizations represent ideal methods for the formation of cyclic organic molecules, as they can fulfil all of these criteria. Computational understanding the reaction mechanism of catalyst-control can provide potential ideas to rationalize and guide in the organic synthesis. In collaboration with experimental group (Prof. Edward Anderson in Oxford), we finally realized highly enantio- and diastereoselective catalysed cycloisomerizations of ynamides using new designed chiral phosphoramidite ligands.

Based on a relevant crystal structure of chiral phosphoramidite ligand [1], which clearly shown an Ar-Rh-P coordination. Detail mechanism study of Rh-catalyzed cycloaddition has performed to understand the key factor of enantioselectiviy by DFT calculation [2] with solvent correction. After evaluating more than 16 transition states, we were able to conclude that the reaction favours metallacyclopentene pathway and UP-Ptrans-Ene coordination. The binaphthol backbone of chiral phosphoramidite is responsible for π-π interaction with the ene-yne substrate, while the electronic withdrawing group on Arene of ligand has positive effect to increase enantioselectivity. Quite noteworthy are the mechanism could be different for the Rh catalysed intermolecular and intramolecular cycloadditions [3]. The results provide a crucial idea for designing new chiral ligands which were tested and proved by our collaborators. These studies set the stage for the development of further computationally-guided enantio- and diastereoselective catalyst systems.

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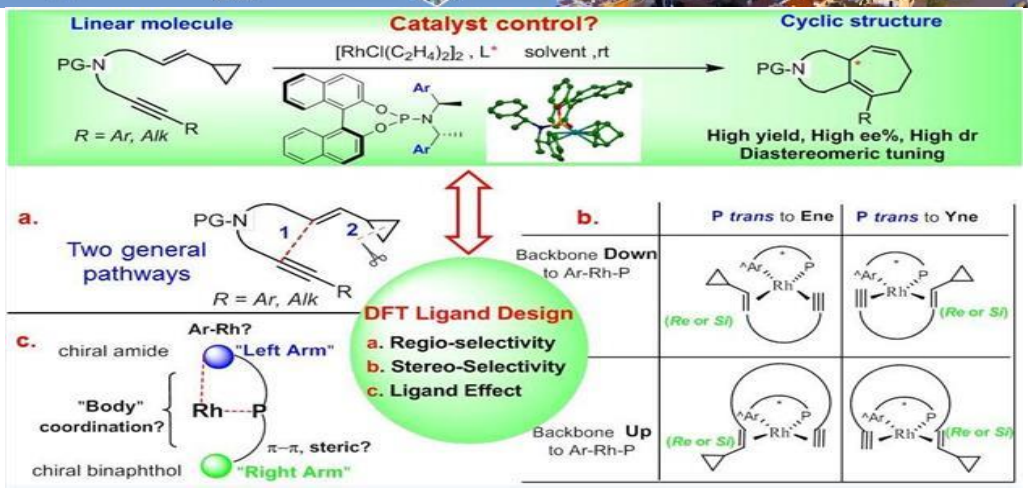
Linear molecule
Catalyst control?
Cyclic structure
PG-N
R = Ar, Alk
[RhCl(C2H4)2]2 , L*
solvent ,rt
High yield, High ee%, High dr
Diastereomeric tuning
a.
Two general pathways
b.
P trans to Ene
P trans to Yne
Backbone Down to Ar-Rh-P
Backbone Up to Ar-Rh-P
(Re or Si)
DFT Ligand Design
a. Regio-selectivity
b. Stereo-Selectivity
c. Ligand Effect
c.
Ar-Rh?
chiral amide
"Left Arm"
"Body" coordination?
Rh---P
π–π, steric?
chiral binaphthol
"Right Arm"

P-059

Well-defined Low Valent Cobalt Complexes for C–H Bonds Activation

Dr Marc Petit[1], Brendan Fallon[1], Sandrine Ventre[1], Dr Muriel Amatore[1], Dr Corinne Aubert[1]
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Poster Session 1

The last decade has seen an explosion of interest in C–H functionalization using more naturally abundant and cheaper metals such as cobalt. Of particular interest is the cobalt based quaternary system consisting of cobalt salt, phopshine, grignard and pyridine developed by Yoshikai to promote the addition of internal alkynes to aromatic imines through chelation-assisted C–H activation.[1] However, the use of bimetallic combinations as catalytic systems for direct C–H functionalization suffers limitations; The nature of the active catalytic species and the precise role of additives remain largely unknown. It is difficult to gain mechanistic insight due to the complexity of the reaction mixture. We reasoned that well-defined electron-rich cobalt catalysts could offer the possibility to achieve C–H functionalization without reducing agents or additives and thus allow us to address some of these issues. Based on our recent results published on the dimerization of arylacetylenes via a C–H activation/hydroalkynylation pathway using $Co(PMe_3)_4$ and $HCo(PMe_3)_4$ we postulated that these catalysts could have the potential to participate in the C–H activation/functionalization of aromatic imines.[2] In this communication we will show that using $Co(PMe_3)_4$ as catalyst we have developed an efficient and simple protocol for the C–H/hydroarylation of alkynes with an anti selectivity. Moreover, based on the simplicity of the catalytic system we were able for the first time to couple deuterium-labeling experiment and DFT calculations in order to shed light on the elusive black box of cobalt catalyzed C–H functionalization.[3]

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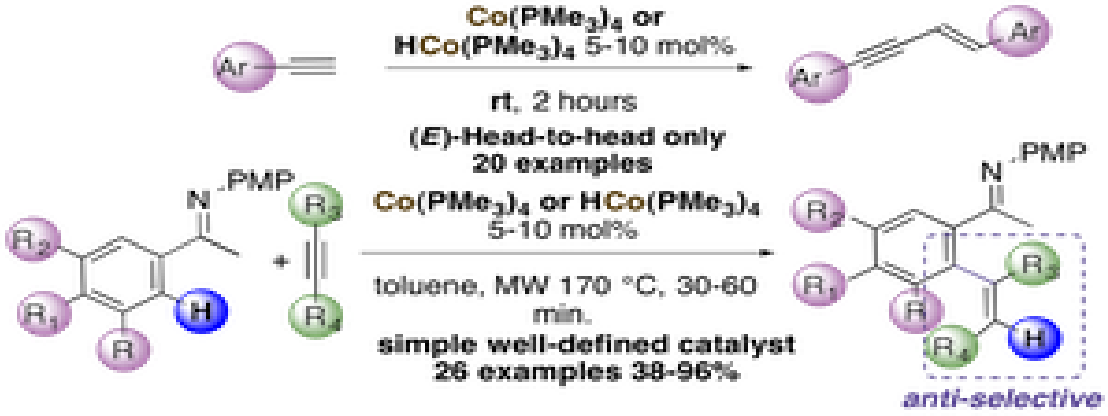

P-060

Catalytic Formation of Sodium Acrylate from CO2 and Ethylene

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Poster Session 1

The catalytic synthesis of acrylates from the cheap and abundant C1 building block CO_2 is an attractive target in academia as well as for industry. In fact, the catalytic synthesis of acrylates from CO_2 and ethylene was considered to be a dream reaction. In 2012, our group reported the first closed cycle for the formation of sodium acrylate (TON = 10) from CO_2, ethylene in a two-stage cycle that included an ethylene rich stage and a CO_2 rich stage.[1] Since then, the rational analysis of the possible side reactions, deactivation pathways and the choice of proper bases a gave access to an one-step catalysed process with TON up to 110.[2] Moreover, this procedure could also be extended to other alkenes.[2] In the same manner, it is possible to obtain sodium acrylate and other unsaturated carboxylic acid salts via a novel one-step palladium catalysed process. This methodology shows a higher base compatibility than the nickel system, which is crucial for a possible industrial process.

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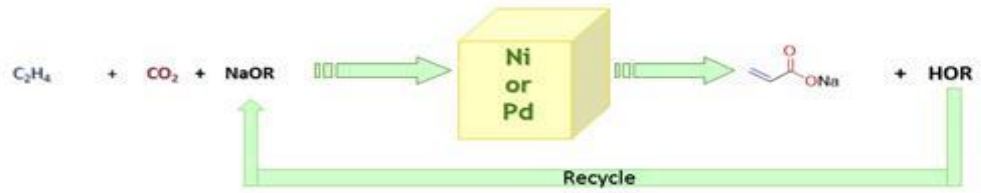

P-061

Recent Achievements about the Novel Radical Polymerization Initiated with Some Kinds of Organoboron Compounds

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Poster Session 1

The author has been continuing the research about many kinds of organoboron compounds as an initiator of radical polymerization, and the unique characteristic of these compounds can be understood by the author's few typical articles.1-6 On the other hand, Muraki's group used diethylmethoxyborane (DEMB) as a simple and effective initiator of living radical polymerization.7-9 This article describes the author's recent studies on the development of novel radical polymerization initiated with some kinds of organoboron compounds. The chemical structure of DEMB is shown in Scheme 1. Table 1 summarizes the results of the methyl methacrylate (MMA)-polymerization initiated with DEMB in tetrahydrofuran (THF) under air at 60 ℃. As can be seen in this table, the polymerization proceeded promptly under such reaction conditions. Noteworthy, the strong inhibition effects of 2,6-di-tert-butyl-p-cresol (BHT) as a radical inhibitor and 1-dodecanethiol (1-DT) as a radical chain transfer agent suggested that the polymerization proceeds via a radical pathway.

References:

1 Kanno, S. , Japanese Patent, Patent Number 3692934.
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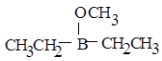

Scheme 1. Diethylmethoxyboran (DEMB)

Table 1. Effect of Additives on the Polymerization of MMA Initiated with DEMB[a]

Time (hr)	Additive (0.282mmol)	Conversion (%)	$\overline{Mn}^{b}$	$\overline{Mw}/\overline{Mn}^{b}$
1	BHT	0.0	—	—
2	BHT	0.0	—	—
3	BHT	0.0	—	—
4	BHT	0.0	—	—
1	HQ	17.4	40000	2.08
2	HQ	28.4	41000	1.60
3	HQ	33.0	37000	1.60
4	HQ	40.0	31000	2.33
1	1-DT	0.0	—	—
2	1-DT	0.0	—	—
3	1-DT	1.0	—	—
4	1-DT	17.5	—	—
1	(Nil)	18.3	47000	1.54
2	(Nil)	23.5	56000	1.61
3	(Nil)	36.8	51000	1.71
4	(Nil)	49.7	37000	1.71

[a]MMA 4.7 mmol, DEMB 0.047 mmol, THF 1 ml, under air, 60 °C.
[b]Determined by GPC with standard polystyrenes (eluent:THF).

P-062

Gold-Catalyzed Cycloisomerization Reactions of Functionalyzed Cyclopropyl Alkynes: An Overview

Dr. Enrique Aguilar[1], Dr. Jesús M. Fernández-García[1], Dr. Alexandra Pérez-Anes[1], Lic. Laura Fernández-García[1], Grad. Eva M. Otero[1], Dr. Patricia García-García[2], Dr. Manuel A. Fernández-Rodríguez[3]
[1]Universidad de Oviedo, Oviedo, Spain, [2]Universidad de Alcalá, Alcalá de Henares, Spain, [3]Universidad de Burgos, Burgos, Spain

Poster Session 1

Gold catalysis has been recognized as a powerful and versatile tool to induce molecular complexity by enabling the mild activation of unsaturated C-C bonds (alkynes, alkenes, allenes), due to the soft and carbophilic Lewis acidic nature of Au(I) cations.[1] Particularly, alkynylcyclopropane derivatives have been claimed as suitable and active substrates for gold-catalyzed transformations.[2] In this communication the scope, limitations and regioselectivity issues of gold-catalyzed cycloisomerizations involving functionalyzed cyclopropyl alkynes (carboxylic acids, carboxamides or cyclopropylmethanols) will be presented. Thus, a synthesis of oxepin-2-ones and azepin-2-ones from alkynylcyclopropanecarboxylic acid derivatives has been developed.[3] This novel cycloisomerization cascade process consists of a nucleophilic addition followed by a cyclopropane ring-opening, where both a donor and an acceptor groups are required as substituents of the cyclopropane ring, as confirmed by isolation of a bicyclic lactone intermediate.[4] Additionally, 4-methoxy-6-oxo-4-enenitriles have been obtained from primary alkyl-substituted alkynylcyclopropanecarboxamides. Finally, a regioselective gold-catalyzed cycloisomerization takes place on alkynylcyclopropylmethanols at low temperature leading to oxabicyclo[4.1.0]heptenes; notably, dihydropyranones are selectively formed under thermal reaction conditions (85 ºC).[5]

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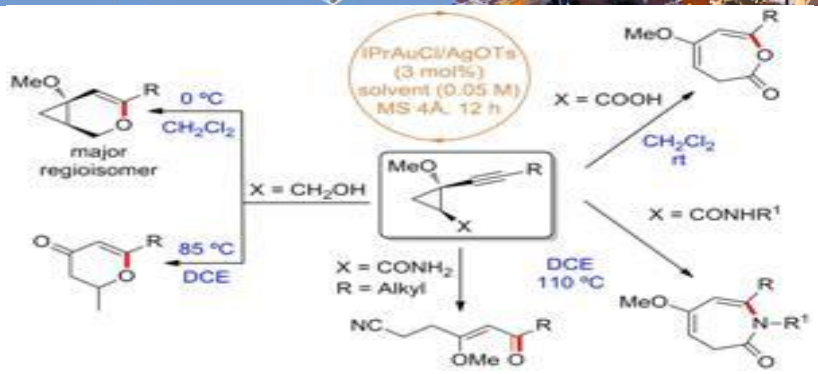

IPrAuCl/AgOTs
(3 mol%)
solvent (0.05 M)
MS 4Å, 12 h
MeO
R
O
major
regioisomer
0 °C
CH2Cl2
X = CH2OH
85 °C
DCE
X = COOH
CH2Cl2
rt
X = CONHR1
X = CONH2
R = Alkyl
DCE
110 °C
NC
OMe
N–R1

P-063

Hydrogen Bond-Controlled meta-Selective C-H Borylation of Aromatic Compounds

Prof. Dr. Yoichiro Kuninobu[1,2], Ms. Haruka Ida[1], Dr. Mitsumi Nishi[1,2], Prof. Dr. Motomu Kanai[1,2]
[1]The University of Tokyo, Tokyo, Japan, [2]ERATO, Japan Science and Technology Agency (JST), Kanai Life Science Catalysis Project, Tokyo, Japan

Poster Session 1

Regioselective carbon-hydrogen (C-H) bond transformations comprise one of the most efficient and ideal methods for synthesizing organic molecules. The presence of many C-H bonds in organic molecules makes regioselective C-H transformations difficult and thus directing groups are usually used to control regioselectivity, especially ortho-selectivity. Here we present a meta-selective C-H borylation of aromatic compounds using a newly designed catalytic system (eq 1).[1] In this system, hydrogen-bonding between the hydrogen donor moiety of a ligand and the functional group of the substrate controls regioselectivity. ^{1}H NMR studies and control experiments support the participation of hydrogen bonds for inducing regioselectivity. Reversible direction of the catalyst through hydrogen bonds is a versatile concept for regioselective C-H transformations.

Reference:

1. Y. Kuninobu, H. Ida, M. Nishi, M. Kanai, submitted for publication.

P-064

Nickel catalysed deprotonative cross coupling reactions: a valuable alternative to palladium.

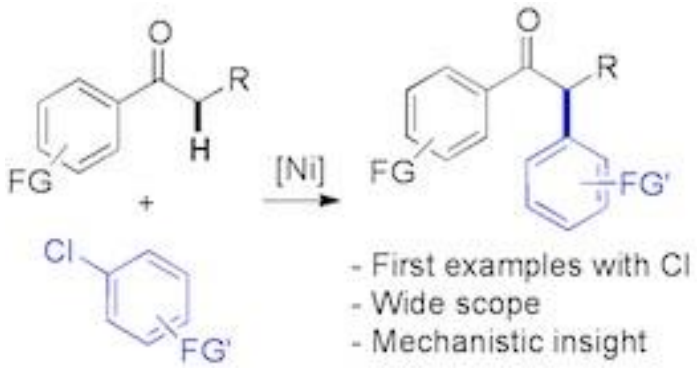
Mr. Enrico Marelli[1], Dr Josè Fernàndez-Salas[1], Dr. David Cordes[1], Prof. Alexandra Slawin[1], Prof. Steven Nolan[1,2]

[1]*University of St Andrews, St Andrews, UK* , [2]*King Saud University, RIyadh, Saudi Arabia*

Poster Session 1

The functionalization of C–H bonds is potentially the most atom economical method for bond formation. The use of pro-nucleophiles bearing acidic C–H bonds, such as organic carbonyl derivatives, is established in Pd catalysis, and highly efficient methodologies have been reported. However, the use of a more Earth-abundant element, such as Ni, represents a crucial goal for synthetic chemists from an economical and environmental perspective. Our recent work disclosed the high activity of the [Ni(NHC)(cinnamyl)Cl] precatalyst family (NHC = N-heterocyclic carbene) in the ketone arylation reaction; this methodology delivers the coupling products in good to excellent yields using a wide variety of challenging substrates. The use of well-defined precatalysts allowed us to investigate the mechanism of this transformation, by isolating the activation products. Our results suggest that a Pd-like, Ni(0)/Ni(II) mechanism is active. This methodology has been further optimised for the synthesis of a key intermediate towards industrially relevant target molecules.

Intrigued by the efficiency of our system, we tested it in the highly challenging arylation of benzophenone-derived benzilymines. Arylation at a benzylic position is much more requiring than the ones discussed above, due to the low acidity of the targeted C–H bond, and only a few examples of such reactivity are reported using Pd. The methodology we developed is competitive with the Pd-based reports, and afforded high yields of an array of (diaryl)methylimines. This is the first example of Ni-catalysed deprotonative cross coupling of a non-activated pronucleophile.

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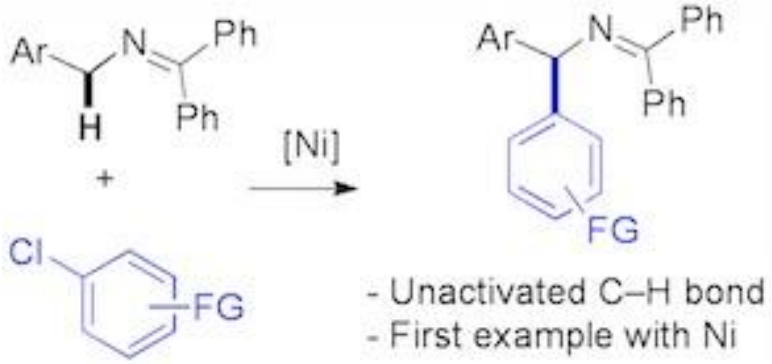
Ar
N
Ph
H
Ph
+
[Ni]
Cl
FG
Ar
N
Ph
Ph
FG
- Unactivated C–H bond
- First example with Ni

P-065

Asymmetric Synthesis of Versatil Benzylic Boronic Esters through a Borylation-Aromation Process

Dr. Alejandro Parra[1], Carlos Jarava[1], Aurora López[1], Fabio Cruz[1], Dr. Mariola Tortosa[1]
[1]*Universidad Autónoma de Madrid, Madrid, Spain*

Poster Session 1

Para-Quinone methides (p-QMs)[1] have been known as reaction intermediates for more than a century. They consist of a cyclohexadiene moiety in para-conjugation with a carbonyl group and an exo-methylene component. As a result of the intrinsic electrophilic reactivity of p-QMs, highly reactive transient p-QM species generated in situ are implicated in many chemical, medicinal, and biological processes. However, p-QMs have been scarcely used as starting materials in asymmetric catalysis.[2]
Recently, our group has been focused on the design of new copper-catalyzed borylation reactions.[3] In this context, we envisioned the synthesis of chiral diarylmethines through the copper-catalyzed borylation-aromatization of p-quinomethanes. The products are enantiomerically enriched dibenzylic boronates that can be transformed into important chiral diarylmethines derivatives (Scheme 1).

Scheme 1

Acknowledgements: We acknowledge the European Research Council (ERC) for the Starting Grant project DAUBOR (337776).

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P-066

Unexpected Syn-Steresoselective Epoxide Ring Opening via Carbenoid Insertion Catalyzed by CpRu Complexes

PhD Thierry Achard[1], PhD Cecilia Tortoreto[2], Assistant Prof. Amalia I Poblador-Bahamonde[2], Research Assistant Laure Guénée[2], Prof. Thomas Bürgi[2], Prof. Jérôme Lacour[2]

[1]*Strasbourg University, Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), Strasbourg, France,* [2]*University of Geneva, chemistry department, Geneva, Switzerland*

Poster Session 1

CpRu complexes are interesting alternatives to copper and dirhodium species for the catalyzed decomposition of diazo compounds.[1] Our group has recently shown that combinations of $[CpRu(CH_3CN)_3][PF_6]$ and diimine ligands catalyze the decomposition of α-diazo-β-ketoesters and allow further condensation, O-H[2] and original 1,3-C-H insertion reactions.[3]

In a recent development, we describe that metal carbenes undergo three-atoms insertions into a large variety of epoxides.[4] Novel 1,4-dioxene motifs (1) are afforded as single regio- and stereoisomers. The process is only possible through ruthenium cyclopentadienyle catalysis as, under Rh(II)-mediated reactions, the corresponding alkenes 2 are predominantly obtained.[5] Mechanistic insights will be given for this reaction; the effective enantiospecificity and syn-stereoselectivity for the opening will be particularly discussed

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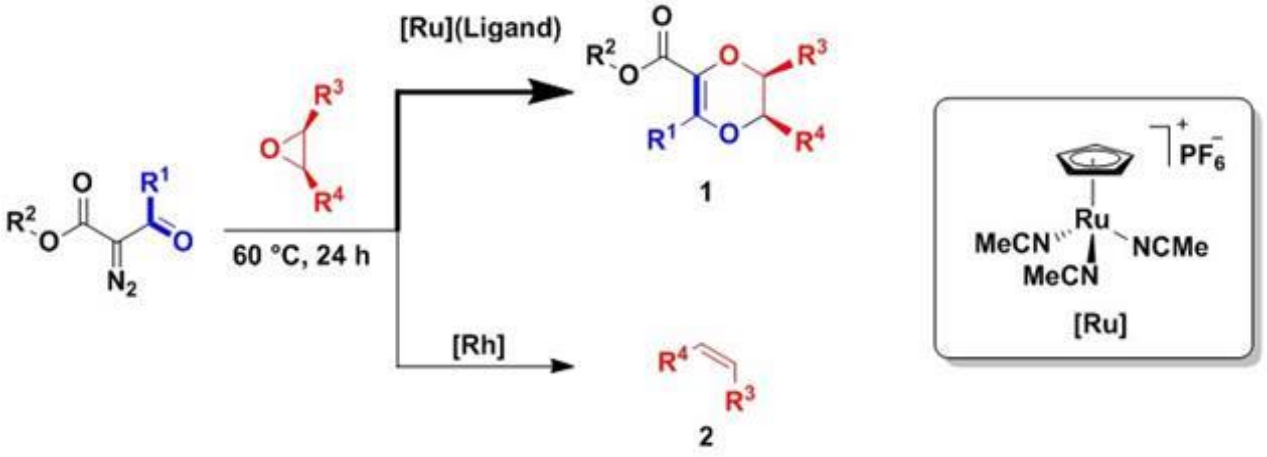

[Ru](Ligand)
60 °C, 24 h
[Rh]
1
2
[Ru]
MeCN
NCMe
MeCN
PF6

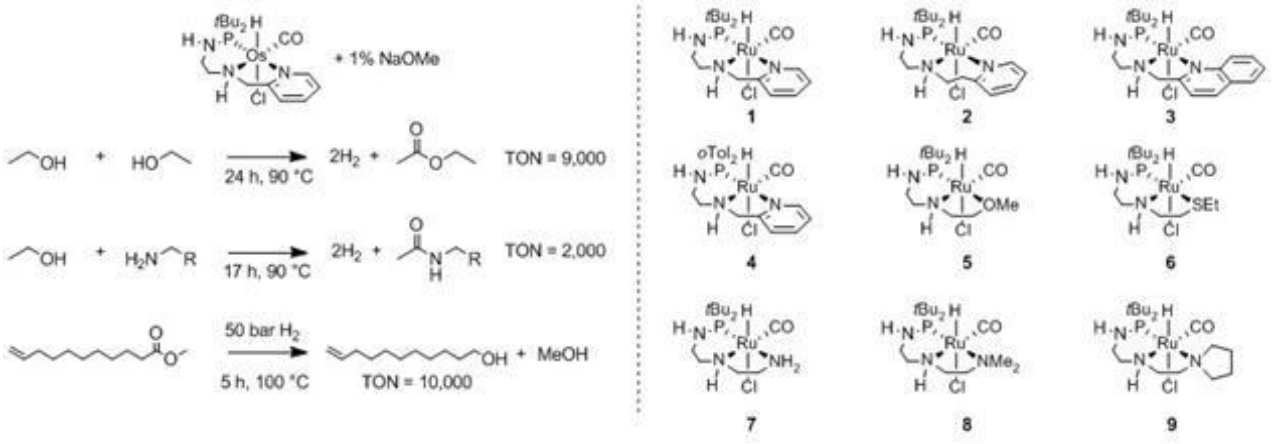
P-067

Selective dehydrogenative coupling of alcohols and hydrogenation of esters

Prof. Dmitri Goussev[1]
[1]*Wilfrid Laurier University, Waterloo, Canada*

Poster Session 1

Our recently reported OsHCl(CO)[PyNNP-tBu] (J. Am. Chem. Soc. 2015, DOI: 10.1021/ja512389y and PCT Application WO 2014/139030) is arguably today's best catalyst for the title reactions (see examples in the Figure included with this Abstract). This study has been extended to investigate the structure, properties, and catalytic activity of a series of related ruthenium complexes. The experimental and computational results will be presented and discussed.



P-069

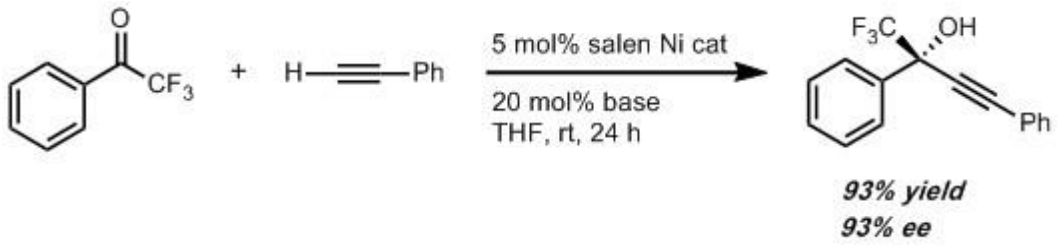
Nickel-Catalyzed Enantioselective Alkynylation of Trifluoromethyl Ketones

Dr. Sukwon Hong[1], Mr. Minsung Park[1], Ms. Jiyun Kim[1], Mr. Yongmin Lee[1], Ms. Woo-ok Jung[1], Dr. Jongwoo Park[2]

[1]*School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Buk-gu, South Korea,* [2]*Department of Chemistry, University of Florida, Gainesville, USA*

Poster Session 1

Chiral cooperative catalysis enabling simultaneous activation of both an electrophile and a nucleophile has emerged as an elegant strategy in catalytic asymmetric synthesis. In our laboratory, a series of novel hydrogen-bond functionalized salen-transition metal catalysts have been developed to facilitate bimetallic or bifunctional activation of both reaction partners. Herein, we wish to report that novel functionalized salen Ni complexes are highly efficient catalysts for the enantioselective direct alkynylation of trifluoromethyl ketones, affording enantioenriched propargyl alcohol products in high yields and enantioselectivities. The current methodology is operationally simple and allows for the substoichiometric use of base. Ligand synthesis, catalyst/reaction optimization, substrate scope study results will be discussed in detail in the presentation.



P-070

Computational Investigations on Catalytic Copper-Mediated Functionalization Processes from Diazo Compounds

Dr. Maria Besora[1], Prof. Feliu Maseras[1,2]

[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, Spain*

Poster Session 1

Coinage-metal complexes have been experimentally used to catalyze the transfer of carbene units from diazo compounds to different types of nucleophiles, notably by the group of Pérez that has developed catalysts with the tris(pyrazolyl)borate or N-heterocyclic carbene based ligands to functionalize a variety of organic compounds.[1,2] This approach has been proven to be very successful as it has even allowed the functionalization of methane.[3] The general reaction scheme presented in the Figure, consists on reaction of the catalyst with the diazo compound to generate and electrophilic metallocarbene. This species will react with a nucleophile to generate a new value-added product.

We have computationally investigated the reaction mechanisms for which a variety of such processes take place.[2,4,5] Our calculations provide information on the nature of the intermediates, the different roles of the catalyst as well as the other species present in the reaction media.

References:

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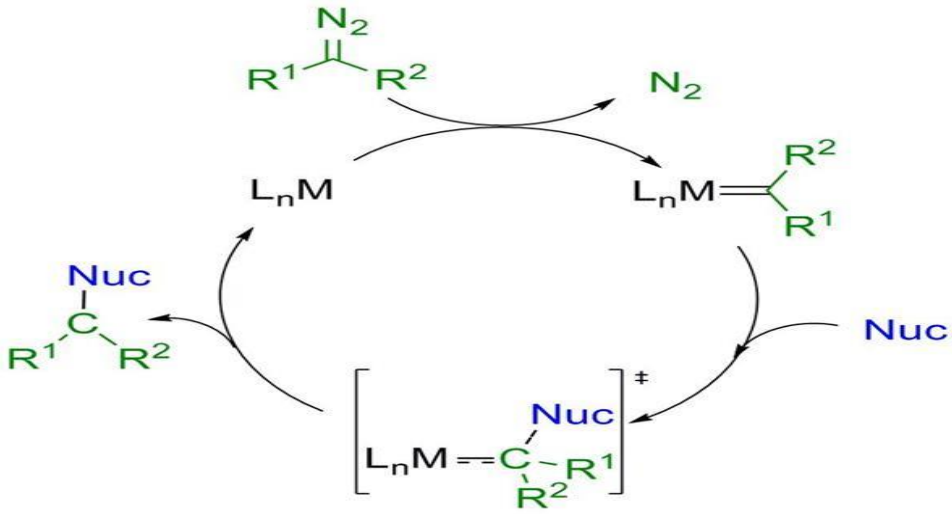
N2
R1
R2
N2
LnM
LnM
R2
R1
Nuc
Nuc
R1
C
R2
Nuc
LnM
C
R1
R2
‡

P-071

Rhodium-Catalyzed Intermolecular Reaction of 1-Naphtoeic Acids with Internal Alkynes Leading to Perinaphthenones

Dr. Takahide Fukuyama[1], Mr. Taiki Sugimori[1], Prof. Ilhyong Ryu[1]
[1]*Osaka Prefecture University, Osaka, Japan*

Poster Session 1

Polycyclic aromatic compounds have attracted much attention due to their presence in many optoelectronically and biologically active compounds. We recently reported that decarbonylative C-H arylation of 2-aryloxybenzoic acids to give dibenzofurans was effectively catalyzed by rhodium complexes.[1] We also reported that rhodium-catalyzed intramolecular C-H acylation took place when 2-arylbenzoic acids was used as the substrate, which gave fluorenones. Herein we will report rhodium-catalyzed cycloaddition reaction of 1-naphthoic acids with internal alkynes. When the reaction of 1-naphthoic acids with internal acetylenes in the presence of rhodium catalyst was carried out, C-H activation/cyclization took place at a peri-position to give perinaphtenone derivatives in good yields.

References:
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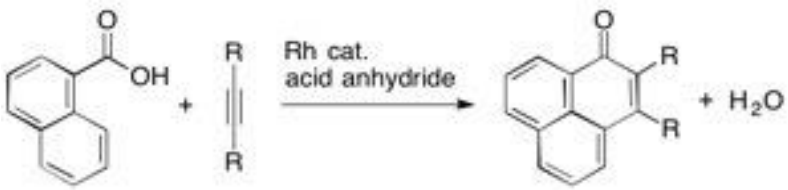

P-072

Norbornadiene as a building block for the synthesis of linked benzazocinones and benzazocinium salts through carbopalladated intermediates.

Dr Jose A. Garcia-Lopez[1], Dr Roberto Frutos Pedreño[1], Prof. Isabel Saura-Llamas[1], Prof. Jose Vicente[1], Dr. Delia Bautista[2]

[1] *Facultad de Química, Universidad De Murcia, Murcia, Spain,* [2]*SAI, Universidad de Murcia, Murcia, Spain*

Poster Session 1

The insertion of unsaturated molecules such as alkenes or alkynes into the reactive Pd–C bond of metallated species has become a tremendously useful and versatile tool in organic synthesis, leading to both stoichiometric[1] and catalytic[2] methods for the functionalization of the unsaturated substrates. In this work we present the double carbopalladation of norbornadiene through the insertion of both double bonds into the Pd–C bond of six-membered palladacycles, giving rise to new norbornene-linked cyclometallated complexes (2a, Scheme 1). The Pd–C bond present in these complexes is still reactive towards RNC or CO affording larger metallacycles in the case of RNC (3a, Scheme 1). In the appropriate conditions, the organometallic intermediates can decompose to give the corresponding norbornene-linked eight-membered double amidinium salts (4a, Scheme 1) or lactams (5a and 5b, Scheme 1) and Pd(0). Interestingly, the regiochemistry of the insertion products is highly dependant on the nature of the starting palladacycle. Further catalytic development of these reactions is currently underway in our group.

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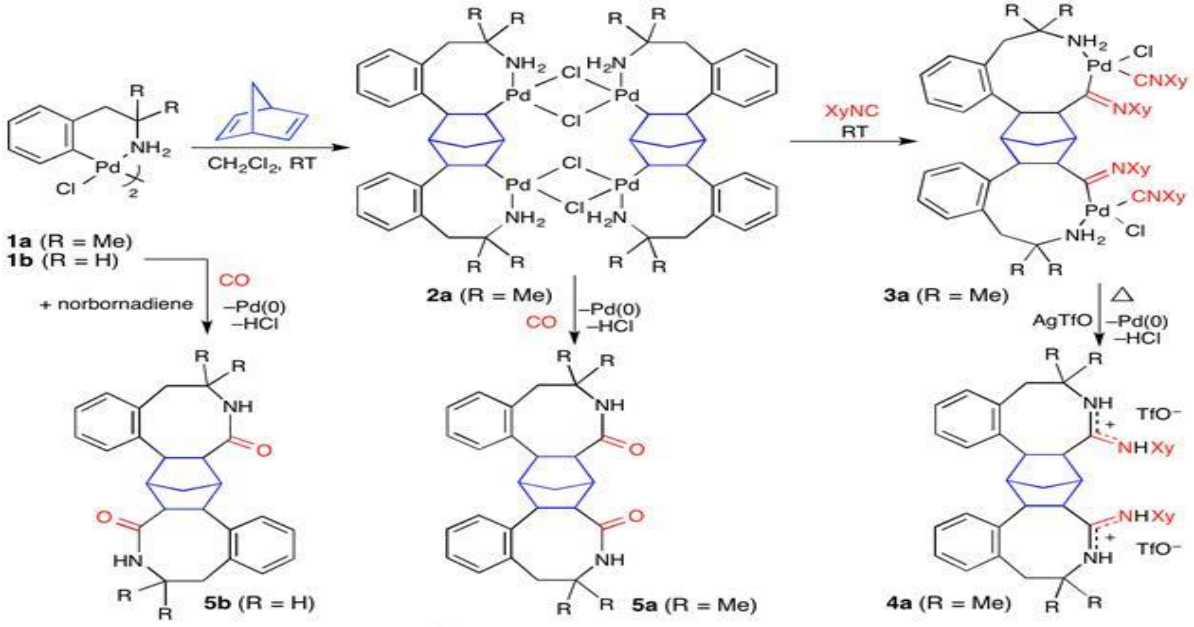
CH2Cl2, RT
XyNC
RT
1a (R = Me)
1b (R = H)
+ norbornadiene
CO
–Pd(0)
–HCl
2a (R = Me)
3a (R = Me)
AgTfO
△
5b (R = H)
5a (R = Me)
4a (R = Me)
TfO⁻

P-073

Mild and efficient trifluoroethylation of aromatic and heteroaromatic systems via C-H functionalization and transition metal catalyzed C-H activation

Dr. Zoltán Novák[1], Mr. Balázs Tóth[1], Dr. Szabolcs Kovács[1], Mr. Gergő Sályi[1], Mr. Gábor Borsik[1]
[1]*MTA-ELTE Lendület Catalysis and Organic Synthesis Research Group, Eötvös University, Institute of Chemistry, Budapest, Hungary*

Poster Session 1

The fluorous functional groups (mainly trifluoromethyl, trifluoromethoxy, trifluoromethylthio) are often used in medical chemistry. Although, several efficient methodologies were developed for the introduction of these functional groups, few synthetic tools are available for trifluoroethylation. Recently several cross-coupling methods were developed using trifluoroethyl iodide to introduce the trifluoroethyl group into the aromatic molecules, but only few examples exist on the direct C-H functionalization of aromatic and heteroaromatic systems.
In our research, we developed an efficient C3 selective trifluoroethylation process for indoles using a new stable hypervalent iodonium salt reagent.[3] We successfully utilized the powerful trifluoroethylating reagent in palladium catalyzed C-H activation for the access of diverse trifluoroethylated compounds. The introduction of 2,2,2-trifluoroethyl group into organic molecules performed efficiently at room temperature in 1-3 hours and provided new fluoroalkylated aromatic compounds with high yields (75-95%).

P-075

Biomimetic catalytic activities of copper (II) ferrocenecarboxylate complexes with nitrogen based ligands as catechol oxidase and phenoxazinone synthase and for oxidative coupling of 2,6-dimethylphenol

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Poster Session 1

Copper is one of the most important metals, beside Fe and Zn, present in several metalloenzymes and is involved in a large number of biological functions including enzyme-catalyzed reactions [1]. Binary and ternary copper carboxylate complexes have been used as biomimetic of copper containing enzymes.
As part of our ongoing research on the study of biomimetic activities of copper (II) carboxylate complexes with biologically important nitrogen based ligands, we report here the results of our studies on the synthesis and oxidase catalytic activities of copper(II) complexes of ferrocenecarboxylate with nitrogen donor ligands pyrazole and 1,2-dimethylimidazole. The complexes, bis(ferrocenecarboxylato) tetrakis(pyrazole) copper(II) (1) and cis-bis (ferrocenecarboxylato) bis(1,2-dimethylimidazole) copper(II) (2) have been prepared from the reaction of tetrakis(ferrocenecarboxylato) bis(tetrahydrofuran) dicopper(II) and the appropriate base. Based on the spectral results for complex (1), the Cu(II) ion is coordinated in the plan with four nitrogen atoms of pyrazoles and the axial sites are occupied by oxygen atoms from two ferrocenecarboxylato groups to yield Cu[N]sub4+ O_2 chromophore. We had previously determined crystal structure of complex (2) by X-ray crystallography. In this complex the copper ion is in a cis- square-planar environment consisting of two imidazole nitrogen atoms and a carboxylate oxygen atom from each ferrocenecarboxylato ligand. The second oxygen atoms of the carboxylate functionalities are involved in weak interactions with the copper ion in the axial positions.
The biomimetic catalytic oxidase activities of complexes 1 and 2 toward the aerobic oxidations of 3,5-di-tert-butylcatechol (3,5-DTBC) to 3,5-di-tert-butyl-o-benzoquinone (3,5-DTBQ) (catecholase activity), and o-aminophenol (OAP) to o-amino-3H-phenoxazine-3-one (APX) (phenoxazinone synthase activity) have been studied and the results will be presented. In addition, the results of the catalytic activities of these complexes for C-O polymerization or C-C dimerization coupling of 2,6-dimethylphenol (DMP) will be presented

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P-076

Gold(I)-Catalysed Dehydrative Formation of Ethers From Benzylic Alcohols and Phenols

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Poster Session 1

The formation of C-O bonds has emerged as a major objective in the construction of pharmaceutical compounds.[1] Disadvantages of traditional procedures (e.g. multiple steps, low atom economy) have challenged chemists to develop novel and greener processes. The most notable approach involves the direct activation of alcohols for nucleophilic substitution.[2] π-Activated alcohols (e.g. allylic, propargylic, benzylic) are now commonly used as sources of "proto-electrophiles" in metal-catalysed procedures.[3] The rapidly growing field of homogeneous gold catalysis has now extended to these dehydrative reactions.[sup]4, 5[/sup] Our group has reported the synthesis of NHC-gold(I) complexes (NHC = N-heterocylic carbene) that have shown good catalytic activity in various transformations.[sup]6, 7[/sup]

We have demonstrated that [Au(IPr[sup]Cl[/sup])(CH_3CN)][BF_4] (IPr[sup]Cl[/sup] = 4,5-dichloro-1,3-bis(2,6-diisopropyl-phenyl)-imidazol-2-ylidene) is a highly effective catalyst for the synthesis of unsymmetrical ethers from readily available phenols and secondary benzylic alcohols.[8] The optimised methodology proceeds under mild reaction conditions and the formation of side-products is suppressed. The synthetic utility is exemplified by forming a range of ethers with various substituents. In addition to providing access to new products, this methodology provides a further example of the remarkable chemoselectivity possible by employing well-defined NHC-gold(I) catalysts.

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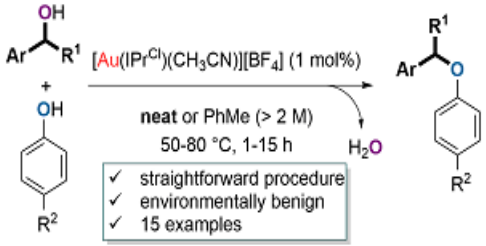

P-077

Stereoselective synthesis of novel chiral cyclopentane scaffolds

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[1]*AstraZeneca Sweden, Mölndal, Sweden*

Poster Session 1

The cyclopentane ring system is an important molecular framework that encounters frequently in both pharmaceuticals and natural products. Therefore, new synthetic approaches for the stereoselective synthesis of cyclopentane scaffolds are of high importance in medicinal chemistry. The heart of our strategy is a diastereoselective Heck reaction of cyclopentene 2, where the approach of the organometallic species should be fully controlled by the remote amine group. Substrate 2, which was prepared in a few steps from (+)-Vince lactam 1, was therefore decorated with different protecting groups on the amine functionality and their impact on the stereochemical outcome was compared in a model reaction. In this study, 2,5-dimethylpyrrole showed excellent diastereoselectivity for both aryl and vinyl electrophiles in the designated Heck reaction. The scope of the reaction was validated by a series of different examples.
Cyclopentene 3 depicts a valuable intermediate for several important structures in medicinal chemistry like γ-amino acids or carbocyclic nucleosides. Therefore, we performed different subsequent transformations of 3 including reductions and deprotection of the amine. During this studies we developed a new methodology for the stereoselective hydrogenation of α,β-unsaturated esters in the presence of a 2,5-dimethylpyrrole protecting group, which illustrates an elegant entry to cyclic γ-amino acids.

References:
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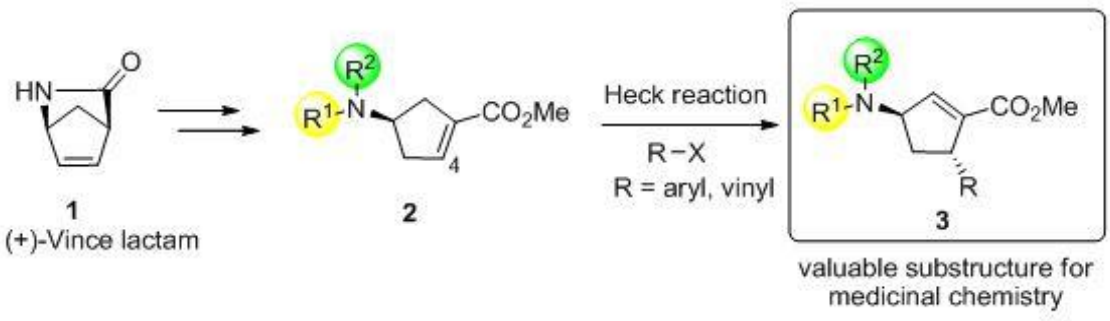

P-080

Palladium-Catalyzed Carbonylations using Paraformaldehyde as a CO Source

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[1]*Leibniz Institute for Catalysis (LIKAT), Rostock, Germany*

Poster Session 1

The functionalized aldehydes represent important class of compounds that are widely used in organic synthesis as versatile intermediates. In addition, they are produced on larger scale in the pharmaceutical, agrochemical and fine chemical industries as valuable building blocks. In recent years palladium-catalyzed coupling reactions have become a “true power” tool for organic synthesis. In this regard, carbonylative coupling reactions have become of importance. Unfortunately, the use of toxic CO and the need for high pressure infrastructure refrain organic chemists to apply these methodologies more often. Hence, there exists significant interest in alternative procedures. In this context, Manabe and co-workers reported an interesting palladium-catalyzed reductive carbonylation of aryl halides using N-formylsaccharin and phenyl formate as CO source [1]. Moreover, Liu and co-workers reported the Pd/C-catalyzed direct formylation of aromatic iodides to aryl aldehydes using CO2 and silanes [2]. Herein, we report the first successful application of readily available paraformaldehyde in a CO gas-free synthetic protocol for the Pd-catalyzed carbonylations of aryl bromides [3]. This novel approach offers a convenient synthesis of a variety of (hetero)aromatic aldehydes and other carboxylic acid derivatives under relatively mild reaction conditions (Figure 1). Notably, paraformaldehyde is a solid, stable, and inexpensive CO Surrogate.

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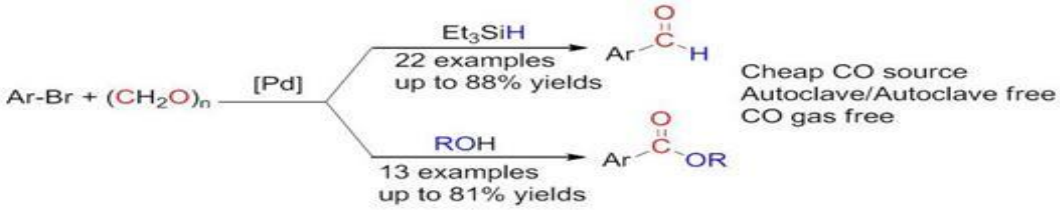
Ar-Br + (CH2O)n
[Pd]
Et3SiH
22 examples
up to 88% yields
Ar
O
C
H
ROH
13 examples
up to 81% yields
OR
Cheap CO source
Autoclave/Autoclave free
CO gas free

P-081

Towards New C2-Symmetric Ferrocenyl Substituted N-Heterocyclic Carbenes for Homogeneous Catalysis

Dr. Maurice Odago[1]
[1]*SUNY ONEONTA, Oneonta, USA*

Poster Session 1

N-Heterocyclic carbenes (NHCs) have become universally used ligands in organometallic and inorganic coordination chemistry. They have been preferred over their phosphine counterparts due to their specific coordination chemistry, where they both stabilize and activate metal centers in quite different key catalytic steps of organic syntheses. Further, many of the NHC precatalysts have been reported to exhibit excellent thermal stability and they do not need excess ligands in their catalysis.
Since the synthesis of the first chiral and optically active carbene by Lappert in 1983, many chiral NHCs acting as monodentate ligands, as well as bidentate ligands have been synthesized by numerous groups and used in asymmetric catalysis. The chiral ferrocenyl-substituted NHCs obtained by deprotonation of imidazolium or imidazolinium salts by strong bases such as potassium tert-butoxide (KOtBu) were reported by Togni et al. Here we report the progress made in an attempt to synthesize new chiral C2-symmetric ferrocenyl-substituted NHCs which have saturated trans-1,2-diaminocyclohexane and trans-1,2-diphenylethanediamine backbones. These ligands have not been synthesized to our knowledge. We believe that incorporating chiral backbones, particularly those that are sterically rich, would offer great advantages to the enantioselective catalysis using these ligands as chiral auxiliaries in nickel catalysis and other metal catalyzed organic transformations by offering unique stereochemical control around the metal centers. The synthesis of these chiral ligands, their crystal structure together with application in homogenous chiral catalysis will be explored.

P-082

Changing the Nature of Anagostic and Agostic Interactions – a Synthesis by Computation Approach.

Prof. Al Nielson[1], Assoc. Prof. John Harrison[1], Mr Arif Sajjad[1], Distinguished Prof. Peter Schwerdtfeger[1]
[1]*Massey University at Auckland, Auckland, New Zealand*

Poster Session 1

High-powered computing facilities and high level calculations allow fully optimised structures to be obtained for organometallic complexes which have very good physical parameter comparisons to X-ray structures. Simplified models of complexes no longer need to be used, and energy-minimised structures can be obtained for complexes which have not been actually prepared. This ideology removes the need for bench syntheses which may be complicated or produce compounds which are difficult to handle. The computational approach gives much more information about a complex and allows a more complete understanding of fundamental characteristics than the normal bench synthesis would provide. We have used this 'synthesis by computation' approach [1] to obtain information about the nature of anagostic and agostic interactions that occur during cyclometallation reactions. DFT calculations using the PBE-D3 functional show that for anagostic interactions in [RhCl(CO)2(L)] complexes (L = 1-tetralone oximes and imines), NOH and NMe groups position the anagostic hydrogen more over the metal and NOCMe and NCMe3 groups more out towards the chloro ligand. QTAIM analysis indicates electrostatic dominance for the Rh••••H interaction. Both σ and π-withdrawing substituents on the ligand aromatic ring lengthening the Rh••••H separation; σ and π-donating substituents decrease the separation and an attractive anagostic approach can develop. [RhCl(CO)2(L)] complexes (L = isoquinoline) show much shorter Rh••••H separations. For the agostic interaction in the palladium complexes [PdCl)2(L)] and [Pd(OAc)2(L)] (L = 1-tetralone oximes and imines, isoquinoline), substituents on the aromatic rings of the ligands have a major effect on the nature of the interaction.

References:

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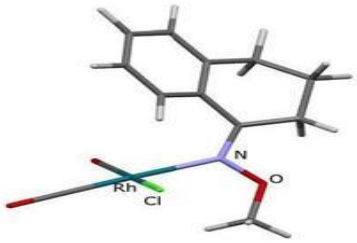
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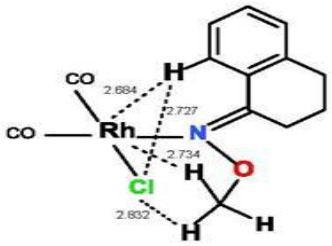
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H
H
2.684
2.727
2.734
2.832

P-084

Regiodivergent Copper-Catalyzed Aminoboration of Unactivated Terminal Alkenes

Dr. Koji Hirano[1], Mr. Ryosuke Sakae[1], Prof. Masahiro Miura[1]
[1]*Osaka University, Suita/Osaka, Japan*

Poster Session 1

The catalytic aminative difunctionalization of alkenes is highly attractive from the synthetic point of view because both positions of the alkene π bond are simultaneously functionalized in one synthetic operation, and relatively simple starting materials can be readily transformed into the highly functionalized alkylamines of high value in medicinal and material chemistry. In this context, we recently developed the copper-catalyzed aminoboration of activated styrenes[1] and some strained alkenes[2] with diboron reagents and hydroxylamines as nucleophilic boryl sources and electrophilic nitrogen sources, respectively. During our continuous studies on the catalytic aminoboration,[3] we focused on unactivated terminal alkenes since they are simple and abundant bulk commodities, and their functionalization is of great importance in organic synthesis. Here, we present a ligand-controlled regiodivergent copper-catalyzed aminoboration of simple terminal alkenes: by proper choice of the ligand, both regioisomeric aminoboration products are obtained with high regioselectivity from a single alkene (Scheme 1).

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Scheme 1

P-085

Catalytic Enantioselective Synthesis of Planar-Chiral Ferrocenes Initiated by C-H Bond Activation

Ph. D Takanori Shibata[1,2], Tomoya Sasaki[1], Tsubasa Shizuno[1]
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Poster Session 1

Ferrocene-containing compounds are attractve, because of their unique structures, chemical and thermal stabilities, and redox properties. The successful application in organic synthesis is chiral ligand. For example, planar-chiral ferrocenyl phosphine “Xyliphos” is an efficient ligand for the Ir-catalyzed asymmetric hydrogenation. But the stoichiometric amounts of metal regents are generally required for the synthesis of chiral ferrocenes.
We realized the first example of enantioselective C-H alkylation of ferrocenes, which was achieved by the Ir-chiral diene catalyst.1 The isoquinolyl moiety as a directing group controlled the regioselectivity and enantioselectivity. This protocol is a new approach to the synthesis of planar chiral ferrocenes and a new application of diene ligands.(equation 1)

Dibenzosilole is an important skeleton of many functional molecules that are useful as conjugated organosilicon materials in organic electronics and photonics. We merged it with ferrocene and created a new class of planar-chiral compounds “benzosiloloferrocenes”. The intramolecular reaction of 2-(hydrosilyl)arylferrocenes gave planar-chiral benzosiloloferrocenes. The enantioselective cross dehydrogenative coupling of an sp2 C-H bond of ferrocene with a Si-H bond proceeded efficiently with the use of a Rh-chiral diene catalyst. The corresponding benzogermoloferrocenes could be also prepared by the same reaction.(equation 2)

References:
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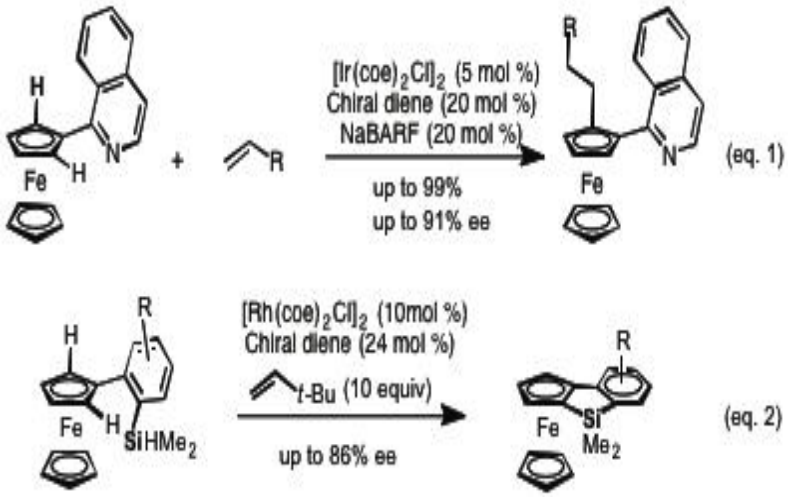

P-086

Access to Silylated and Germylated Heterocycles by Anionic Rearrangement

Dr Muriel Durandetti[1], Dr. Cyril François[1], Dr. Thomas Boddaert[1], Dr. Laetitia Mistico[1], Dr. Olivier Querolle[2], Dr. Lieven Meerpoel[2], Dr. Patrick Angibaud[2], Dr. Jacques Maddaluno[1]

[1]COBRA UMR CNRS 6014 - University of Rouen, Mont-Saint-Aignan, France, [2]Dept of Medicinal Chemistry - Janssen, Val de Reuil, France

Poster Session 1

Replacing a carbon atom by silicon in heterocycles can be regarded as an innovative strategy to develop new drugs.[1] So the C/Si swap of known drug skeletons has been widely investigated.[2] But the lack of general synthetic procedures, prompted us to develop a new access to sila-heterocycles.

Figure 1

In this presentation, a simple access to silylated and germylated binuclear heterocycles, based on an anionic rearrangement, will be described.[3] In presence of butyllithium, the intramolecular cyclisation of the precursor 1 did not furnish only the desired product (a-isomer) but also the regioisomer (b-isomer). The formation of this latter could be explained by a hypervalent-silicon specie which would evolve either by migration of the aromatic ring (path a) or the CH_2-Si bond (path b). A set of electron-rich and electron-poor silylated and germylated (hetero)aromatic substrates have been tested, in order to understand the mechanism and the factors controlling the rearrangement, and the regioselectivity.

References:

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P-087

Intermolecular nucleophilic addition to allenes catalysed by platinum: unveiling the Pt-allene interaction

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Poster Session 1

For some time allenes were considered simple curiosities due to their apparent unstable nature. However, in the last few years the chemistry of allenes has been extensively developed since they have shown interesting reactivity and selectivity affording complex structures in a limited number of steps.[1] Probably the most widely explored reactions of allenes are the metal catalysed additions of nucleophiles, among which, the intermolecular version has shown to be very versatile.[2] In 2010, our group reported a novel platinum-catalysed dihydroalkoxylation of allenes, leading to aliphatic acetals through a double addition to the terminal carbon of the allene moiety. This reaction was also extended to indoles affording the synthesis of bis-indolyl compounds, interesting scaffolds from a biological point of view.[3] Understanding the mechanism of this reaction is essential to gain a better control of the process. Although this manifold is not fully understood yet, preliminary studies suggest a η^1-coordination of the Pt atom to the central carbon of the allene, instead of the more common η^2-structure.[4] The present project attempts to shed light in the platinum-allene interaction with the preparation of some platinum-allene complexes, the study of their behaviour in solution and the implications of these findings in the reaction mechanism. Moreover, kinetic studies and labelling experiments are showing interesting results that highlight the uncommon behaviour of the platinum in this process, and will be presented in this communication.

References:
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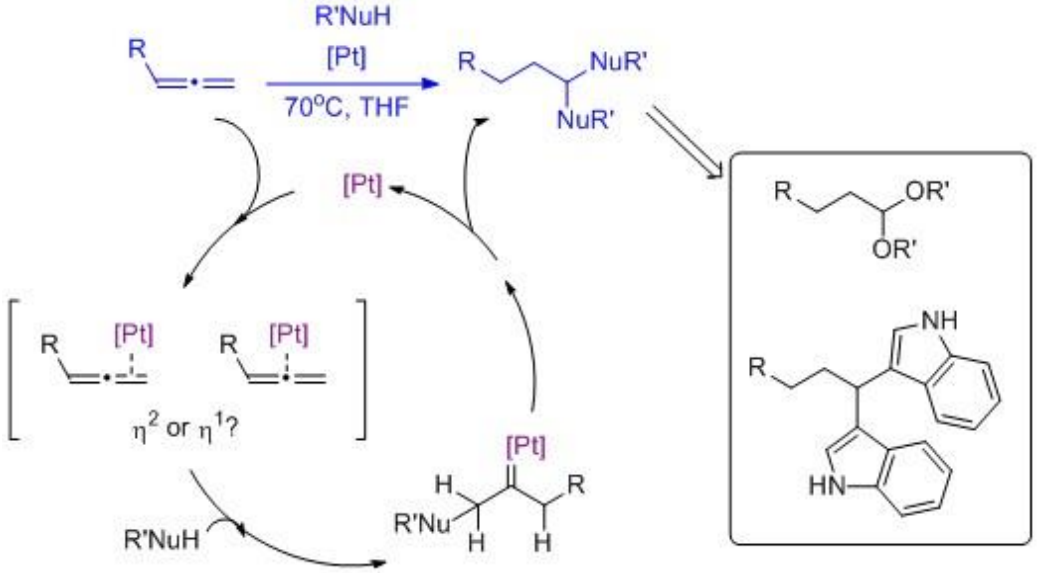
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η2 or η1?
R'NuH
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R
R'Nu
H
H
R
OR'
OR'
NH
R
HN

P-089

Understanding the stereochemical outcomes of reactions involving organo(bi)metallic reactants: beyond the Curtin-Hammett principle

Dr Anne Harrison-Marchand[1], Dr Nicolas Duguet[1], Dr Gabriella Barozzino Consiglio[1], Pr Hassan Oulyadi[1], Dr Jacques Maddaluno[1]

[1]*UMR CNRS 6014 - University of Rouen, Mont Saint Aignan Cédex, France*

Poster Session 1

Recent investigations on the asymmetric nucleophilic addition of organolithiums (RLi) onto highly reactive prochiral electrophile substrates (aldehydes) will be presented. Although this reaction is one of the simplest way to create new C-C bonds, it has not found efficient solutions yet when it comes to an enantioselective version.

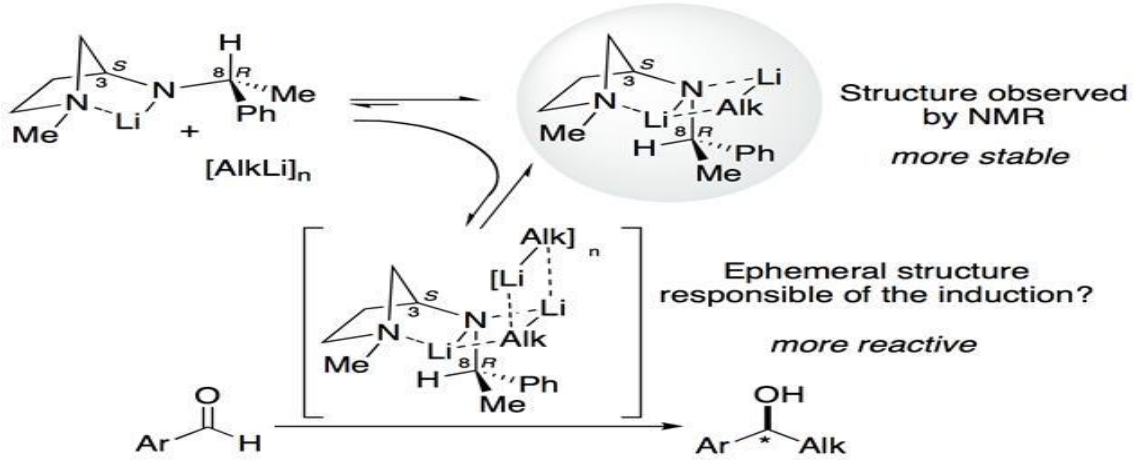
Our strategy consists in resorting to organo(bi)metallic systems in which a highly nucleophilic RLi is associated to chiral lithium amides (CLAs) which become the source of asymmetry. In our methodological approach, the structures in solution of the intermediate mixed aggregates are systematically characterized by NMR.

Figure

The Curtin-Hammett principle forbids to correlate the complexes observed in solution to the enantiomeric excesses measured at the end of the reaction. Thus, complementary experiments have been run to shine some light on the key-intermediates at the origin of the induction. The results we will present lead us to propose the participation of an ephemeral, but very reactive, triptych supramolecular aggregate.

Reference:

Top. Organomet. Chem. 2014, 47, 43-62



P-090

SYNTHESIS OF HETEROCYCLIC RINGS: STUDY OF THE REACTIVITY OF M-C BONDS

Dr Barbara Villa Marcos[1], Mr Joseph Walker[1], Miss Yuk Ki Lee[1], Mr Kevin Carr[2], Prof. Stuart A. Macgregor[2], Prof. David L. Davies[1]

[1]*University of Leicester, Leicester, UK* , [2]*Heriot-Watt University, Edinburgh, UK*

Poster Session 1

Catalytic C-C/N/O bond formation by functionalisation of C-H bonds is a step-economical approach for the synthesis of complex organic molecules.[1] In particular, annulation reactions have emerged as a very attractive synthetic tool to produce fused derivatives. It typically consists of a C-H activation step forming a cyclometallated complex with a subsequent alkyne insertion into the M-C bond.[2] Understanding the reactivity of cyclometallated M-C bonds with alkynes will facilitate the design of more efficient and selective catalysts.

Insertion of alkynes into M-C(Ph) bonds usually forms 7-membered rings (Fig. 1, a)[3] which can give isoquinolinium salts (Fig. 1, d) after oxidation. Here we show that cyclometallated heterocyclic or vinylic imines react with alkynes to give C,N coupled products directly. Heterocyclic imines give Ir(III) complexes of bis-fused η^5-anionic ligands (Fig. 1, b) whereas vinylic imines result in Ir(I) complexes of η^4-diene ligands (Fig. 1, c). In both cases oxidation can lead to formation of heterocyclic cations d. In addition to experimental studies, DFT calculations are used to reproduce observed mechanistic data.

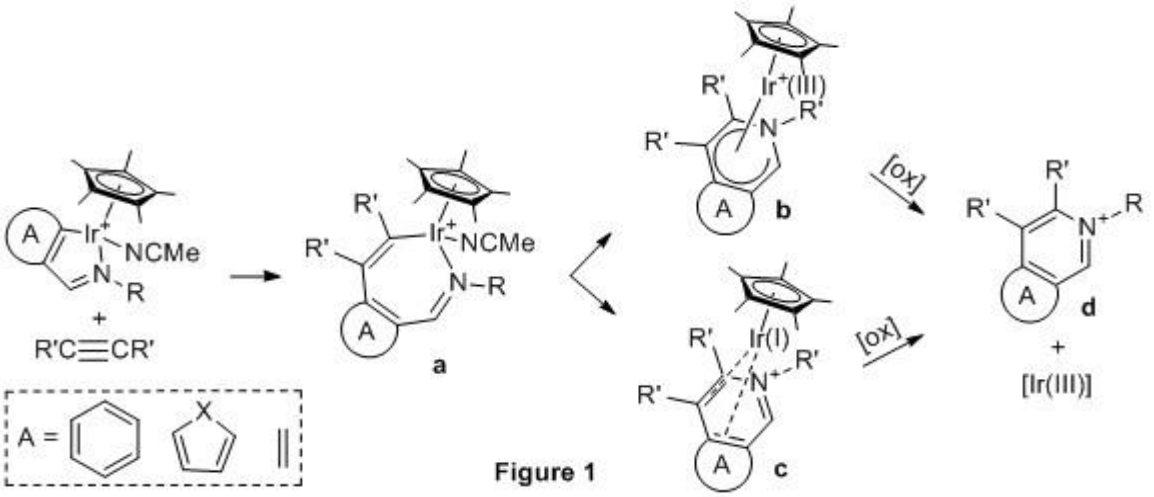


Figure 1

P-092

Synthesis of 8-Membered Lactones via Rh(I)-Catalyzed [6+2] Cycloaddition of Allenyl Aldehydes and Carbonyl Compounds

Dr. Yoshihiro Sato[1], Dr. Yoshihiro Oonishi[1], Kenya Takeda[1], Dr. Akihito Hosotani[1]
[1]*Hokkaido University, Sapporo, Japan*

Poster Session 1

The transition-metal-catalyzed [m+n] cycloaddition is one of the promising ways for construction of complex polycyclic skeletons in one-pot reaction with a highly stereoselective and atom-economical fashion. On the other hand, the [m+n] cycloadditions employing multiple bonds containing a heteroatom (e.g. carbonyl group, imine, nitrile, etc) are still limited. We have reported a Rh(I)-catalyzed intramolecular [6+2] cycloaddition producing 8-membered cycloalkanone derivatives.[1] More recently, the [6+2] cycloaddition was successfully expanded to an intermolecular cycloaddition, in which monocyclic cyclooctanones 3 were obtained from allene-aldehydes 1 and alkynes 2 in a stereoselective manner.[2] The cycloaddition proceeds via oxo-rhodacycle 4 formed by hydroacylation of 4-allenal moiety in 1. Insertion of alkynes 2 into Rh-carbon bond in 4 followed by reductive elimination occurs to give cyclooctanone 3. We envisaged if insertion of carbonyl groups instead of alkynes into 4 occurred, 8-membered lactone derivatives would be obtained through the [6+2] cycloaddition. When the reaction of allene-aldehydes 1 and N-methyl isatin (5) was carried out using 10 mol% of [Rh(SIMes)(cod)]BArF in dichloroethane at room temperature, 8-membered lactone 6 was obtained in 96% yield in a stereoselective manner. The mechanistic aspects as well as the scope and limitations of this reaction will be also discussed.

References:
(1) Oonishi, Y.; Hosotani, A.; Sato, Y. J. Am. Chem. Soc. 2011, 133, 10386.
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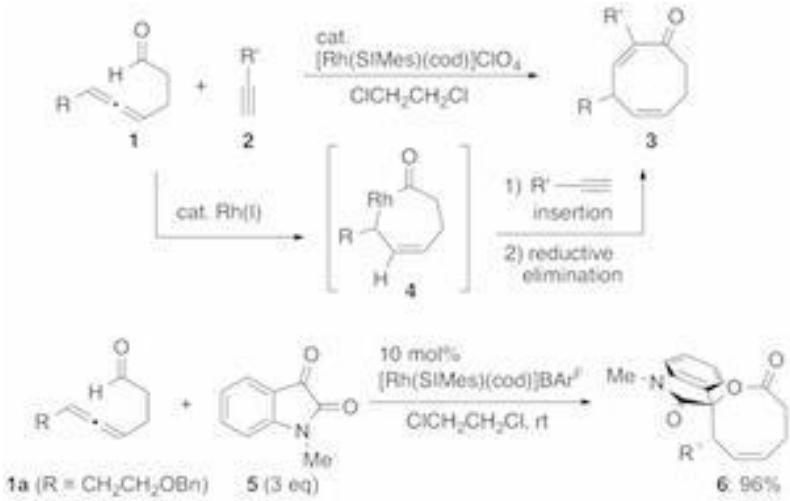

P-093

Visible Light-Mediated C-N Cross-Coupling Reactions Enabled by the Productive Merger of Copper and Photoredox Catalysis

Dr. Woo-Jin Yoo[1], Mr. Tatsuhiro Tsukamoto[1], Dr. Shu Kobayashi[1]
[1]*The University of Tokyo, Bunkyo-Ku, Japan*

Poster Session 1

Harnessing visible light as an alternative source of clean energy to mediate organic transformations has garnered much attention in recent years. This is, in part, due to the emergence of photoexcited metal polypyridyl complexes as redox mediators that can activate organic substrates via single-electron oxidation/reduction to facilitate challenging bond constructions.[sup]1[sup] Moreover, it has been found that the combination of visible light photoredox catalysis with other catalytic systems (organocatalysis, transition metal catalysis, Lewis acid catalysis) could lead to useful chemical transformations that are not easily accessible by a single catalytic system.[sup]2[sup]

In this presentation, our efforts to merge copper catalysis with photoredox catalysis to enable C-N cross-coupling reactions will be described (Scheme 1). In particular, it was found that the copper-catalyzed Chan-Lam[sup]3[sup] (X = $B(OH)_2$) and Ullmann-type[sup]4[sup] (X = I) coupling reactions occurs under milder conditions and with broad substrate scope when performed under visible light photoredox catalytic conditions.

References:
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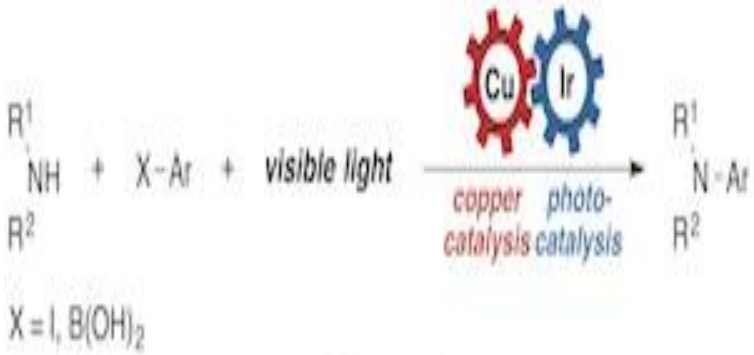
3. W.-J. Yoo, T. Tsukamoto, S. Kobayashi, Angew. Chem Int. Ed. 2015, DOI: 10.1002/anie.201500074R1.
4. W.-J. Yoo, T. Tsukamoto, S. Kobayashi, manuscript in preparation.



Scheme 1

P-095

Enantioselective Allylation of (2E,4E)-2,4-Dimethylhexadienal: Synthesis of (5R,6S)-(+)-Pteroenone

Petr Koukal[1], Martin Kotora[1]
[1]*Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Praha, Czech Republic*

Poster Session 1

Enantioselective allylation (R = H) of aldehydes 1 has become a standard tool for highly enantioselective synthesis of secondary alcohols 2[1]. Resulting homoallylic alcohols are prepared either by stoichiometric addition of chiral reagents or by catalytic addition of allylmetal species promoted by Lewis acid, Lewis base[2] or Brønsted acid catalysts. Enantioselective crotylation (R = Me) introduces another centrum of chirality into the molecule and the syn/anti diastereoselectivity of the product 2 is controlled by cis/trans configuration of the crotylation reagent.
Asymmetric crotylation of α,β,γ,δ-unsaturated aldehydes has been scarcely explored although the motive of alcohol 2 occurs within many natural products. Therefore a comparative study of enantioselective allylation, cis- and trans-crotylation of 1 using various methodologies was undertaken. Alcohol 2 was obtained in moderate to very good yields and enantiomeric excess up to 96 %.
The optimal reaction condition were then applied for synthesis of natural compound (5R,6S)-(+)-pteroenone 3, a defensive metabolite isolated from Clione Antarctica. This ketol was obtained in excellent diastereoselectivity and enantioselectivity over 95 %.[3]

This work was supported by grants from Ministry of Education, Youth, and Sports (MSM0021620857) and the Czech Science Foundation (P207/11/0587).

References:

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2. a) Kadlčíkova, A.; Valterová, I.; Ducháčková, L.; Roithová, J.; Kotora, M. Chem. Eur. J. 2010, 16, 9442-9445 and references therein; b) Cadart, T.; Koukal, P.; Kotora, M. Eur. J. Org. Chem. 2014, 34, 7556–7560.
3. Koukal, P.; Kotora, M. Chem. Eur. J. 2015, in press, doi: 10.1002/chem.201500050.

P-096

A NEW DESULFINLYLATION AND METAL TRANSPOSITION REACTION IN SILVER MESIOINIC CARBENES

Maria Frutos[1], M. Carmen de la Torre[1], Alma Viso[1], Roberto Fernández de la Pradilla[1], Miguel Ángel Sierra[2]
[1]*Instituto de Química Orgánica Genera, Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain,* [2]*Departamento de Química Orgánica. Facultad de Química, Universidad Complutense, Madrid, Spain*

Poster Session 1

N-Heterocycle carbenes (NHC) are nowadays a powerful tool in different areas of Chemistry, such as ligands in catalysis. Sulfinyl groups are also very interesting due to their hemilabile character: they can be coordinated to the metal or they can also create a vacant position for the catalytic process. Despite this exceptional feature, there are not so many examples in the literature of NHC bearing sulfoxyde functionality in their structures.

We were interested in the synthesis of new chiral ligands based in 1, 2, 3 triazol incorporating a sulfinyl moiety in the C-4. During the functionalization of the triazol units, we discovered that sulfinyl group was lost instantaneously by the reaction of Silver carbene 5 in the presence of methanol. Transmetalation of products 6, 7, and 8 with AuSMe2Cl gave two Gold carbene regioisomers: the 1, 2, 3-triazolium-5-gold chloride 8 and the unexpected 1, 2, 3-triazolium-4-gold chloride 9.

To gain more insights into the mechanism of this process we have carried out different experiments: the study of the role of electronic effects by using a variety of aromatic azides (phenyl, p-methoxyphenyl, p-nitrophenyl and naphtyl); changes in the alcohols (ethanol, isopropanol, butanol), the use of bulkier sulfinyl groups or the presence of a sulfone group.

Theoretical studies, in order to shed light into the mechanism of this reaction, have also been displayed.


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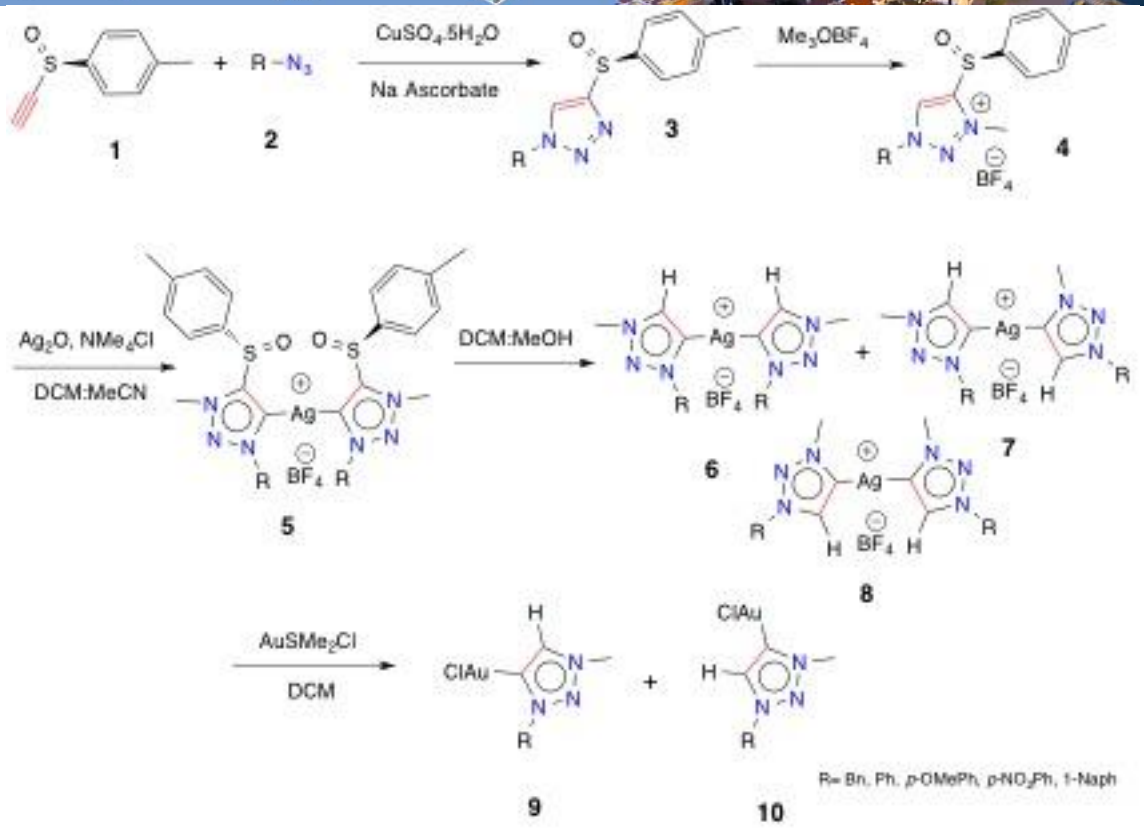

CuSO4.5H2O
Na Ascorbate
Me3OBF4
Ag2O, NMe4Cl
DCM:MeCN
DCM:MeOH
AuSMe2Cl
DCM
R= Bn, Ph, p-OMePh, p-NO2Ph, 1-Naph

P-098

A steric-controlled C–H activation strategy for primary amino alcohols

Dr Jonas Calleja[1], Mr. Timothy W. Gorman[1], Dr. Daniel Pla[1], Dr Victoriano Domingo[1], Dr Benjamin Haffemayer[1], Prof Matthew J. Gaunt[1]

[1]*Chemistry Department, University of Cambridge, Cambridge, UK*

Poster Session 1

Aliphatic amines are central to the function of many biologically active molecules as evidenced by their prevalence in numerous pharmaceutical agents. Primary amines such as α-amino alcohols are among the most versatile of such structures and this basic motif is present in many functional molecules.[1] The corresponding derivatives containing a fully substituted carbon atom appended to the nitrogen motif are a key class of this fundamental molecular framework due to the high level of directional functionality that can be built into these systems. However, their efficient synthesis is limited to a relatively small number of strategies. A streamlined synthetic solution to this problem could involve a catalyst capable of transforming simple, readily available fully substituted amino alcohols into complex variants via selective functionalization of C–H bonds.

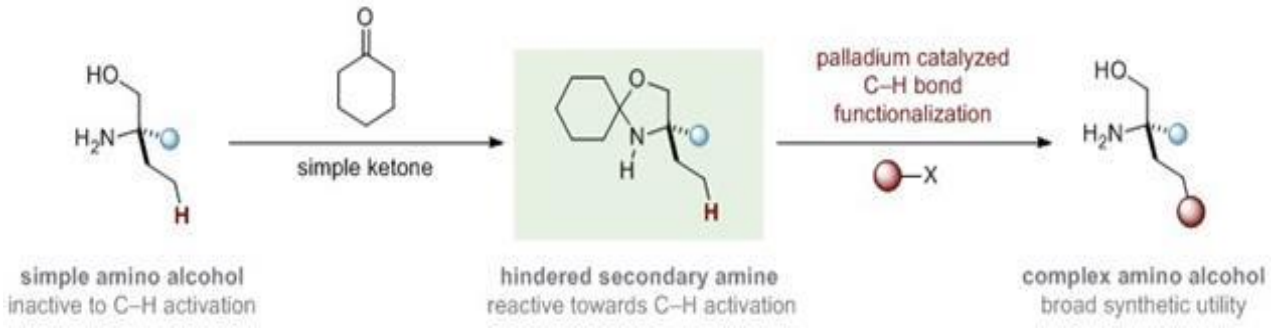
Methods enabling the practical and selective functionalization of inert aliphatic C–H bonds have synthetic applications in fields ranging from fine chemical production to drug discovery. While the core versatile functionality of carboxylic acids and alcohols has been shown to direct a number of useful C–H activation reactions,[2],[3] strategically important reactions on aliphatic amines remain a major challenge and successful cases require strongly electron withdrawing groups or directing auxiliaries to effect the desired reactions. We describe a simple activation strategy for amino alcohols and showcase this through the development of a palladium-catalyzed C–H alkenylation transformation (Scheme 1). We present a broad substrate scope and mechanistic basis for the new transformation and highlight how this process can expedite the synthesis of complex molecules.

References:

[1]. K. Bera, I.N.N. Namboothiri, Asian J. Org. Chem. 2014, 3, 1234-1260.

[2]. A. McNally, B. Haffemeyer, B.S.F. Collins, M.J. Gaunt, Nature 2014, 510, 129-133.

[3]. R. Giri, N. Maugel, J.-J. Li, D.-H Wang, S.P. Breazzano, L.B. Saunders and J.-Q. Yu, J. Am. Chem. Soc. 2007, 129, 3510-3511.



P-100

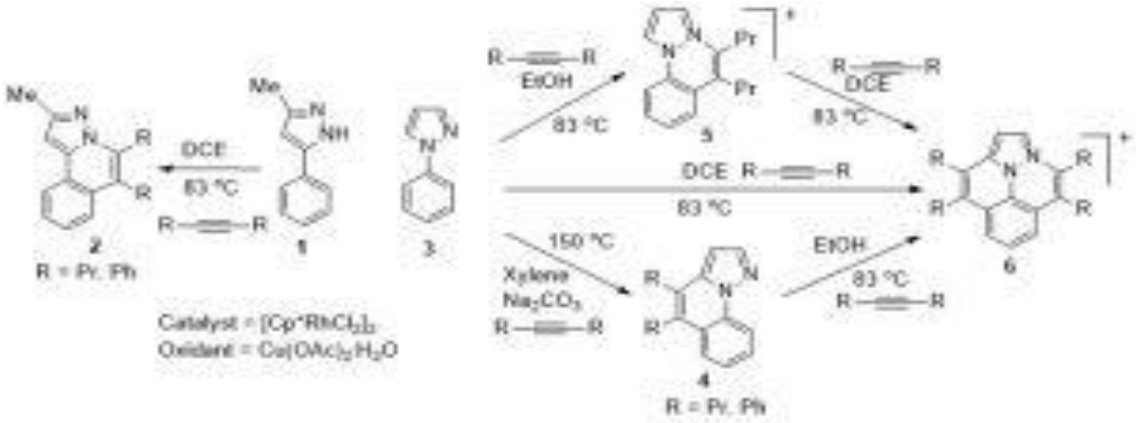
Experimental and Computational Investigation of Rhodium-Catalysed Oxidative Coupling

Prof. David Davies[1], Dr Charles Ellul[1], Dr Qudsia Khamker[1], Dr Claire McMullin[2], Prof. Stuart Macgregor[2]
[1]*University of Leicester, Leicester, UK,* [2]*Heriot-Watt University, Edinburgh, UK*

Poster Session 1

Directed C-H functionalisation catalysed by $[Cp^*RhCl_2]_2$ and related derivatives has recently attracted a large amount of interest as a convenient, atom economical route to new C Y bonds (Y = C, N, O).[1] We recently reported the reactions of 3-phenylpyrazole (1) with internal alkynes to form heterocycles (2) via CH and NH activation.[2] Previously Miura showed 1-phenylpyrazole (3) will undergo C,C coupling to form (4).[3] Now we demonstrate that (3) may also undergo facile C,N coupling to form cationic heterocycles (5, 6) (Scheme 1). Furthermore, we show that combined experimental and computational studies can help identify the key steps within the catalytic cycles which control product selectivity. Our results suggest that product selectivity is dependent on directing group, anion coordination and the reductive elimination step, enabling rational control over product selectivity by altering the nature of the alkyne and reaction conditions.

References:
[1] Song, G.; Wang, F.; Li, X.,. Chem. Soc. Rev. 2012, 41, 3651-3678.
[2] Algarra, A. G.; Cross, W. B.; Davies, D. L.; Khamker, Q.; Macgregor, S. A.; McMullin, C. L.; Singh, K. J. Org. Chem. 2014, 79, 1954-70.
[3] Umeda, N.; Hirano, K.; Shibata, N.; Sato, H.; Miura, M.,. J. Org. Chem. 2011, 76, 13-24.



Scheme 1 Product scope of phenylpyrazoles in oxidative coupling with internal alkynes

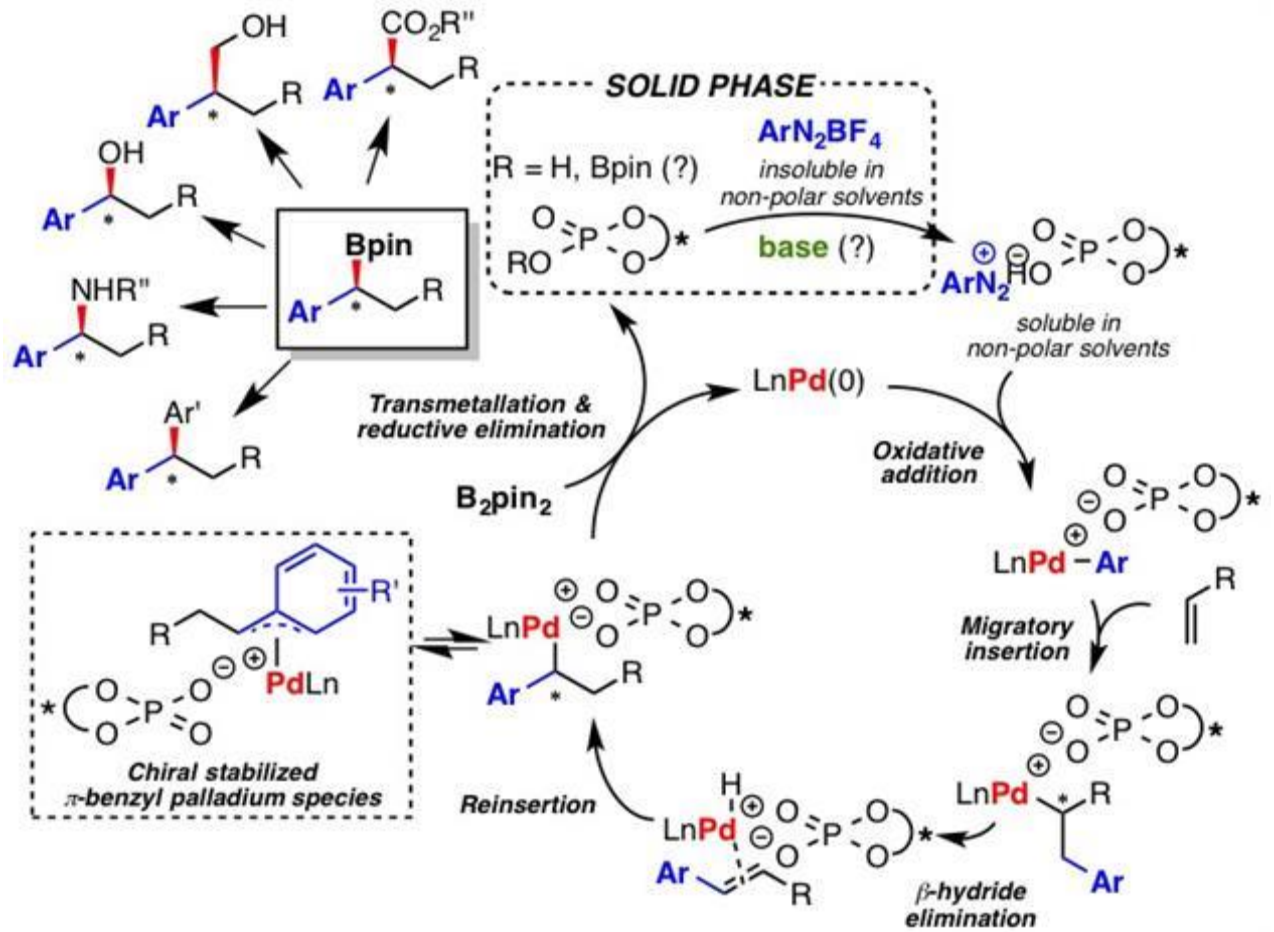
P-101

Enantioselective 1,1-Arylborylation of Alkenes: Merging Chiral Anion Phase Transfer with Pd Catalysis

Javier Miró[2], Dr Hosea M Nelson[1], Dr Brett D Williams[1], Prof F Dean Toste[1]
[1]*University of California, Berkeley, USA,* [2]*University of Valencia, Valencia, Spain*

Poster Session 1

Catalytic enantioselective synthesis of benzyl boronic esters through the innovative combination of chiral anion phase transfer (CAPT) and transition metal catalysis in a novel Heck-Matsuda 1,1-arylborylation cascade reaction. Methodology that provides synthetically valuable scaffolds and is anticipated to be highly impactful in the area of diversity oriented synthesis.



P-102

Bisphosphine-cross-linked Polystyrenes: Application to Heterogeneous Ni Catalysis for C-H/C-O Coupling

Prof. Masaya Sawamura[1], Mr. Tomoya Harada[1], Dr. Tomohiro Iwai[1]
[1]*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan*

Poster Session 1

Polystyrene(PS)-supported phosphines are widely used for heterogeneous transition metal catalysis. The phosphine moieties have generally significant mobility even in cross-linked PS resins, and hence exhibit ligand properties similar to those of their homogeneous counterparts, except for their insoluble nature. In many cases, however, the polymer chain causes unfavourable steric effects in the catalytic environment, resulting in reduced catalyst efficiency. Thus, using the PS backbone for designing phosphine ligands to favour a specific structure desirable for an increase in catalytic activity is difficult.[1]

A new type of PS-phosphine hybrid (PS-DPPBz) was prepared through radical emulsion copolymerization of styrene monomers in the presence of tetravinylated 1,2-bis(diphenylphosphino)benzene. PS-DPPBz (dried beads) exhibited moderate swelling properties with aprotic organic solvents.

The use of PS-DPPBz as a ligand enabled the Ni-catalyzed cross-coupling reactions such as C–H/C–O coupling between azoles and phenol derivatives.[2] The catalytic activity of the Ni-PS-DPPBz system was comparable with that of the reported homogeneous Ni catalysts with the electron-rich and bulky bisphosphine ligand Dcype.[2]
On the other hand, the homogeneous bisphosphine ligand (DPPBz) featuring the bisphosphine core of PS-DPPBz gave no catalytic activity. Thus, the fourfold cross-linking was crucial for the high catalytic performance of the Ni-PS-DPPBz heterogeneous catalyst system.

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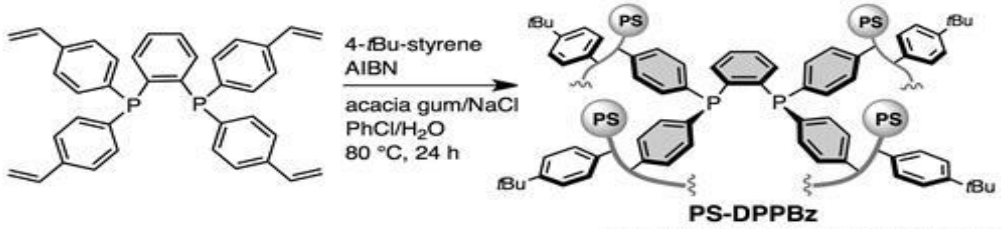
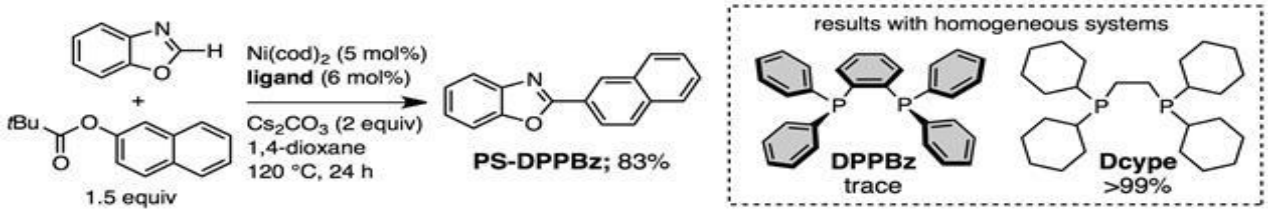

4-tBu-styrene
AIBN
acacia gum/NaCl
PhCl/H2O
80 °C, 24 h
PS
tBu
PS-DPPBz


Ni(cod)2 (5 mol%)
ligand (6 mol%)
Cs2CO3 (2 equiv)
1,4-dioxane
120 °C, 24 h
1.5 equiv
PS-DPPBz; 83%
results with homogeneous systems
DPPBz
trace
Dcype
>99%

P-103

Cross-Coupling and Addition Reactions of Trifluoromethyltriolborate Salt

Kazuya Ikizakura[1], Associate Prof. Yasunori Yamamoto[1]
[1]*Hokkaido University, Sapporo, Japan*

Poster Session 1

Trifluoromethyl-substituted compounds are known to provide significant changes in chemical and physical properties of pharmaceutical and organic materials. For this reason, many methods for the trifluoromethylation reactions have been developed. Recently, in the cross-coupling reactions and addition reactions, Ruppert's reagents that act as a source of trifluoromethyl anions are often used. However, its storage and handling are limited, because it is a highly volatile liquid, and is sensitive to air and moisture. On the other hand, we have developed organotriolborate salts[1], that have exceptionally high levels of stability in air and water and reasonable solubility in organic solvents, for cross-coupling reactions[2] and catalyzed asymmetric addition reactions[3]. In this presentation, we will report a newly synthesized trifluoromethyltriolborate salt for cross-coupling reactions and addition reactions.

References:
[1] (a) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. Angew. Chem. Int. Ed., 2008, 47, 928. (b) Yamamoto, Y.; Sugai, J.; Takizawa, M.; Miyaura, N. Org. Synth., 2011, 88, 79. (c) Li, G.-Q.; Kiyomura, S.; Yamamoto, Y.; Miyaura, N. Chem. Lett., 2011, 40, 702. (d) Yamamoto, Y. Heterocycles, 2012, 85, 799.
[2] (a) Yu, X.-Q.; Yamamoto, Y.; Miyaura, N. Chem. Asian J., 2008, 3, 1517. (b) Yamamoto, Y.; Takizawa, M.; Yu, X. Q.; Miyaura, N. Heterocycles, 2010, 80, 359. (c) Li, G.-Q.; Yamamoto, Y.; Miyaura, N. Synlett, 2011, 1769. (d) Li, G.-Q.; Yamamoto, Y.; Miyaura, N.; Tetrahedron, 2011, 67, 6804. (e) Yamamoto, Y.; Ikizakura, K.; Ito, H.; Miyaura, N. Molecules 2013, 18, 430. (f) Sakashita, S.; Takizawa, M.; Sugai, J.; Ito, H.; Yamamoto, Y. Org. Lett. 2013, 15, 4308.
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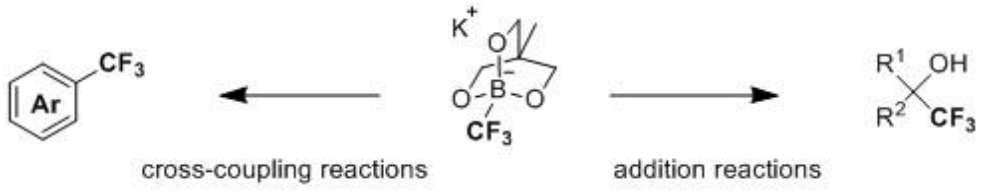


P-104

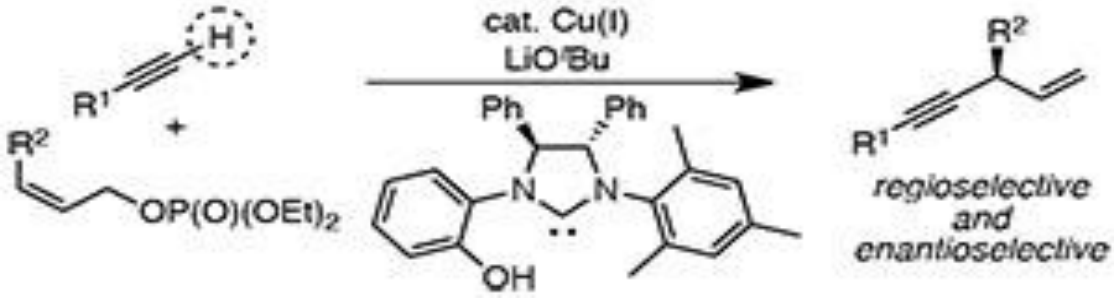
Copper-Catalyzed Enantioselective Allylic Alkylation of Terminal Alkyne Pronucleophiles

Dr. hirohisa ohmiya[1], Ayumi Harada[1], Heng Zhang[1], Dr. Masaya Sawamura[1]
[1]*Hokkaido University, Sapporo, Japan*

Poster Session 1

Catalytic enantioselective allylic alkylation of alkynyl nucleophiles is a powerful strategy for asymmetric organic synthesis. Readily available precursors are easily transformed into chiral 1,4-enynes (skipped enynes), which are versatile synthetic intermediates with two different handles for further transformations connected to the stereogenic carbon center. This paper reports copper-catalyzed enantioselective allylic alkylation of terminal alkynes with primary allylic phosphates using a new chiral N-heterocyclic carbene ligand bearing a phenolic hydroxy group at the ortho position of one of the two N-aryl groups.[1] This reaction occurred with excellent γ-branch-regioselectivity and high enantioselectivity, forming a controlled stereogenic center at the allylic/propargylic position. Various terminal alkynes including silyl, aliphatic, and aromatic alkynes could be used directly without premetalation of the C(sp)-H bond. Based on the results of experiments using an isomeric secondary allylic phosphate, which gave a branched product through an α-selective substitution reaction with retention of configuration, a reaction pathway involving 1,3-allylic migration of Cu in a ([σ+π]-allyl)copper(III) species is proposed.

Reference:
1. A. Harada, Y. Makida, T. Sato, H. Ohmiya, M. Sawamura, J. Am. Chem. Soc. 2014, 136, 13932.



P-105

Palladium-Catalyzed Alkoxycarbonylation of Conjugated Enyne Carbonates and Oxiranes: A Stereoselective Method in Synthesis of 2,3,5-Trienoates.

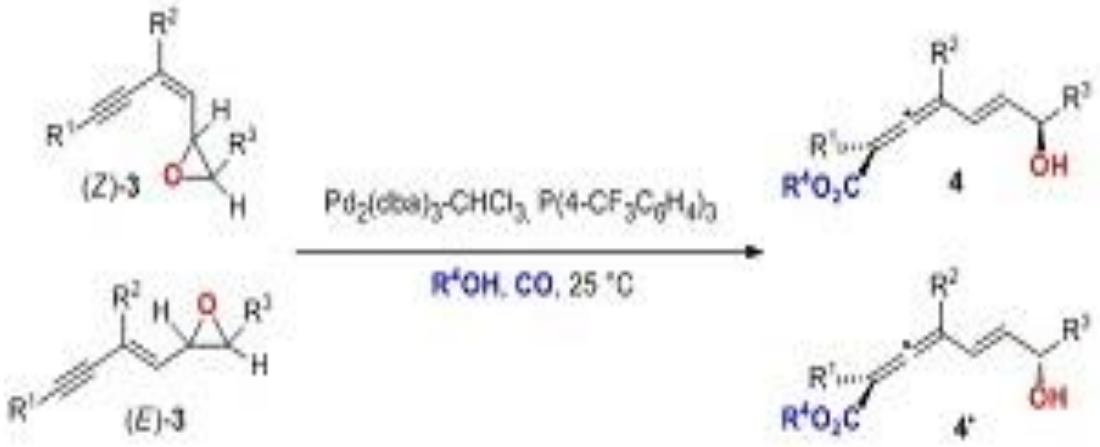
Prof. Dr. Levent Artok[1], Melih Kuş[1], Ezgi Şule Karagöz[1], Eray Gürkan Akpınar[1]
[1]*Izmir Institute of Technology, Urla, Turkey*

Poster Session 1

It is well-known that the Pd(0)-catalyzed alkoxycarbonylation of allylic compounds usually leads to β,γ-unsaturated esters through the involvement of a π-allylpalladium complex. However, the analogous experiments with alkynyl substituted allylic compounds proceeded through a 1,5-substitution to afford ester functionalized vinylallene structures.[1]

References:

[1] a) Akpınar, G. E. Kuş, M. Üçüncü, M. Karakuş E. Artok, L. Org. Lett. 2011, 13, 748. b) Karagöz, E.Ş., Kuş, M., Akpınar, E.G., Artok, L. J. Org. Chem. 2014, 79, 922.



P-106

Synthesis and Reactivity of Late Transition Metal Complexes with Phosphorus Ligands Containing Lewis Acidic Metals

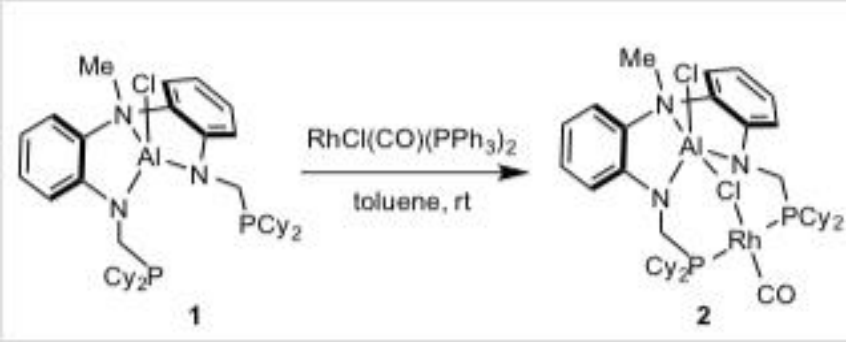
Dr. Teruhiko* Saito[1], Prof. Yoshiaki* Nakao[1,2]

[1]*Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan,* [2]*CREST, Japan Science and Technology Agency (JST), ,*

Poster Session 1

Heterobimetallic complexes derived from transition metals with Lewis acidic metals have received increasing attention in coordination chemistry due to their unique electronic properties and coordination modes to activate organic molecules. In this presentation, we report that synthesis of heterobimetallic complexes bearing group 9 or 10 transition metals with aluminum has been achieved by utilizing phosphino–aluminum ligand 1.

The reaction of aluminum–containing phosphorus ligand 1 with $RhCl(CO)(PPh_3)_2$ gave Rh/Al heterobimetallic complex 2 (eq 1). X-ray diffraction analysis of complex 2 revealed that aluminum and rhodium metal centers were bridged by a chloride ligand, and rhodium metal center possess square planar geometry. In a similar manner, we successfully obtained Ir/Al, Ni/Al, and Pd/Al heterobimetallic complexes using ligand 1. Furthermore, reduction of these metal complexes was examined to generate late transition metal–aluminum bonds.



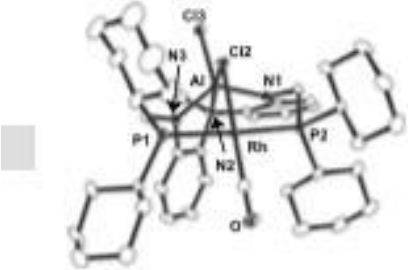


Figure 1. Crystal Structure of Complex **2**

P-107

Synthesis of Boryl Aryne Precursors via Catalytic C-H Activation and Their Orthogonal Derivatisation

Dr Lukasz Pilarski[1], Dr Emilien Demory[1], Mr Karthik Devaraj[1], Dr Andreas Orthaber[1], Dr Paul Gates[2]
[1]*Uppsala University, Uppsala, Sweden,* [2]*Bristol University, Bristol, UK*

Poster Session 1

(Hetero)arylboronates have become established as extremely versatile reagents for the arylation of many different functional groups. Iridium C-H borylation has proven to be a mild, selective and efficient method for their generation.[1] However, few methods exist for the postfunctionalization of arylboronates themselves.[2] Meanwhile, the development of ortho-silyl aryl triflates as precursors for the generation of arynes under mild conditions[3] has inspired a surge in recent developments around aryne capture as an arylation strategy.[4] Their postfunctionalization has remained unexplored to date, meaning each precursors typically has to be made de novo.

We report here[5] a new set of boryl aryne precursors that undergo orthogonal derivatisation of either the boronate or aryne functionality. These uniquely versatile building blocks are obtained in good-to-excellent yield via Ir catalysis and open up vast possibilities for access to new (het)arylboronates and (het)arynes with previously difficult-to-access substitution patterns. Moreover, the B(pin) units undergo facile and high-yielding deprotection to the corresponding boronic acids (2) and can be derivatised using 1,4-conjugate additions, Tsuji-Trost allylation, Chan-Lam amination, and other approaches to give a very broad range of substituted aryne precursors.

References:
[1] Chem. Rev. 2010, 110, 890-931. [2] Limited examples include: (a) Angew. Chem. Int. Ed. 2012, 51, 12723-12726 (b) Angew. Chem. Int. Ed. 2014, 53, 1822-1826. [3] Chem. Lett. 1983, 1211-1214. [4] Angew. Chem. Int. Ed. 2012, 51, 3766-3778. [5] Manuscript submitted.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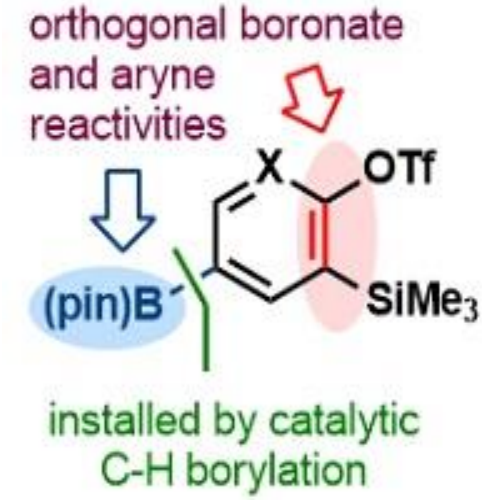

orthogonal boronate
and aryne
reactivities
X
OTf
(pin)B
SiMe3
installed by catalytic
C-H borylation

P-108

Pd-Catalyzed α-Alkenylation of Ketones: Synthesis of the ABCD Core of Calyciphylline A-Type Alkaloids

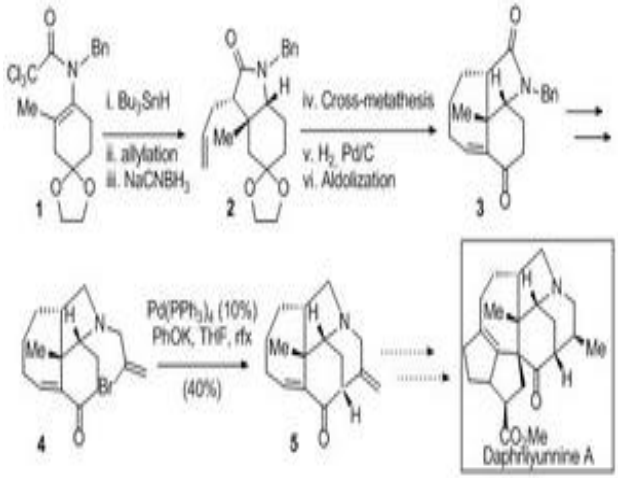
Prof. Josep Bonjoch[1], Guilhem Coussanes[1]
[1]*Laboratori de Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona, Barcelona, Spain*

Poster Session 1

New strategies for the synthesis of the vast array of Daphniphyllum alkaloids[2] have appeared in the last five years, reflecting a renewed interest in this area since the initial synthetic work of Heathcock. However, very few total syntheses have been reported to date.[3] Here, following our synthetic methodology of Pd-catalyzed intramolecular enolate alkenylation,[4] an approach to the ABCD fragment of calyciphilline A-type alkaloids is reported.

The tetracyclic core ring of calyciphylline A has been synthesized, the key steps being: (a) a 5-endo radical cyclization of trichloroenamide 1, which after diastereoselective allylation and reduction of the enamide gave 2; (b) a seven-membered ring formation (D ring) by a ring-closing aldolization leading to 3 and (c) a palladium-catalyzed intramolecular coupling of an amino-tethered vinyl bromide with a ketone (i.e. 4) using potassium phenoxide as the base to generate azatetracyclic compound 5 embodying the ABCD-ring. Studies on the transformation of 5 to the targeted alkaloids are in course.

References:
1. FP7Marie Curie Actions: ITN ECHONET Network (MCITN-2012–316379).
2. B. Kang, P. Jakubec, D. J. Dixon, Nat. Prod Rep. 2014, 31, 550.
3. Z. Lu, Y. Li, J. Deng, A. Li, Nature Chem. 2013, 5, 679.
4. D. Solé, X. Urbaneja, J. Bonjoch, Adv. Synth. Catal. 2004, 346, 1646.



P-109

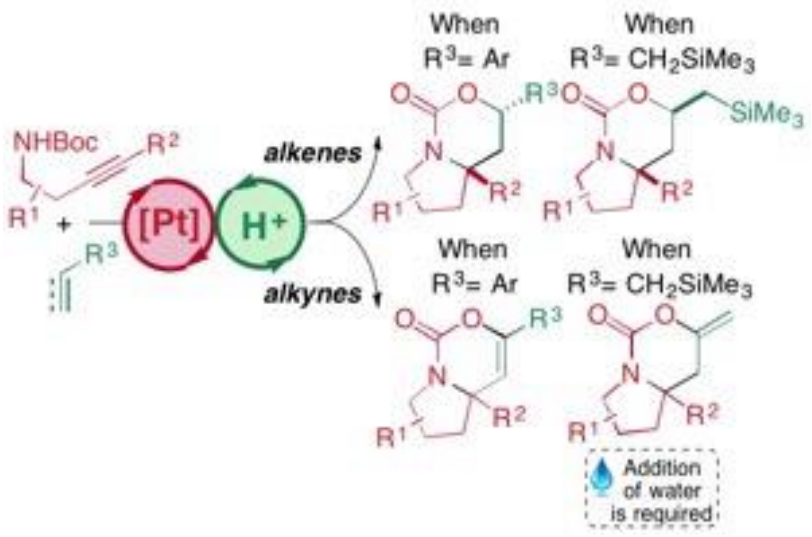
A Platinum/Brønsted Acid Relay Catalytic Cascade Reaction for the Synthesis of Pyrrolidine Derivatives

Alicia Galván[1], Dr. Jonás Calleja[1], Prof. Dr. Francisco Javier Fañanás[1], Prof. Félix Rodríguez[1]
[1]*Universidad de Oviedo, Oviedo, Spain*

Poster Session 1

The pyrrolidine nucleus is one of the most ubiquitous heterocyclic structural motifs found in Nature, present in many biologically active natural products, pharmaceutical drugs and, additionally, in a number of ligands and organocatalysts.[1] Although numerous methods for their preparation have been reported, the development of new protocols based on atypical disconnections is a topic of undoubted interest. Here, a new catalytic cascade reaction for the synthesis of pyrrolidine derivatives is presented. The method implies the coupling of N-Boc-protected alkynamine derivatives and appropriate alkenes or alkynes in a process catalysed by a platinum/triflic acid catalytic binary system. This cascade reaction involves an initial platinum-catalysed cycloisomerisation of the alkynamine derivative followed by a triflic acid promoted nucleophilic addition of the alkene or alkyne and trapping of the cationic species formed by the Boc group. Moreover, when allyltrimethylsilane is used interesting bicyclic compounds containing a trimethylsilyl group are obtained and when propargyltrimethylsilane is used in the presence of water formation of a related bicyclic compound lacking the trimethylsilyl group and containing an exocyclic carbon−carbon double bond was observed.[2]

References:
1. a) J. Buckingham, K. H. Baggaley, A. D. Roberts, L. F. Szabó, in Dictionary of Alkaloids, 2nd ed., CRC, Boca Raton, 2009. b) Privileged Chiral Ligands and Catalysts (Ed: Q.-L. Zhou), Wiley-VCH, Weinheim, 2011.
2. A. Galván, J. Calleja, F. J. Fañanás, F. Rodríguez, Chem. Eur. J. 2015, 21, 3409 – 3414. Highlighted as “Hot Paper”.



P-110

Gas-Phase Investigations on Transmetalation step in Sonogashira Reactions

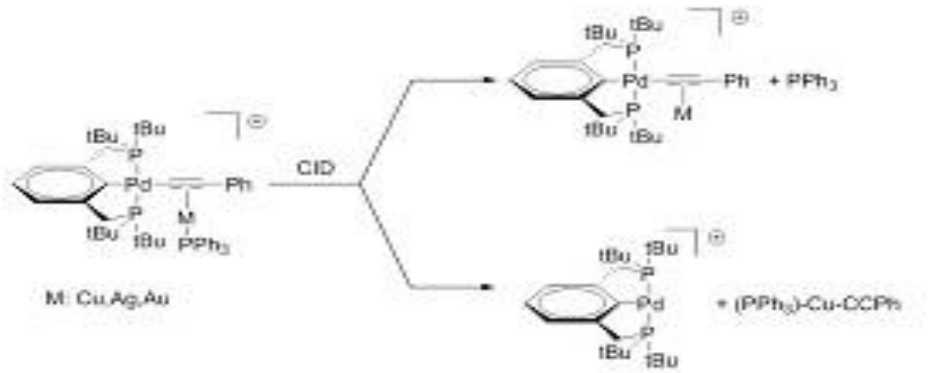
Mr. Raphael J. Oeschger[1], Dr. David H. Ringger[1], Prof. Dr. Peter Chen[1]
[1]*ETH Zürich, Zürich, Switzerland*

Poster Session 1

Bimetallic Pd/M (M: Cu, Ag, Au) catalyzed C–C bond-forming reactions have received significant attention in recent years. Even though the Sonogashira reaction is probably the most well-known of such reactions, its mechanism is still not well understood. Since Lei and coworkers determined that transmetallation was rate limiting1 this step has been of particular interest. We will describe a mass-spectrometric study on the microscopic reverse of a Sonogashira-type transmetallation. Measuring the activation energies by quantitative energy-resolved collision induced dissociation experiments2 provides an upper bound for the internal rearrangement energies of the transmetallation step. The associated potential energy surface was calculated by DFT and compared to the experimental results. Short Pd-Cu/Ag/Au distances in the optimized ground-state structures suggest that stabilizing metal-metal interactions are responsible for the low barriers of the bond-breaking/bond-forming step.

References:
1. He, C.; Ke, J.; Xu, H.; Lei, A., Synergistic Catalysis in the Sonogashira Coupling Reaction: Quantitative Kinetic Investigation of Transmetalation. Angewandte Chemie International Edition 2013, 52 (5), 1527-1530.

2. Couzijn, E. P. A.; Zocher, E.; Bach, A.; Chen, P., Gas-Phase Energetics of Reductive Elimination from a Palladium(II) N-Heterocyclic Carbene Complex. Chemistry – A European Journal 2010, 16 (18), 5408-5415.



Observed reactivity of bimetallic Pd/Cu,Ag,Au complexes upon collision induced dissociation.

P-112

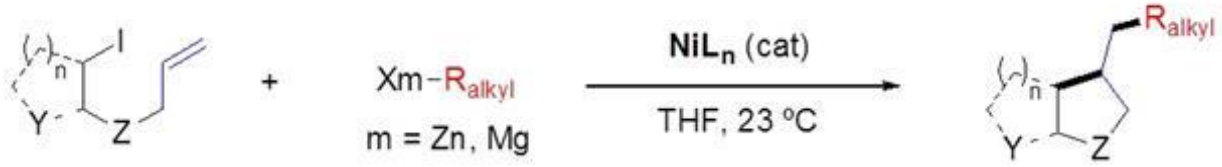
Ni and Fe catalyzed cross-coupling reactions for the formation of C-C(sp(sup)3(sup)) bonds

Prof. Dr. Diego J. Cárdenas[1], Dr. Manuel Guisán-Ceinos[1], Miss Rita Soler-Yanes[1], Dr. Francisco Tato[1], Dr. Elena Buñuel[1], Mr Daniel Collado-Sanz[1]
[1]*Universidad Autónoma de Madrid, Madrid, Spain*

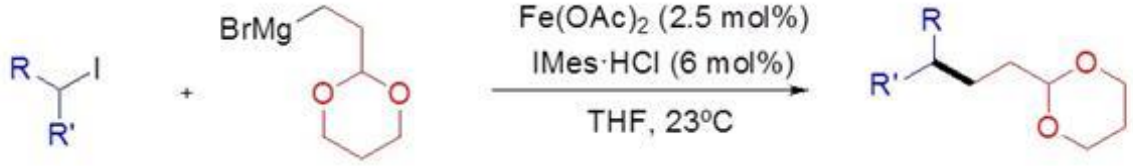
Poster Session 1

The use of first-row transition metal complexes, mainly Ni, Fe and Cu, as catalysts for cross-coupling reactions has experienced a renaissance during the last years. These metals have demonstrated to be especially useful for the coupling of alkyl electrophiles with a variety of metal-based nucleophiles. In addition to their convenience for economic and environmental reasons, these reactions also address fundamental aspects. Thus, wider scope can be covered, and novel mechanisms involving radical species, different from the usually accepted pathways for Pd chemistry, seem to be involved.
We have developed Ni-catalyzed cascade cyclization-coupling reactions of alkyl halides containing alkenes with alkyl-Zn or alkyl-Mg halides, which allow the formation of at least two C-C bonds in a single operation.(sup)1(sup) Several functional groups may be present within the structure of both cross-coupling partners. Mechanistic experimental and computational studies support the intermediacy of radical species.
On the other hand, Fe-NHC complexes catalyze Kumada-type alkyl-alkyl cross coupling reaction in the presence of functional groups. Mechanistic evidence point to Fe(I) complexes as the catalytically active species.(sup)2(sup)
We will present an overview of the scope and mechanism of Ni and Fe-catalyzed cascade and cross-coupling reactions for the formation of several C-C(sp3) bonds in a single operation. Recent results, as well as the possible reaction mechanisms will be discussed.

References:
[1] a) M. Guisán-Ceinos, R. Soler-Yanes, D. Collado-Sanz, V. B. Phapale, E. Buñuel, D. J. Cárdenas, Chem. Eur. J. 2013, 19, 8405. b) V. B. Phapale, E. Buñuel, M. García-Iglesias, D. J. Cárdenas, Angew. Chem. Int. Ed. 2007, 46, 8790.
[2] M. Guisán-Ceinos, F. Tato, E. Buñuel, P. Calle, D. J. Cárdenas, Chem. Sci. 2013, 4, 1098.



Z = CH_2, O, NTs, $C(CO_2Et)_2$; Y = CH_2, O; n = 0, 1



P-113

Origin of anti-Markovnikov hydroamination of alkenes catalyzed by Rh(I) complexes

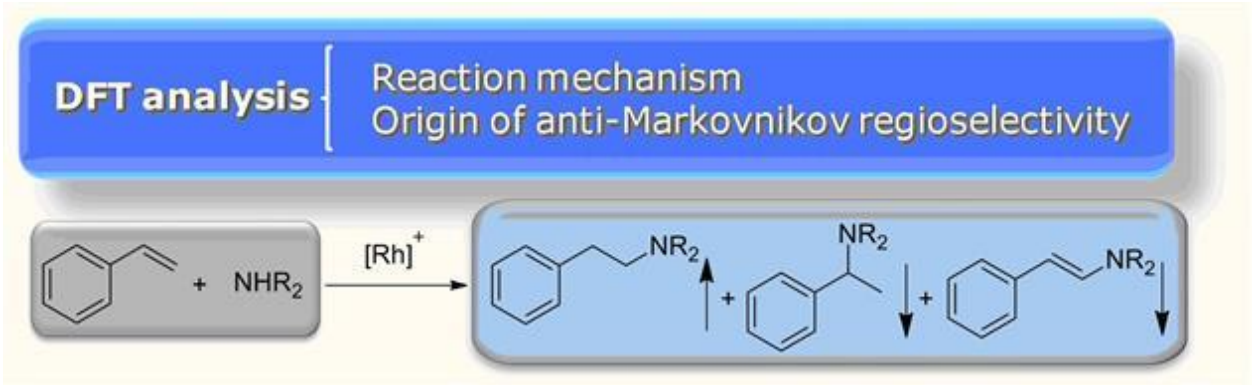
Dr Gregori Ujaque[1], Dip. Chem. Almudena Couce-Rios[1], Prof. Agustí Lledós[1]
[1]*Universitat Autonoma De Barcelona, Barcelona, Spain*

Poster Session 1

Nitrogen containing compounds such as amines, imines and enamines are very valuable and important due to their industrial and pharmaceutical applications. Improving synthetic methods for forming N-C bonds is thus stimulating.

In general, in acid catalyzed hydroamination reactions, the Markovnikov regioisomer is favored due to the higher stability of the secondary carbocation. Obtaining anti-Markovnikov products, however, is much more challenging. At the end of XX Century, Beller reported the first intermolecular anti-Markovnikov oxidative amination and hydroamination of styrenes catalyzed by the cationic [Rh(COD)2]BF4/PPh3 complex. Later, Hartwig published the first example of selective hydroamination of olefins (unactivated vinylarenes) with secondary amines to generate terminal amines as the major product (and oxidative amination as a side product). Several Rh(I) complexes were tested obtaining the best performance when using [Rh(COD)(DPEphos)]+ as catalyst (DPEphos = Bis[(2-diphenylphosphino)phenyl] ether).

Despite the detailed mechanistic studies of some Rh and Ir catalyzed intramolecular hydroamination of unactivated alkenes, the mechanism of the more challenging intermolecular version is not well understood yet. We carried out, by means of theoretical methods, a mechanistic analysis in order to elucidate the reaction mechanism (for the main and the side products), as well as the origin of the regioselectivity: Markovnikov vs anti-Markovnivov products.



P-114

Carbonyl Directed Carbonylative Ring Expansions of Aminocyclopropanes: Rhodium Catalysed Multicomponent Synthesis of N-Heterobicyclic Ketones

Mr. Niall McCreanor[1], Dr. Megan Shaw[1], Dr. John Bower[1]
[1]*University of Bristol, Bristol, UK*

Poster Session 1

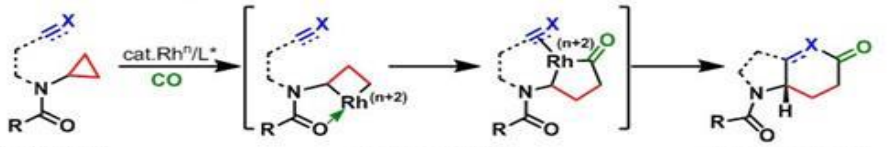
Previous work within the Bower group has demonstrated rhodium catalysed ring expansions of aminocyclopropanes bearing tethered alkynes.1[2] Here, the oxidative addition of the rhodium catalyst into the cyclopropane moiety is facilitated by an appropriate directing group (Scheme 1A).2[2]

Work described herein expands on this methodology by trapping the amino-rhodacyclopentanone intermediate with a tethered olefin generating complex N-heterobicyclic ketones. Several different substrate classes can be synthesised easily from commerically available cyclopropanecarboxylic acid. Under rhodium catalysed carbonylative conditions access to three different core scaffolds are attainable (Scheme 1B). These could prove useful for further synthesis or as pharmaceutical candidates.

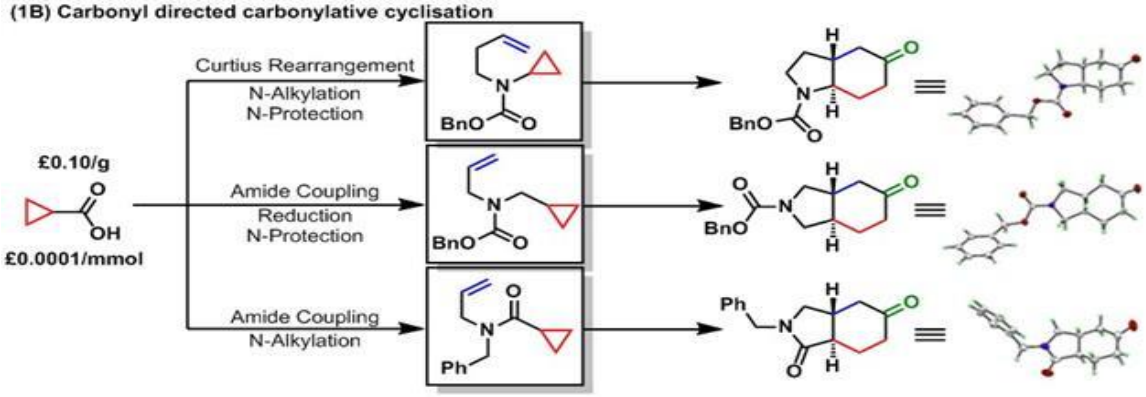
This process is highly diastereoselective yielding complex nitrogen containing scaffolds with multiple stereogenic centres that would be otherwise difficult to synthesise.3[2]

References:
1. Shaw, M. H.; Melikhova, E. Y.; Kloer, D. P.; Whittingham. W. G.; Bower, J. F. J. Am. Chem. Soc. 2013, 135, 4992
2. For directed insertion of rhodium into cyclopropanes see: Bart, S. C.; Chirik, P. J. J. Am. Chem. Soc. 2003, 125, 886.
3. Shaw, M. H.; McCreanor, N. G.; Whittingham, W. G.; Bower, J. F.; J. Am. Chem. Soc. 2015, 137, 463.

(1A) Multicomponent carbonylative ring expansions of aminocyclopropanes:



(1B) Carbonyl directed carbonylative cyclisation



P-115

Iron Catalyzed Reductive Functionalization of CO2

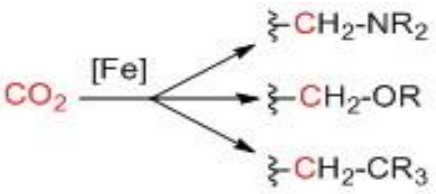
Dr Sébastien Bontemps[1], Dr Sylviane Sabo-Etienne[1], Guanghua Jin[1], Dr Yannick Escudié[1], Dr Gunnar Werncke[1]
[1]*LCC-CNRS, Toulouse, France*

Poster Session 1

CO_2 is an attractive source of carbon because it is an abundant and rather non-toxic molecule when compared to other C1 sources. Despite its high thermodynamic stability, CO_2 has been reduced to HCOOH, CO, CH_{3OH} and CH_4 under mild conditions. The next challenge is now to transform CO_2 into more complex and thus more valuable molecules. Cantat, Beller and others reported the access to formamides (R_2NCHO) and methylamines (R_2NCH_3) from amines, but the scope of CO_2 functionalization is restricted to these two functions and thus to the formation of C-N bond.

We recently reported the reduction of CO_2 into CH_2O by using ruthenium polyhydride catalysts. This was a significant finding on the fundamental point of view since it fully completed the C1 list of reduction products from CO_2. In addition such a system should give an easier access to more complex molecules, since formaldehyde is a reactive and versatile source of carbon.

By a careful control of the reductive process, we are now able to use CO_2 as a source of methylene to generate not only C-N bonds but also C-O and C-C bonds. Moreover, in the context of replacing noble metals by earth abundant metals, we are able to transfer our expertise from ruthenium to iron complexes. In this presentation, we will disclose a very efficient iron catalyst for the transformation of CO_2 into a large variety of compounds under mild conditions.



P-116

Synthesis of Unsymmetrically Substituted Fluorenes

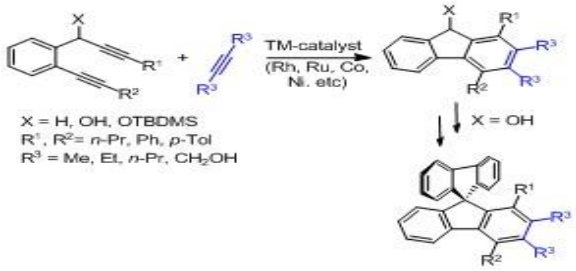
M.Sc. Reinhard Kaiser[1], Prof. RNDr. Martin Kotora[1]
[1]*Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Praha, Czech Republic*

Poster Session 1

Cyclotrimerization reaction of substituted diynes with alkynes was investigated as a new synthetic pathway to form regioselectively substituted fluorenes. Fluorenes, very similar to indenes are used as ligands in various complexes with transition metals[1] and important organic material chemistry components for light emitting devices like dyes in diodes.[2] Thus, appropriately substituted diynes with variable residues R[1] and R[2] (Scheme 1) as precursors for fluorenes or fluorenols were prepared by using sequential cross-coupling reactions of acetylides with o-halobenzyl halides or by Sonogashira coupling. These compounds were suitable starting materials for subsequent transition metal catalyzed cyclotrimerization reactions with symmetrically substituted alkynes, bearing various aliphatic substituents (Scheme 1, substituent R[3]). As far as transition metals were concerned, Rh, Ru, Co and Ni metals capable of performing cyclotrimerization were investigated. A major task of the project was the screening of various aliphatic and aromatic R[1], R[2] and R[3] residues.
Beside, also cyclotrimerization reactions with terminal alkynes (R[3]= Ph, Fc) were carried out and the substantial effect of the bulky moiety on the preferential insertion into one of two non-equivalent C-metal bonds in the intermediate metallacyclopentadiene was investigated.
With unsymmetrically substituted fluorenoles as suitable precursors for further elaboration the conversion of 9,9'-spirobifluorenes (Scheme 1) and their optical property was investigated.

Reference:
[1] Janková, Š.; Schulz, J.; Hybelbauerová, S.; Císařová, I.; Štěpnička, P.; Kotora, M. Eur. J. Org. Chem. 2013, 44.
[2] (a) Poriel, C.; Rault-Berthelot, J.; Thirion, D. J. Org. Chem. 2013, 78, 886. (b) Kumar, D.; Thomas, K.; Lee, C.; Ho, K. J. Org. Chem. 2014, 79, 3159.

This work was supported by the Czech Science Foundation (reg. No. 13-15915S).

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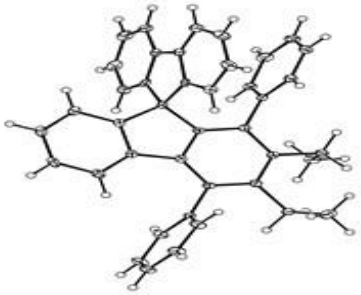


P-117

Asymmetric catalytic hydrogenation of enamines towards the synthesis of (-)-cytisine and heterocyclic building blocks

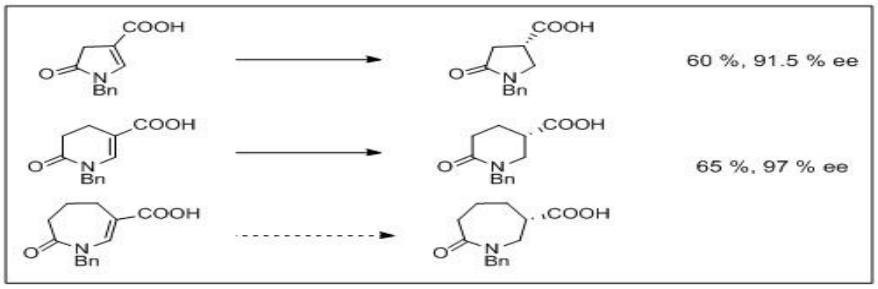
Mr Hugo Rego Campello[1], Prof. Timothy Gallagher[1]
[1]*School of Chemistry, University of Bristol, Bristol, UK*

Poster Session 1

Asymmetric catalytic hydrogenation of enamines in a transition metal catalyzed reaction has been established as a readily available pathway for the synthesis of several heterocyclic building blocks. The scope of the reaction has been investigated over 5-, 6-, and 7-membered-cyclic enamines, generating the resulting amides in high enantiomeric excess.

Figure 1: Asymmetric heterocyclic building blocks which may be used as future templates to synthesize many asymmetric organic compounds.

Furthermore, this chemistry provides a novel asymmetric route towards the synthesis of the naturally occurring alkaloid ( ) cytisine 1, enabling a general way to synthesize core and pyridone modified derivatives asymmetrically. Cytisine 1 behaves as a partial agonist of nicotinic acetylcholine receptors in the brain, and it was taken by Pfizer as the lead compound in the development of Varenicline, a smoking cessation agent. Moreover, one interesting pyridone modified cytisine analogue, which is thought to hold greater biological activity than cytisine, has been synthesized.

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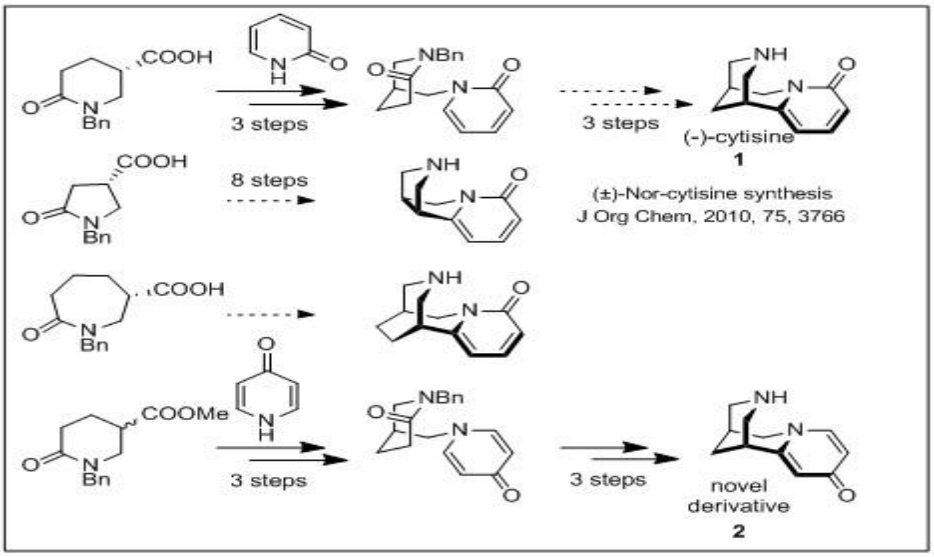
COOH
N
Bn
3 steps
NBn
3 steps
NH
(-)-cytisine
1
8 steps
(±)-Nor-cytisine synthesis
J Org Chem, 2010, 75, 3766
COOMe
3 steps
3 steps
novel
derivative
2

P-118

Gold-catalyzed Hydroamination of C-C Multiple Bonds with Small Nucleophiles: Substrate and Ligand Effects

Dr. Agusti Lledos[1], Ms. Almudena Couce-Rios[1], Dr. Gregori Ujaque[1]
[1]*Universitat Autonoma de Barcelona, Cerdanyola Del Valles, Spain*

Poster Session 1

Hydroamination with small nucleophiles as ammonia or hydrazine represents a challenging task. In 2008, Bertrand reported gold(I) complexes with bulky cyclic (alkyl)(amino)carbene ligands as the first homogeneous catalysts active in the hydroamination of alkynes and allenes with ammonia.[1] Recently, Betrand's and Hashmi's groups showed that related gold-N-heterocyclic carbenes also promote the hydroamination of alkynes and allenes with parent hydrazine.[2] We have theoretically addressed the mechanism of such transformations. The general mechanism we described for the reaction with ammonia[3] is also operating in the case of the hydrohydrazination of alkynes (Figure 1).[4] Aspects such as the associative or dissociative nature of the ligand exchange between hydrazine and the substrate, the generation of the catalytically active π-complex, the inner or outer-sphere mechanism for the nucleophilic attack, the nitrogen to carbon proton transfer or the relative importance of the ligand substitution, the nucleophile addition and the proton transfer barriers in the catalytic cycle are analyzed in the light of the DFT results, taking into account the nature of the carbene ligand and the substrate.

References:

1. Lavallo, V.; Frey, G. D.; Donnadieu, B.; Soleilhavoup, M.; Bertrand, G. Angew. Chem. Int. Ed. 2008, 47, 5224.
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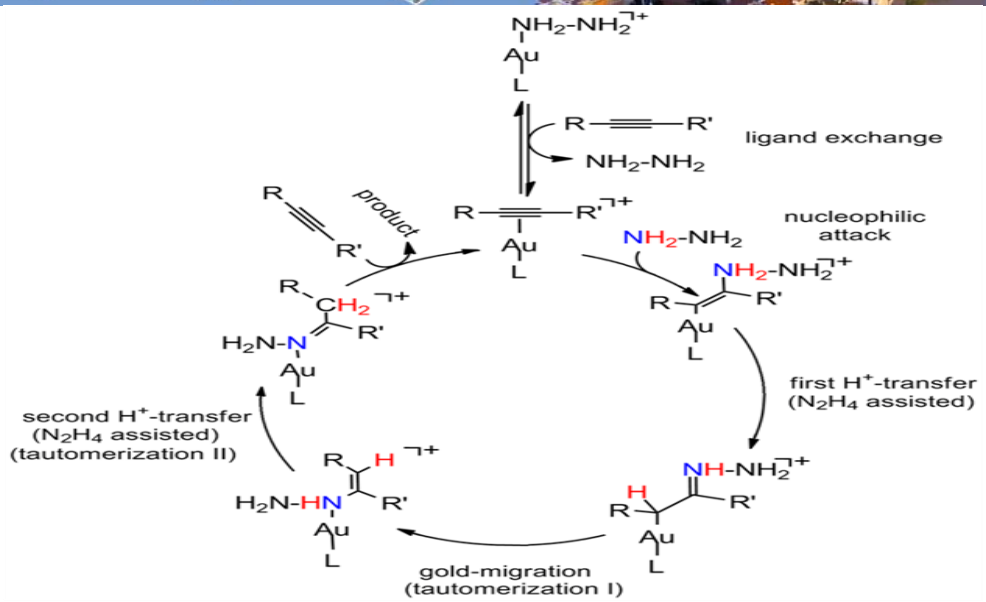

ligand exchange
nucleophilic attack
product
first H+-transfer (N2H4 assisted)
gold-migration (tautomerization I)
second H+-transfer (N2H4 assisted) (tautomerization II)

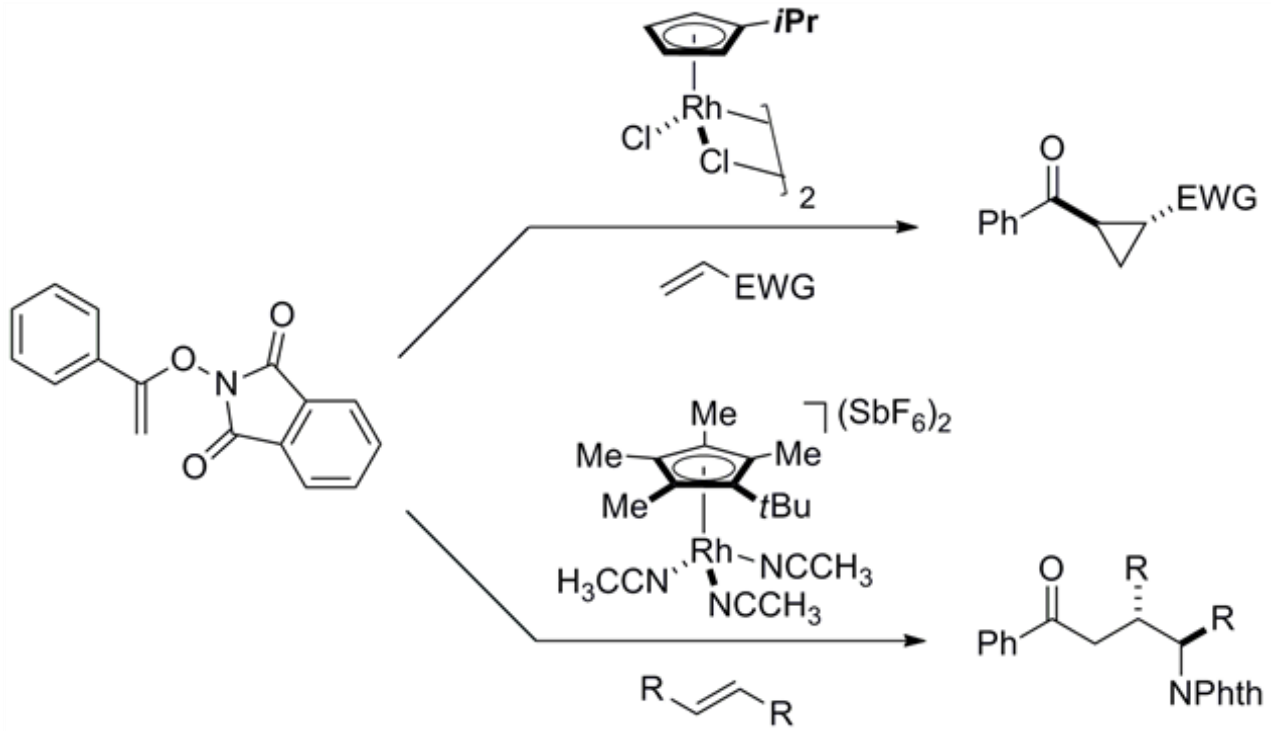
P-119

Rh(III)-Catalyzed C-H Activation of N-Enoxyphthalimides: The Design of New Cyclopentadienyl Ligands to Control Selectivity

phD Tiffany Piou[1], Prof. Tomislav Rovis[1]
[1]*Colorado State University, Fort Collins, USA*

Poster Session 1

Rh(III)-catalyzed C-H activation of aromatic C-H bonds represents a valuable strategy for the synthesis of N-heterocycles. With prominent exceptions, this approach has not been widely used for the synthesis of saturated compounds. Furthermore, the limited number of cyclopentadienyl ligands available for catalysis has hindered progress in the field. Herein, we report our recent discovery of N-enoxyphthalimide reactivity and our design of new cyclopentadienyl ligands to solve selectivity issues. We discovered N-enoxyphthalimides undergo a Rh(III)-catalyzed C-H activation initiated cyclopropanation of electron deficient alkenes. The design of a new monosubstituted isopropylcyclopentadienyl ligand enables the synthesis of trans-1,2-disubstituted cyclopropanes in high yield and diastereoselectivity. During the course of our study, we discovered a divergent syn-carboamination pathway leading to acyclic saturated α-aminoacid derivatives. The chemoselectivity outcome of this transformation was controlled by tuning of the cyclopentadienyl ligand with in situ formation of an “active” bidentate directing group. The generated compounds could be cyclized to efficiently access polysubstituted pyrrolidines.



P-120

Synthesis of Highly Substituted Azoles via Direct C–H Bond Arylation Catalyzed by Palladium–Nitrogen-based Ligands Complexes

Dr. Fumitoshi Shibahara[1], Mr. Takayuki Yamauchi[1], Dr. Eiji Yamaguchi[2], Dr. Toshiaki Murai[1]
[1]Gifu University, Gifu, Japan, [2]Gifu Pharmaceutical University, Gifu, Japan

Poster Session 1

Polyarylated azoles are an important motif for pharmaceuticals and functional materials, and the synthesis of these compounds has been extensively studied for over a century. Recently, direct C–H bond arylation of the parent azoles has emerged as a significant alternative to conventional transition-metal-catalyzed C–C bond-forming reactions to obtain polyarylated azoles. Particularly, palladium-catalyzed those reactions have been extensively studied owing to wide applicability for C-H bonds on (hetero)arenes. Meanwhile, most of the previous examples have used phosphine-based ligands, but some limitations remain such as reaction positions. On the other hand, we have developed the reaction catalyzed by palladium–1,10-phenanthroline complexes.[sup]1-5[/sup] This catalytic system made it possible to achieve direct arylation of all C–H bonds on azoles including less-reactive C4 position in a catalytically controlled manner that can hardly be achieved by other catalytic systems. With our system, stepwise sequential triarylations such as three steps synthesis of Tie2-tyrosine kinase inhibitor from unsubstituted N-methylimidazole are achieved (eq 1).[3] One-pot sequential direct C-H bond arylations of azoles was also developed by our system with simple sequential addition of aryl iodides to the reaction mixture.[5] In addition, C-Br bonds on azoles were intact under the reaction conditions. With this feature in hand, syntheses of the other types of functionalized azoles have also been demonstrated.[6] Those details will be presented.

References:
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[4] Yamaguchi, E.; Shibahara, F.; Murai, T. Chem. Lett. 2011, 40, 939.
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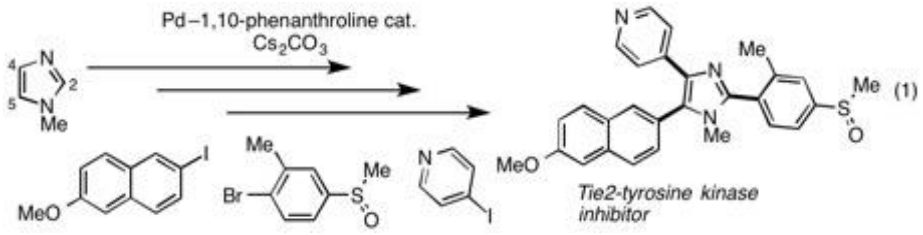


P-121

Rhodium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzosiloles and Related Compounds by Enantioselective [2+2+2] Cycloaddition

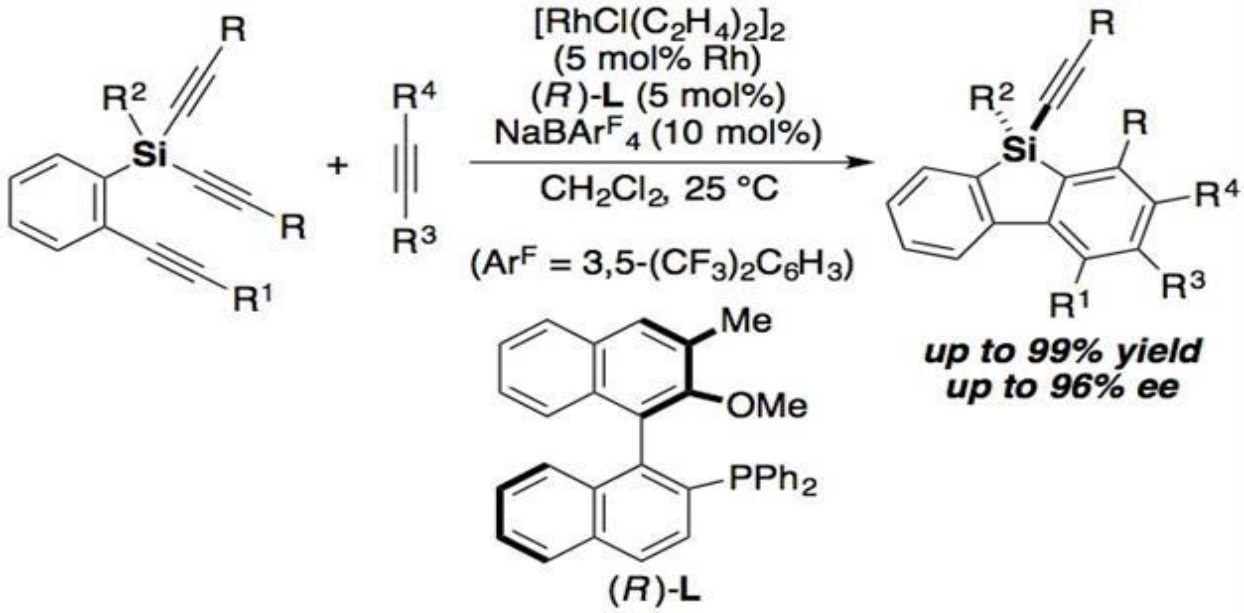
Dr. Ryo Shintani[1], Mr. Chihiro Takagi[1], Mr. Tomoaki Ito[2], Mr. Ryo Takano[1], Dr. Masanobu Naito[3], Dr. Kyoko Nozaki[1]

[1]Graduate School of Engineering, The University of Tokyo, Bunkyo-Ku, Japan, [2]Graduate School of Science, Kyoto University, Sakyo, Kyoto, Japan, [3]National Institute of Materials Science, Tsukuba, Japan

Poster Session 1

Dibenzosiloles constitute a class of compounds that can be applied to various useful materials due to their unique optoelectronic properties based on the π-conjugation system. Considering the wide utility of dibenzosiloles in materials science, the preparation of enantioenriched chiral dibenzosiloles would be of high significance in view of their potential future applications. In this context, we envisioned that the preparation of silicon-stereogenic dibenzosiloles would be highly attractive because the requisite biaryl moiety of the dibenzosilole can be flexibly tuned without the necessity of introducing extra carbon stereocenters, but available methods for the construction of silicon stereocenters in a catalytic asymmetric manner are very limited compared to those for the construction of carbon stereocenters.

In this context, here we describe the asymmetric synthesis of silicon-stereogenic dibenzosiloles and related compounds through a rhodium-catalyzed [2+2+2] cycloaddition of silicon-containing prochiral triynes with appropriate reaction partners. High yields and enantioselectivities have been achieved by employing an axially chiral monophosphine ligand, and this process could also be applied for the asymmetric synthesis of a germanium-stereogenic dibenzogermole.



P-122

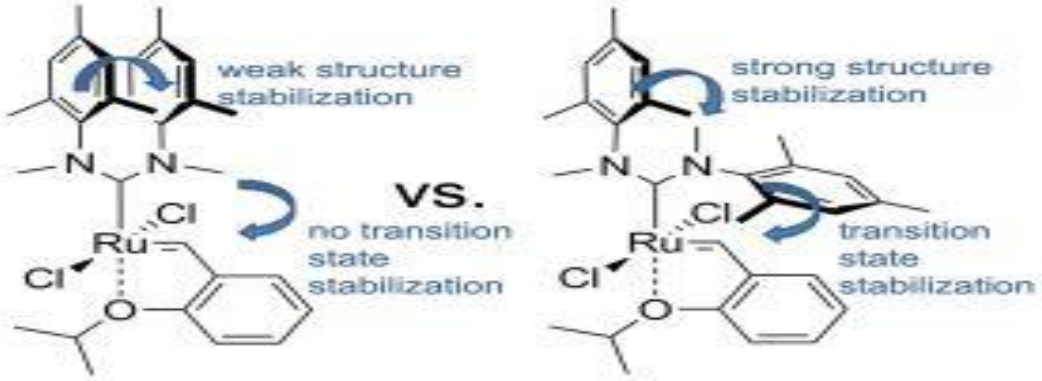
The role of C_{ipso}-$C_{alkylidene}$ interaction in the stabilization of acyclic Ruthenium-based metathesis catalysts.

Dr Bartosz Trzaskowski[1], Aleksandra Pazio[1,2], Prof Karol Grela[2], Prof Krzysztof Woźniak[2]
[1]*Centre of New Technologies, University of Warsaw, Warszawa, Poland,* [2]*Faculty of Chemistry, University of Warsaw, Warszawa, Poland*

Poster Session 1

We used the density functional theory to gain insight into the conformational flexibility of acyclic diaminocarbenes (ADC) and their corresponding Hoveyda- and Grubbs-class ruthenium complexes. Remarkably, all known crystal structures of acyclic carbenes and their Hoveyda-type Ru complexes show only one specific conformer. We demonstrate that rotation about the C-N bonds in the free acyclic diaminocarbenes is thermally accessible (~20 kcal/mol), but is relatively restricted upon coordination, primarily due to steric constraints. In consequence, the capacity of the ADC ligands to sample multiple conformations is reduced following coordination.

In addition, we show that the conformation of the carbene part of both the ADC-Hoveyda and ADC-Grubbs catalysts has a major impact on the energy barriers of the initiation step of metathesis reaction. First, we demonstrate that the presence of the interaction between the H atom of the isopropoxy-styrene part and the C_{ipso}atom of the neighboring mesityl ring. Our results suggest that this interaction has little impact on the rotational energy barriers. On the other hand the importance of the C_{ipso}-$C_{alkylidene}$ interaction is immediately obvious when we consider the energetic outcome of the precatalyst activation. The amphi-L and syn conformers, both with the mesityl ring close to the $C_{alkylidene}$ atom, have substantially lower energy barriers and more stable products of the initiation step than those conformers with the mesityl ring rotated away from the Ru center (amphi-R and anti). As a result the structures of both the dissociative and intermediate path transition states as well as the products are stabilized by this subtle, yet important interaction.



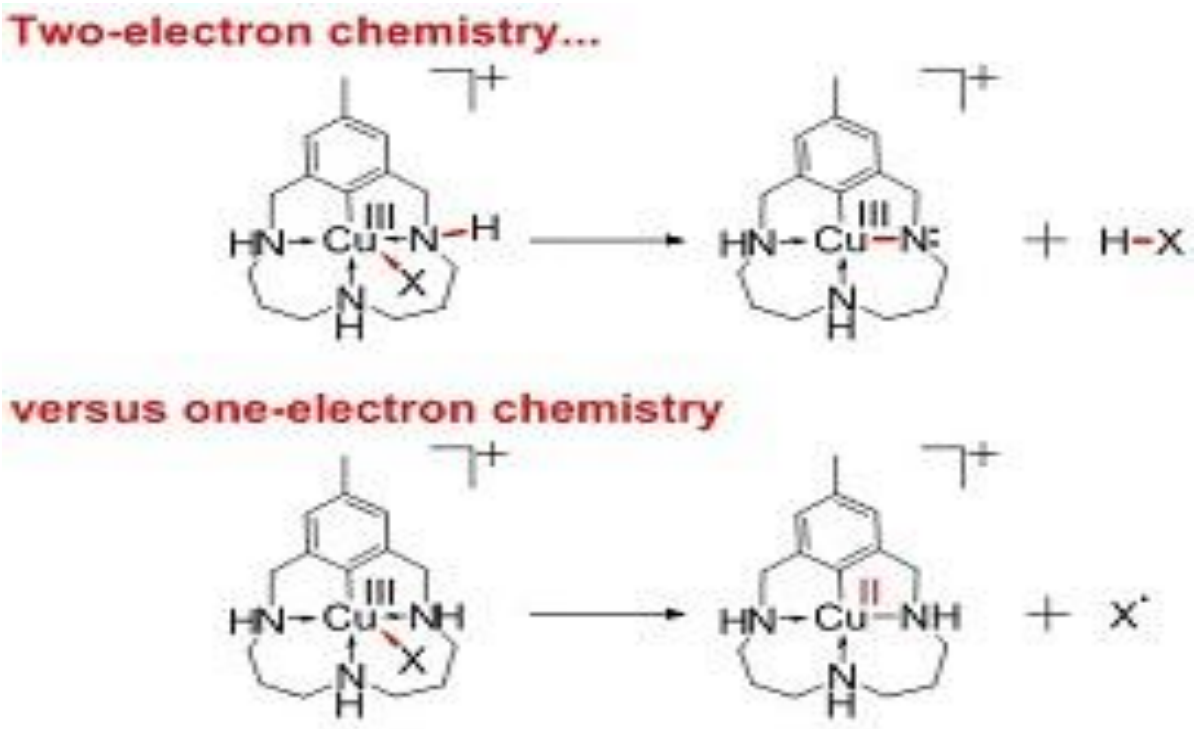
P-123

An up-close look at catalytic organocopper(III) intermediates: Using gas-phase chemistry to validate DFT methods and inform solution-phase chemistry.

Dr. Krista Vikse[1], Prof. Dr. Peter Chen[1]
[1]*ETH Zurich, Zurich, Switzerland*

Poster Session 1

Selecting suitable DFT methods for elucidating organometallic mechanisms is not straightforward. Different DFT functionals can give dramatically different results for the same system and there exists very little thermochemical data on ligated metal catalysts (especially those in unusual oxidation states) against which the performance of these functionals can be judged. Here we will present the results of a quantitative gas-phase mass spectrometry study on a series of organocopper(III) complexes (see graphic, X = Cl, Br, I) that are known reactive intermediates in copper-catalyzed Ullmann-type reactions. The results of our DFT benchmarking study will be presented. Furthermore, factors which affect the propensity of these organocopper(III) complexes to participate in one-electron versus two-electron chemistry will be discussed and an emphasis will be placed on relating the observed gas-phase reactivity to known solution-phase chemistry.



P-125

Iridium Catalyzed Cyclodimerization of Imines to Substituted Piperazines

Dr. María Pilar del Río[1], Dr. José Antonio López[1], Prof. Dr. Miguel Ángel Ciriano[1], Dr. Cristina Tejel[1]
[1]*ISQCH (Instituto de Síntesis Química y Catálisis Homogénea), Zaragoza, Spain*

Poster Session 1

Piperazine is the basic skeleton of a broad class of organic compounds, which display a wide variety of biological activities.[1] This pharmacophore is found in about 6% of all orally administered drugs due to its antitumor, antiviral, antifungal, and antibacterial properties. The synthesis of piperazines is usually achieved by reduction of (di)oxopiperazines, α-lithiation of Boc-protected piperazines, or by different cyclization reactions such as dialkylation of amines with bis(2-chloroethyl)amine, reductive cyclization of diimines, alkene carboamination, and the Mitsunobu reaction. However, the efficient synthesis of substituted piperazines often requires lengthy sequential synthesis, making the developments of diverse and efficient synthetic approaches highly desirable.

In 2012, the groups of Li [2] and Wolczanski [3] reported the stoichiometric synthesis of substituted piperazines from deprotonated imines through the formation of binuclear titanium complexes. Although some valuable intermediates could be isolated, all the attempts to carry out the reactions in a catalytic manner were unsuccessful.

In this communication we report a good catalytic method yielding fully substituted piperazines (2,3,5,6-tetraRpiperazines) mediated by the iridium complex [Ir(cod)Cl(PPh3)], and the characterization of related complexes. The formation of the desired heterocycle is produced by the cyclodimerization of the imine in a C-C diastereoselective coupling process. The scheme shows the proposed catalytic cycle for the bis(picolyl)imine (bpi) cyclodimerization.

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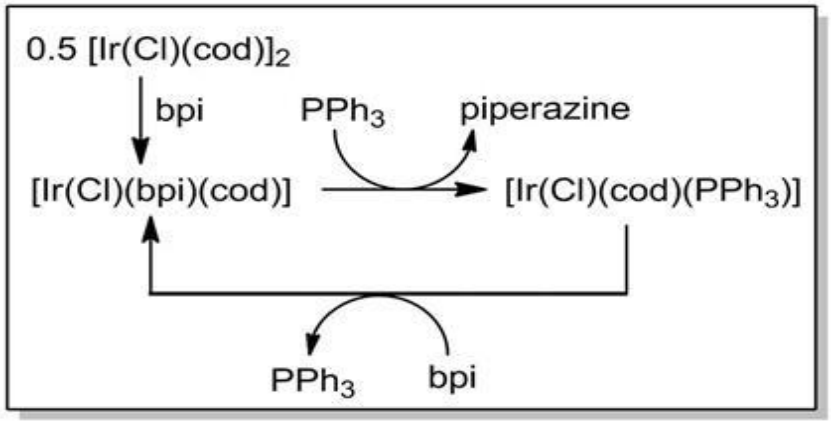
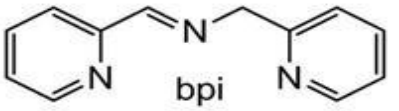

0.5 [Ir(Cl)(cod)]2
bpi
PPh3
piperazine
[Ir(Cl)(bpi)(cod)]
[Ir(Cl)(cod)(PPh3)]
PPh3
bpi


N
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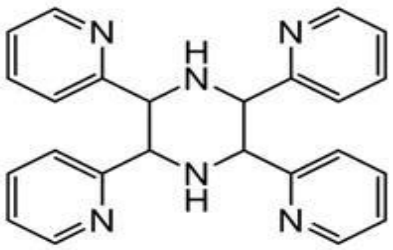
N
H
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N
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H
N
N
N

piperazine

P-126

Ni-catalyzed Mild Chemo-, Regio- and Diastereoselective Bond-Formation via Proximal C–C Cleavage of Benzocyclobutenones

Dr Francisco Juliá-Hernández[1], Dr Asraa Ziadi[1], Dr Akira Nishimura[1], Prof Rubén Martín[1,2]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain*

Poster Session 1

The field of metal-catalyzed C-C bond-activation has evolved over the last years from a mere curiosity to a powerful tool for advanced organic synthesis. While oftentimes visualized as exotic cyclobutane analogues, benzocyclobutenones (BCB) have shown to be superb reaction intermediates in a myriad of transformations.[1] Unfortunately, the reactivity of BCB remains confined to their innate proclivity for distal C1-C8 cleavage.

Our new protocol describes the first intermolecular bond-formation via proximal C1–C2 cleavage of BCB using non-precious noble Ni(0) catalysts and without requiring prior activation of carbonyl groups.[2] This method allows the preparation of a variety of otherwise inaccessible carbocyclic skeletons depending on the synthon utilized, including elusive benzofused eight-membered rings via formal [4+4]-cycloaddition and at room temperature.

References:
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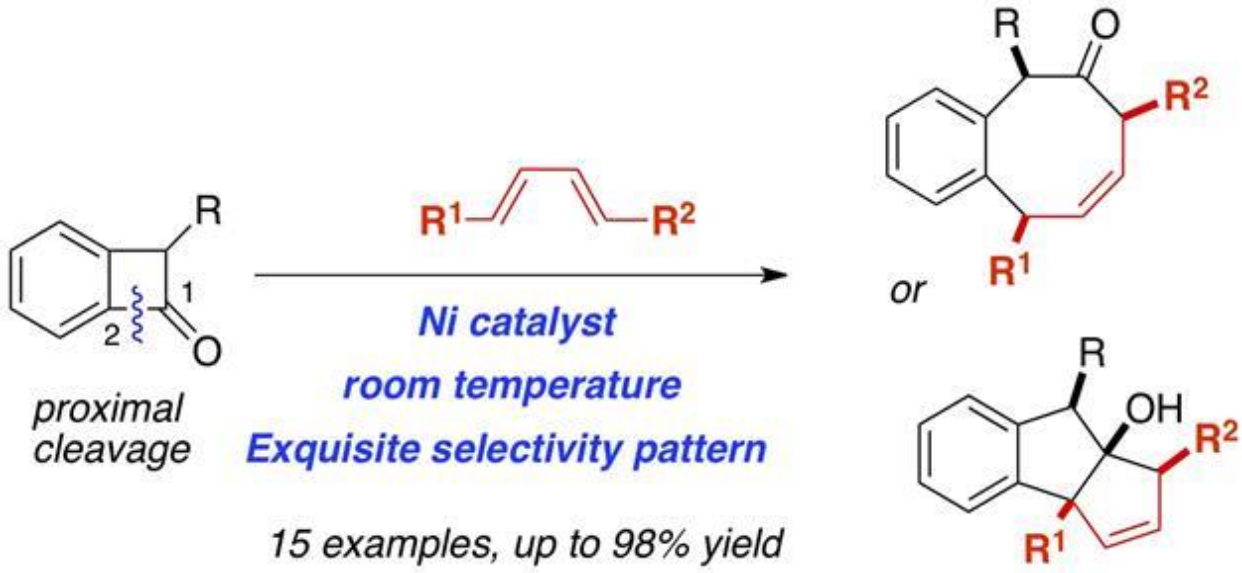
(2) (a) Xu, T.; Dong, G. Angew. Chem. Int. Ed. 2012, 51, 7567. (b) Ishida, N.; Sawano, S.; Masuda, Y.; Murakami, M. J. Am. Chem. Soc. 2012, 134, 17502.



P-127

Metal catalysed synthesis of boron-oxygen heterocycles from alkene containing boronic acids: novel strategies for the synthesis of poly-substituted boron enolates and benzooxaboroles.

Dr Laure Benhamou[1], Mr Daniel Walker[1], Dr Tom Sheppard[1]
[1]*University College London, London, UK*

Poster Session 1

Enolates are versatile intermediates in organic chemistry and are employed in a range of useful transformations.(1) Boron enolates are a very attractive class of enolates because when they are involved in a C-C bond formation process they induce good stereocontrol via a compact transition state.(2)
The main application of boron enolates is in the aldol reaction where an enolate reacts with another carbonyl precursor to synthesise β-hydroxy-carbonyl compounds. Since the two reaction partners come from carbonyl compounds, selective deprotonation to form the enolate remains a challenge and usually the procedure requires a two-step sequence. New strategies in the research area are now focusing on the development of a "one-pot" aldol reaction and more particularly on the formation of enolates or their equivalents from non-carbonyl precursors. To date two strategies are reported that rely on metal-catalysed alkyne activation or isomerisation of allylic alcohols.(3) Our group has previously reported a gold catalysed synthesis of boron enolates by an intramolecular addition of a boronic acid to an alkyne (A).(4) To extend our methodology and reach a greater diversity of enolates, we have developed a novel strategy to generate enolates from alkenes following a palladium catalysed Wacker-type oxidation (B). Careful identifications of by-products at the early stage of our study allowed us to optimise three procedures for the preparation of three different types of boron-oxygen heterocycles from alkenes containing boronic acids: boron enolates, halo-boron enolates and benzooxaboroles.

References:

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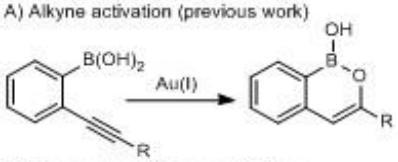
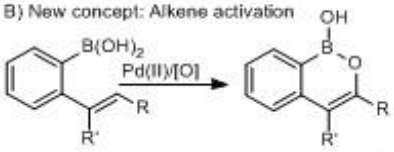
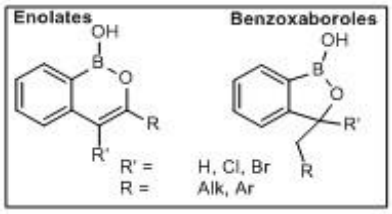
A) Alkyne activation (previous work)



B) New concept: Alkene activation





P-129

Synthesis, Characterization and Application of N-Trifluoromethyl N-Heterocyclic Carbene Ligands and Their Complexes

Mr. Pascal Engel[1], Remo Senn[1], Prof. Antonio Togni[1]
[1]*ETH Zürich, Zürich, Switzerland*

Poster Session 1

Since their discovery by Arduengo et al. in 1991, stable N-heterocyclic carbenes (NHCs) are extensively used as bulky and electron-rich ligands for transition metals in homogeneous catalysis.
Only very recently NHCs bearing electron-withdrawing groups on their backbone or side chains were shown to outperform their electron-rich analogs in gold(I)- and platinum(II)-catalyzed carbocyclisations [1].
Starting from N-trifluoromethyl benzimidazole, which was synthesized according to a procedure recently reported by our group [2], we present the synthesis and characterization of a series of complexes bearing an electron-poor N-trifluoromethylated NHC ligands [3]. Furthermore the performance of gold- and platinum-complexes bearing these novel N-trifluoromethylated ligands in a variety of carbocyclisation and hydrosilylation reactions was investigated.

References:
[1] Alcarazo, M.; Stork, T.; Anoop, A.; Thiel, W.; Fürstner, A. Angew. Chem., Int. Ed. 2010, 49, 2542−2546.
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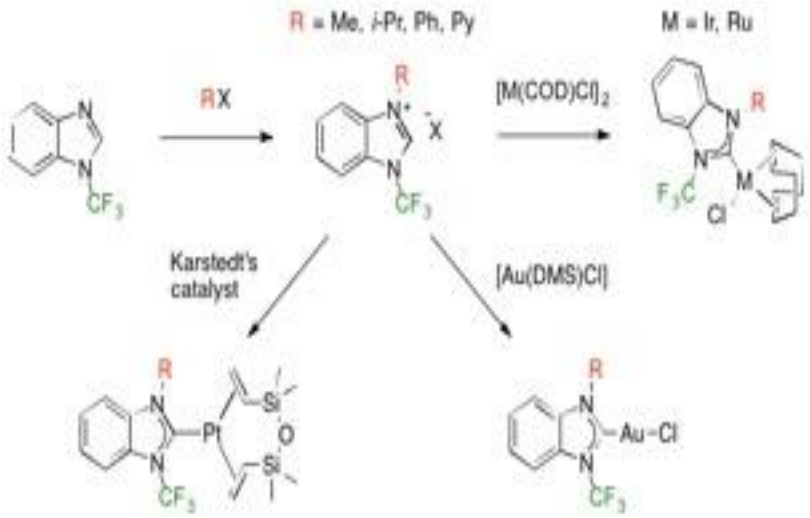

P-130

Amino Acid-derived N-Heterocyclic Carbene Palladium Complexes for Suzuki-Miyaura Couplings in Water: The Control of Hetero- and Homogeneity

Bsc, MChem Elliot Steeples[1], Prof. Markus Antonietti[1], Dr. Davide Esposito[1]
[1]*Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

Poster Session 1

The demand for petrochemical-derived solvents is unsustainable. The search for alternatives has driven research towards catalytic systems designed for the earth's most abundant solvent: water. One particular approach is designing homogeneous catalysts featuring water-soluble ligands for reactions within fine chemical synthesis, however water solubility is typically induced using toxic sulfonated alkanes and arenes.1,2

Here we present a two-step synthesis for "green", novel N-heterocyclic carbene ligand precursors featuring amino acid "R" groups to induce water-solubility;3 and their subsequent complexation with Palladium. These were characterized using NMR, mass spectrometry and X-ray crystallography, allowing for comparison with the steric and electronic properties of traditional NHC ligands.4 Complexes featuring both bis-carbene ligands and pyridine-enhanced complexes were synthesized. These complexes were utilized as catalysts in aqueous phase Suzuki C-C cross coupling reactions of bromoarenes with phenylboronic acid; whereby the active catalyst is generated by hydrolyzing the "arms" of the imidazolium under the same reaction conditions.

By NMR analysis of the aqueous phase, we report evidence of heterogeneous palladium nanoparticles forming during the reaction, supported by TEM imaging. We aim to control this nanoparticle formation to optimize yield, which is a common issue associated with aqueous C-C couplings.2b

Yields of >97% were reached at 60°C in roughly 2 hours with the use of a phase-transfer catalyst; one of the fastest full conversion couplings to date.

References:

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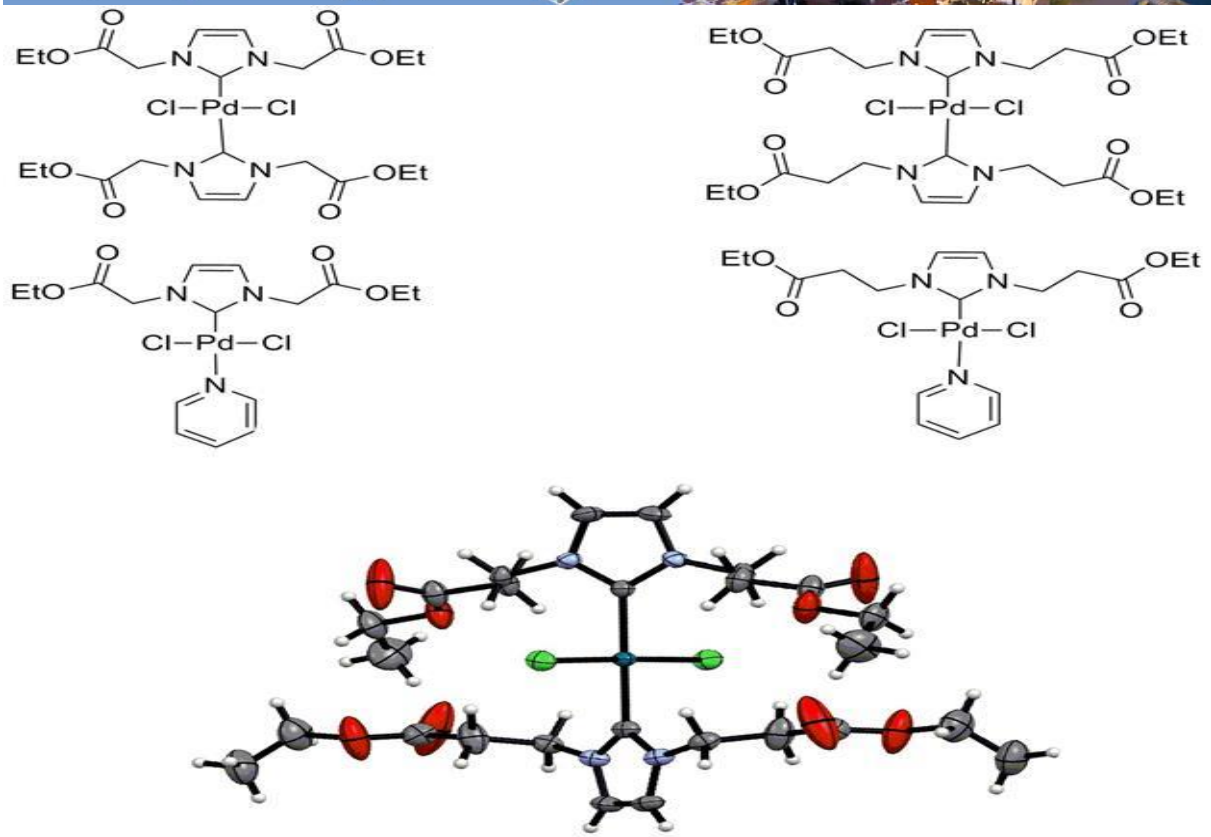


Figure 1: Synthesized Pd-NHC pre-catalysts with an example ORTEP X-ray image

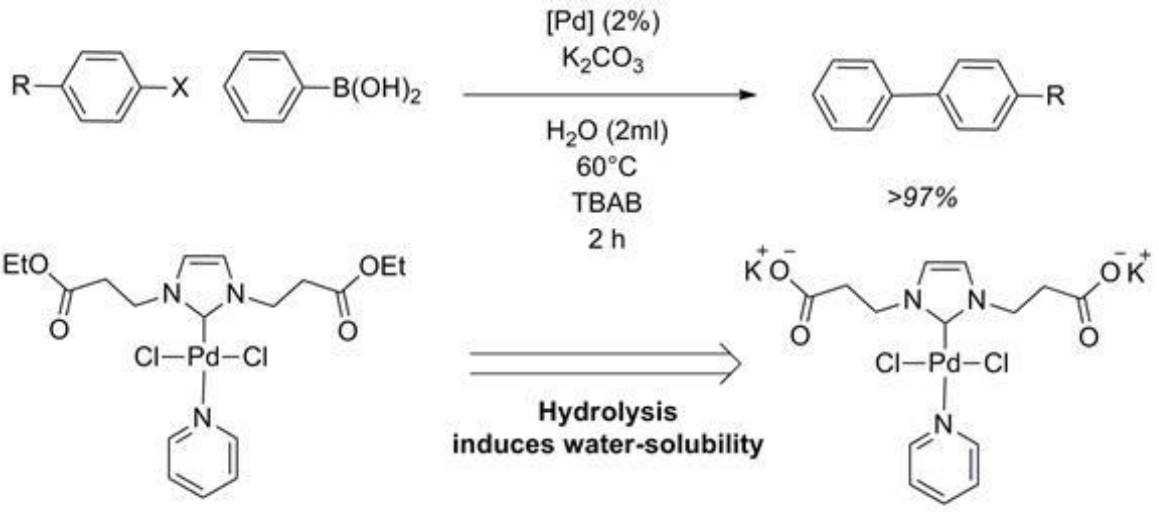


Figure 2: General procedure for Suzuki-Miyaura couplings of phenylbornic acid with various aryl halides featuring *in-situ* water-soluble catalyst generation.

P-132

Hydroformylation applied to the synthesis of indoles

Dr Tyler Bredenkamp[1], Prof. Emeritus Cedric Holzapfel[1], Ms. Etelinda da Silva[1]
[1]*University of Johannesburg, Johannesburg, South Africa*

Poster Session 1

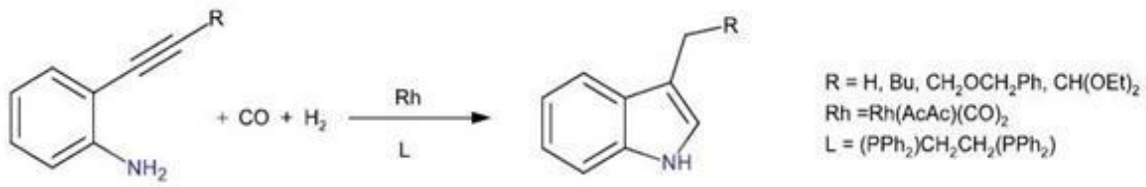
The pharmacological importance of indoles has prompted the development of new synthetic methodologies. [1] Our interest in the synthesis of tryptophans and their precursors stems from our earlier development of a synthetic route to lavendamycin analogues. [2] We now report ring synthetic routes to 3-substituted indoles aimed at generalising and improving hydroformylation approaches. [3]

The first method involves the Rh-catalysed hydroformylation of the Sonogashira derived 2-(alk-1-yn-1-yl) anilines (Scheme 1). Hydroformylation of 2-(alk-1-yn-1-yl) anilines.

Reactions were performed at 80-100 °C and 25 bar syngas. Ligand selection was critical to ensure that the required regioselectivity of the reaction was met. The second method involves the bimetallic (Rh and Pd) hydroformylation of 2-nitro-cinnamaldehyde acetals (Scheme 2). Hydroformylation of 2-nitrocinnamaldehyde derivatives.

Reactions were performed under the conditions described above. In both cases yields in excess of 75% for the desired indole were obtained. Further improvements to the latter (near quantitative conversions) were obtained by the addition of a Pd-complex in DMF to the reaction mixture at ≈ 3 hours after the reaction had started.

References:
1) D.R. Stuart, M.B. Laperle, K.M.N, Burgess, K. Fagnou J. Am. Chem. Soc. 2008, 130, 16474 – 16475 (and references cited therein).
2) C.W. Holzapfel, W. Marais J. Chem. Research. 2002, 22 – 24.
3) Y. Dong, C.A. Busacca J. Org. Chem. 1997, 62, 6404, b) M. Marchetti, S. Paganelli, D. Carboni, F. Ulgheri, D. Del Ponte, J. Molec. Catal. A: Chemical 2008, 288, 103 – 108.

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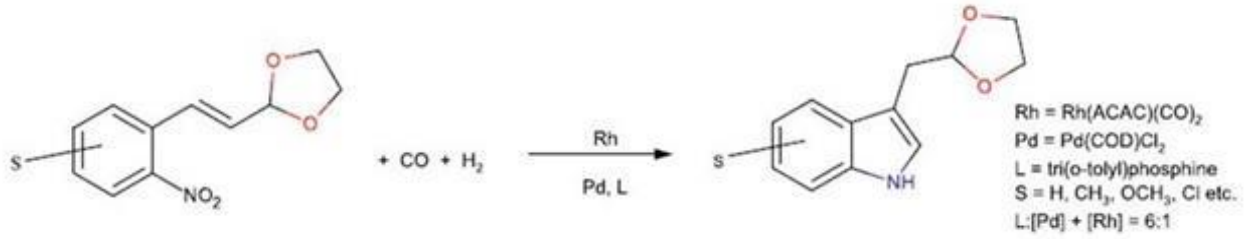
S
NO2
+ CO + H2
Rh
Pd, L
S
NH
Rh = Rh(ACAC)(CO)2
Pd = Pd(COD)Cl2
L = tri(o-tolyl)phosphine
S = H, CH3, OCH3, Cl etc.
L:[Pd] + [Rh] = 6:1

P-133

Catalytic enantioselective hydrogenation of unactivated enamines: factors affecting the rate and enantioselectivity

Tamara Fanjul[2], Mr Sergey Tin[1]

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Poster Session 1

In contrast to the extensively studied hydrogenation of enamides and (Z)-aminoacrylates, hydrogenation of enamines lacking coordinating groups is a significant challenge. While being one of the most desirable transformations for the synthesis of pharmaceuticals,1 no papers report a catalyst that is active enough for industrial application. The aim of our research is to solve this problem. One starting point was the finding of Clarke and Bühl that in hydroaminomethylation, electron withdrawing ligands unexpectedly speed up the reaction due to a change in the rate determining step.2

A number of enamines were prepared using either branched-selective intramolecular hydroaminovinylation (using BOBPHOS as ligand)3 or known lewis-acid catalysed routes.4 These enamines were then tested for hydrogenation using Rh catalysts of electron-withdrawing phosphorus ligands. TON's of up to 4550 mol mol-1 were achieved5 which is, to the best of our knowledge, the highest TON ever reported for catalytic enamine hydrogenation. Highly deactivated tetrasubstituted enamines could also be hydrogenated using these catalysts.

An alternative strategy towards highly active catalysts was to use co-catalysts. It was found that Rh catalysts of certain cyclic phosphines in the presence of co-catalysts can show high activities and good selectivities. Up to date, in enantioselective hydrogenation of enamines TON's of 1800 mol mol-1 were achieved by our group, as well as up to 77% ee (Scheme 1).6 We are now making further refinements of these catalysts and seeking to apply them in the production of pharmaceuticals.

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2. J. A. Fuentes, P. Wawrzyniak, G. J. Roff, M. Bühl, M. L. Clarke, Catal. Sci. Technol., 2011, 1, 431
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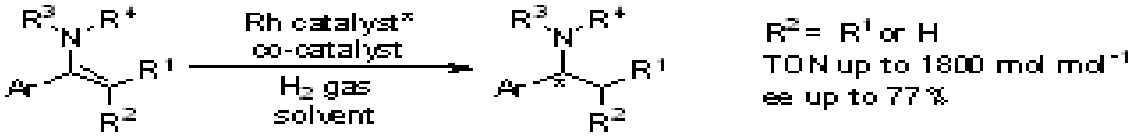
6a. S. Tin, T. Fanjul, M. L. Clarke, Patent filed.
6b. S. Tin, T. Fanjul, M. L. Clarke, Manuscript in preparation.



P-135

Application of non-stabilized nucleophiles to dynamic kinetic asymmetric transformations

Dr Mireia Sidera Portela[1], Mr Hengzhi You[1], Ms Emeline Rideau, Prof. Stephen P. Fletcher
[1]*University of Oxford, Oxford, UK*

Poster Session 1

Processes that allow racemic mixtures of starting materials to be converted to a single enantiomer of the product are highly desirable both from an academic and industrial point of view. In particular, dynamic kinetic asymmetric transformations (DYKATs) have received vast attention in the past years [1][2]. In these processes mainly one of the enantiomers of the product is formed in more than 50% yield. The reaction can proceed in two pathways: i) both enantiomers of the starting material can interconvert in the reaction conditions and only one of them reacts with the catalytic system or ii) both enantiomers of the starting material form a common prochiral intermediate that is transformed later on into solely one enantiomer of the product. There exists a limited number of examples using non-stabilized nucleophiles due to their higher reactivity. Our group recently reported a method that employs organozirconium reagents prepared in situ by hydrozirconation of terminal alkenes using the Schwartz reagent in Cu-catalyzed DYKATs to racemic allyl chlorides[3]. The reaction conditions are smooth, it uses readily available materials and it is robust. We were able to scale-up the reactions and apply the method to synthesise cyclopentene-based natural products with activity against tuberculosis and leprosy (b). We also expanded the method to sp2-hybridized nucleophiles[4].

References:
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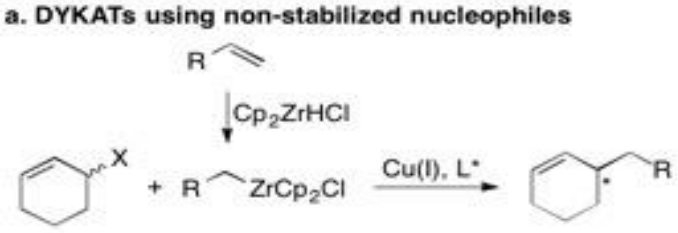
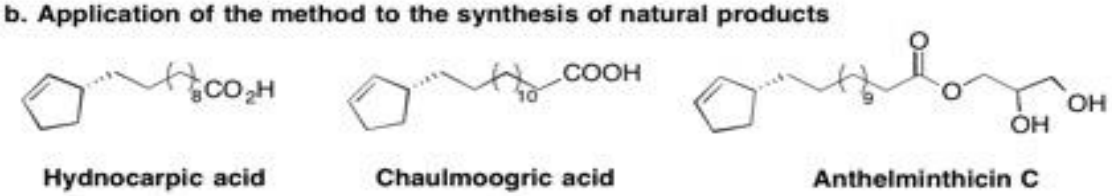
[2] D. R. Trost, Barry M., Fandrick, Aldrichimica Acta 2007, 40, 59–72.
[3] H. You, E. Rideau, M. Sidera, S. P. Fletcher, Nature 2015, 517, 351–355.
[4] M. Sidera, S. P. Fletcher, Chem. Commun. 2015, 51, 5044–5047.





P-136

Ni-catalyzed reductive carboxylation of unactivated alkyl chlorides with CO2

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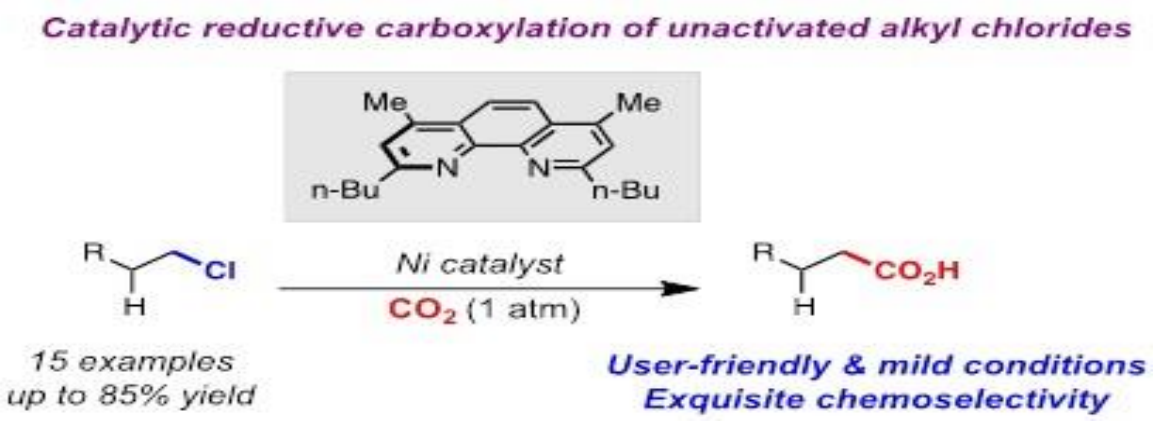
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 1

The direct catalytic fixation of carbon dioxide (CO2) into organic molecules represents a user-friendly, cost-efficient and powerful strategy for the synthesis of valuable organic compounds. Among these, the synthesis of carboxylic acids constitutes an ideal target in CO2 fixation since these molecules are privileged motifs in a myriad of pharmaceuticals with important biological activities. As part of our investigations towards catalytic CO2 fixation into organic matter,2 we have developed a Ni-catalyzed reductive carboxylation of unactivated primary alkyl chlorides. 3 This methodology is characterized by its simplicity and exquisite chemoselectivity profile, providing a rapid access to carboxylic acids from simple and cheap precursors without the need to handle air- or moisture-sensitive reagents.



P-137

Chelate-Assisted Site-Selective Direct Chalcogenation of Aryl C–H Bonds with Disulfides, Diselenides, and Elemental Selenium Catalyzed by Palladium or Nickel

Dr. Masayuki Iwasaki[1], Yuta Tsuchiya[1], Wataru Kaneshika[1], Miki Iyanaga[1], Natsumi Miki[1], Yugo Nishimura[1], Dr. Wenjuan Li[2], Prof. Zhiping Li[2], Prof. Kiyohiko Nakajima[3], Prof. Yasushi Nishihara[1,4]

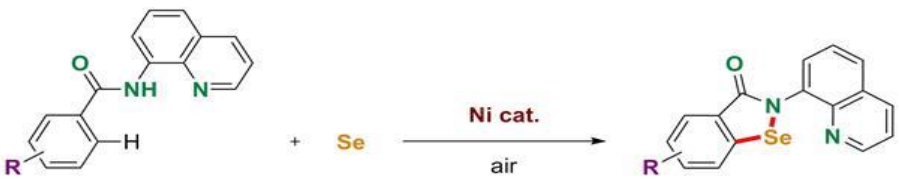
[1]Okayama University, Okayama, Japan, [2]Renmin University of China, Beijing, China, [3]Aichi University of Education, Kariya, Japan, [4]ACT-C, Japan Science and Technology Agency, Kawaguchi, Japan

Poster Session 1

Organosulfur compounds are one of the most important motifs in organic chemistry because of their potential biological activities. Among these compounds, aryl sulfide scaffolds are often found in drug candidates and bioactive compounds. Transition-metal-catalyzed thiolation of aryl halides represents a powerful and reliable synthetic method of aryl sulfides. Although such reactions afford the target aryl sulfides efficiently, starting materials have to be prefunctionalized. Therefore, more straightforward synthetic route to aryl sulfides is desirable.

Herein, we report direct thiolation of aryl C–H bonds with transition-metal catalysts, which provides a facile synthetic method of aryl sulfides. Treatment of arenes bearing directing groups with disulfides in the presence of a palladium catalyst in dimethyl sulfoxide gave the desired aryl sulfides in good yields. We confirmed that the reaction proceeded at the ortho-position of directing groups to give the single product whose structure was confirmed by X-ray crystal structural analysis. Notably, 0.6 equivalents of disulfide based on the substrates was enough to complete the reaction, which suggests that both of sulfenyl moieties of disulfides can be incorporated into the products. In addition, peri-thiolation of naphthylamine derivatives proceeded by using the appropriate directing group. We also found that chelate-assisted direct selenation with diselenides catalyzed by palladium. N-(8-Quinolyl)amide, picolinamide, and pyridyl groups can be utilized as directing groups. Moreover, we disclosed nickel-catalyzed synthesis of benzoselenazolones by direct selenation of aryl C–H bonds. Benzamides and elemental selenium were treated with sodium carbonate and tetrabutylammoium chloride in the presence of a nickel catalyst in air to yield the corresponding benzoselenazolones in good yields. The reaction consists of C–Se and N–Se bond formations through a C–H bond cleavage, providing a direct approach to heterocycles containing selenium and nitrogen.

DG = *N*-(8-quinolyl)amide, picolinamide, and 2-pyridyl groups



P-138

Highly regioselective asymmetric hydroformylation and asymmetric transfer hydroformylation (ATHF) of alkenes. Scope and mechanistic studies.

Dr Jose A. Fuentes Garcia[1], Dr Matthew L Clarke[1]
[1]*University of St Andrews, St Andrews, UK*

Poster Session 1

Asymmetric catalysis, chiral ligands, hydroformylation, paraformaldehyde.

Rhodium catalysed hydroformylation of alkenes is of huge importance to the commodity chemicals industry 1[1] and is increasingly used in the synthesis of fine chemicals and pharmaceutical intermediates.2[2]

For general synthetic applications the use of syngas is sometimes not desired due to its high toxicity, flammability and the need to use expensive pressure equipment. In order to solve this problem, paraformaldehyde has been successfully used as a syngas substitute in carbonylation reactions, but finding catalytic systems delivering high turnover numbers remain elusive.3[3],4[4]

The asymmetric hydroformylation of 1,2-disubstituted alkenes is a challenging process due to their lower reactivity compared to terminal alkenes. Surprisingly, better results can be obtained using asymmetric transfer hydroformylation.

The first example of a rhodium catalysed asymmetric transfer hydroformylation of 1,2-disubstituted alkenes using paraformaldehyde as a syngas substitute that affords the corresponding chiral aldehydes with reaction times down to 5 minutes and with high enantioselectivity (up to 96% ee) will be described.[5]5

Mechanistic insights into the highly regio- and enantioslective hydroformylation of alkyl alkenes using BOBPHOS will also be presented.

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P-139

DFT study of selectivity and mechanism in the Au(I)-catalysed direct etherification of allylic alcohols

Dr. David Johnson[1], Prof. Stuart A. Macgregor[1], Dr. Graeme Barker[1], Ms. Lorena Herkert[1], Ms. Samantha L. J. Green[1], Dr. Paul C. Young[1], Dr. Ai-Lan Lee[1]
[1]*Heriot-Watt University, Edinburgh, UK*

Poster Session 1

Gold catalysis has seen a significant increase in interest in the last 15 years.[1] In particular the Lewis-acidic Au(I) centre is known to activate carbon-carbon multiple bonds allowing for nucleophilic attack. Previous work has investigated the use of Au(I) catalysts in the regioselective etherification of allylic alcohols with O-based nucleophiles[2] as well as thioetherification with S-based nucleophiles.[3] These processes both involve a formal SN2' nucleophilic substitution with C-O (or C-S) bond formation at the C3 position (cf. III Figure 1).

Here we describe DFT studies into the mechanism of these direct etherification reactions. These SN2' reactions are thought to proceed via a 6-membered intermediate (or transition state) such as II (Figure 1), involving proton transfer and loss of water. Under this mechanism enantiopure starting materials will react with transfer of chirality.[4] This result was seen in experiments with a range of enantiopure substrates, often showing excellent (>90% ee) chiral transfer. However it was noted that this outcome only occurred in the presence of molecular sieves that were also found to improve the reaction efficiency. In the absence of the sieves racemization occurred with most substrates.

This presentation shall report on the DFT investigation of the mechanism of direct etherification and the potential reasons for the loss of the expected chiral transfer.

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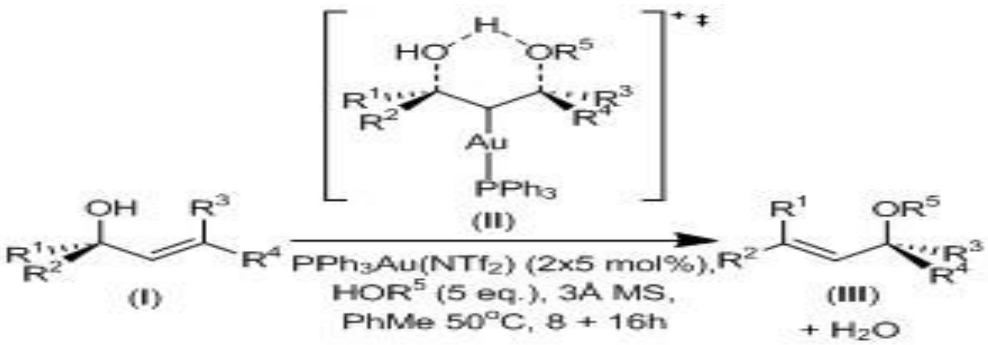

P-140

Ni-catalyzed Borylation of Aryl Methyl Ethers via C–OMe Cleavage

Cayetana Zarate[1], Ni-catalyzed Borylation of Aryl Methyl Ethers via C–OMe Cleavage Rubén Manzano[1], Ni-catalyzed Borylation of Aryl Methyl Ethers via C–OMe Cleavage Ruben Martin[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 1

In recent years, C–O electrophiles have emerged as powerful alternatives to aryl halides as coupling partners in the cross-coupling arena (1). However, the use of aryl methyl ethers, the simplest derivatives in the phenol area, has scarcely been investigated. Indeed, at present, such methodologies remain essentially confined to C–C bond-formation protocols utilizing stoichiometric and well-defined organometallic species (2). The pivotal role of organoboron reagents as synthetic intermediates has attracted the attention of both industrial and academic laboratories.3 Not surprisingly, the recent years have witnessed the development of a myriad of catalytic methods for their synthesis from available precursors (3,4). As part of our interest in C-O bond-activation, we describe herein the first Ni-catalyzed borylation of aryl ethers via C(sp2)– and C(sp3)–OMe cleavage (Scheme 1) (5). The transformation is characterized by its wide substrate scope under mild conditions and an exquisite divergence in site-selectivity that can be easily switched by an appropriate selection of the boron reagent.

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(5) Zarate, C.; Manzano, R.; Martin, R. Submitted.

P-141

Design and Application of a Broadly Applicable Evolutionary Catalyst for Cross-Coupling Reactions

Dr. Yee Hwee Lim[1], Dr. Howard Jong[1], Dr. Yong Yang[1], Dr. Fui Fong Yong[1], Mr. Xinying Chew[1], Miss Wenqin Wu[1], Dr. Charles W. Johannes[1], Dr. Daniel Weiliang Tay[2], Mr. Saei Weng Chia[2], Dr. Edward G. Robins[2], Dr. Adrian Matthew Mak[3]

[1]Institute of Chemical and Engineering Sciences, Singapore, Singapore, [2]Singapore Bioimaging Consortium, Singapore, Singapore, [3]Institute of High Performance Computing, Singapore, Singapore

Poster Session 1

Recently, our group has uncovered some impactful evolutionary design elements in the ligand architecture could enable the catalyst performance to surpass many of the modern phosphine-based palladium systems. The Pd-catalyst based on a novel meta-terarylphosphine ligand, named Cy*Phine has displayed significant board-based catalyst outperformance relative to the state-of-the-art commercial alternatives in cross-coupling reactions. Herein, the presentation will describe the discovery and developmental journey of this evolutionary ligand, and attempt to rationalize the source of this enhancement in catalyst efficiency. Several publications involving the Pd-Cy*Phine catalyst in the copper-free Sonogashira coupling,[1] the Mizoroki-Heck reaction[2] and the Buchwald-Hartwig amination will be highlighted. Opportunities for future design improvement of this promising and tunable ligand platform will also be discussed.

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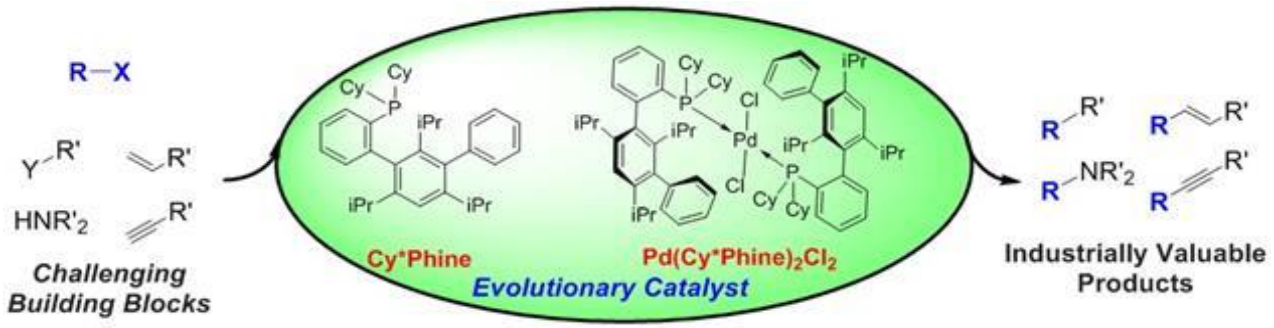

P-143

Pyridylidene-mediated dihydrogen activation coupled with catalytic imine reduction

Dr. Pablo Mauleón[2], Dr. J. Auth[1], J. Padevet[1], A. Pfaltz[1]
[1]*University of Basel, Basel, Switzerland,* [2]*Universidad Autónoma de Madrid, Madrid, Spain*

Poster Session 1

Catalytic hydrogenation with H2 as reductant is of central importance in organic synthesis. In general, a transition metal catalyst is required for H2 activation, dissociation of the H–H bond, and transfer of the hydrogen atoms to the substrate. However, there are examples of transition metal-free systems for H2 activation. A breakthrough in this field was achieved by Stephan and Erker, based on the concept of Frustrated Lewis Pairs (FLPs).[1] FLPs consisting of a perfluorinated arylborane and a sterically demanding base that due to steric constraints cannot form a stable Lewis acid-base complex were shown to reversibly split H2 and to catalyze the hydrogenation of various functional groups.[1,2] Although a range of Lewis bases has been used, the choice of the Lewis acid component appears to be restricted to highly reactive fluorinated aryl boranes, which show limited functional group compatibility and require glove-box or Schlenk techniques. Thus, it would be desirable to explore other types of systems, in order to generalize the concept of non-metal mediated H2 activation. Here, we describe our efforts along these lines: based on the concept of isolobality between singlet carbenes and transition metals, we have studied the behavior of highly reactive pyridylidenes in these transformations. Our findings demonstrate the potential of pyridinium salts for H2 activation and catalytic hydrogenation. (Figure 1)

References:
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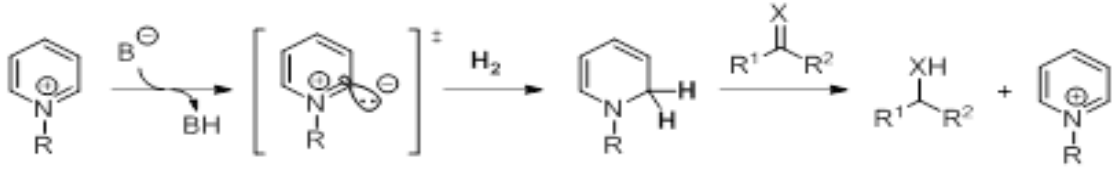

P-144

New Unsymmetrical Iron(II)PNNP' Asymmetric Transfer Hydrogenation Catalysts

Ms. Samantha Smith[1], Prof. Robert Morris[1]
[1]*University of Toronto, Toronto, Canada*

Poster Session 1

Enantiomerically pure alcohols are used in the pharmaceutical, fragrance and flavour industries and are generally obtained via reduction of prochiral ketones using complexes based on precious metals.[1] Previously, our group has developed iron-based catalysts for the asymmetric transfer hydrogenation (ATH) of ketones with high turn-over frequency (up to 200 s[sup]-1[/sup]) and high ee.[2] Here we describe new iron complexes with varying properties that have been conveniently synthesized using a modular Fe(II)-assisted template approach developed in our lab. This library of catalysts allow the discovery of suitable catalysts for the reduction of a particular substrate, such as acetophenone to high e.e. One particular iron(II) complex with a dicyclohexylphosphino group trans to the NH group (R = Cy in the figure) has been found to catalyze the ATH of a variety of ketones with high enantioselectivity, up to 99 % ee and a turn-over number of up to 4300.[3]

References:
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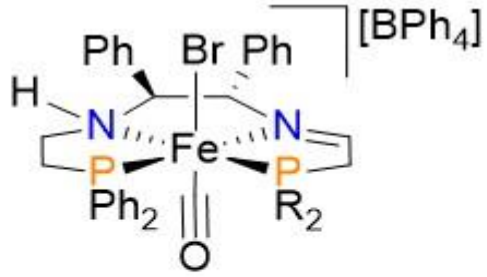

R = Et, iPr, Cy, p-Tol,
p-CF_3Ph,
3',5'-$(CF_3)_2$Ph

P-145

Asymmetric Grignard Synthesis of Tertiary Alcohols

Dr Bartosz Bieszczad[1], Prof Declan Gilheany[1]
[1]*University College Dublin, Dublin, Ireland*

Poster Session 1

Chiral tertiary alcohols constitute an important class of biologically active molecules. Most conveniently they can be prepared by a stereoselective addition of organometallic reagents to ketones. Among organometallics, the Grignard reagents present the widest scope and greatest versatility. However, stereoselective synthesis of tertiary alcohols by direct 1,2-addition of Grignard reagent to ketones is extremely challenging and most of the successful cases involve transmetallation using transition metals.[1] To best of our knowledge, only a single case was reported to date where high enantioselectivity was obtained in the absence of metals other than magnesium.[2]

The challenges of asymmetric Grignard synthesis of tertiary alcohols lie in: the reduced enantioface discrimination between the prochiral sides of a ketone (as compared to an aldehyde), competitive non-stereoselective reactions, low yields due to enolization/reduction side reactions, and dynamic processes originating from the Schlenk equilibrium. We focused our research on development of a general methodology of 1,2-addition of Grignard reagents to arylalkyl ketones in the presence of a new class of chiral ligands. By using stoichiometric amounts of readily available enantiopure ligand L*[3] it was possible to prepare tertiary alcohol products with high enantioselectivities (up to 94%) and high yields (up to 99%). The method was found to be general for a range of ketones and Grignard reagents. The chiral ligand L* can easily be recycled from the crude reaction mixture.

References:
[1] zinc, J. Ramon, M. Yus, Angew. Chem. Int. Ed. 2004, 43, 284-287; copper, A. V. Madduri, S. R. Harutyunyan, A. J. Minnaard, Angew. Chem. Int. Ed. 2012, 51, 3164-3167; titanium, D. J. Ramón, M. Yus, Tett. Lett. 1998, 39, 1239–1242
[2] B. Weber, D. Seebach, Angew. Chem. Int. Ed. 1992, 31, 84-86
[4] A patent application is pending: upon its projected publication in May 2015 the structure of the ligand L* can be revealed.

P-146

Rh(I)/Rh(III) catalyst-controlled divergent C-H functionalization of picolinamide derivatives with alkynes

Dr. Nuria Rodríguez[1], Ángel Manu Martínez[1], Javier Echavarren[1], Dr. Inés Alonso[1], Dr. Ramón Gómez Arrayás[1], Dr. Juan Carlos Carretero[1]

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Poster Session 1

Recent progress on rhodium-catalyzed C-H bond functionalization has opened new possibilities for an ideal chemical synthesis enabling straightforward formation of new C-C bonds without previous functionalization steps.[1] However, investigations of catalyst controlled divergent C-H functionalizations of distinct C-H bonds are relatively uncommon, yet highly appealing.[2] The concept herein presented illustrates a divergent high site-selective control in the direct functionalization of both aryl and heteroaryl C-H bonds of N-substituted picolinamide substrates.[3] By simply switching the oxidation state of the Rh(I)/Rh(III) catalyst precursor, it is possible to access either isoquinoline derivatives or ortho-olefinated benzylamine and phenethylamine derivatives, respectively.[4]

Experimental mechanistic studies based on isolation and X-ray characterization of Rh(I)- and Rh(III)-picolinamide complexes and deuterium labeling studies, as well and DFT theoretical calculations have been performed to explain the factors that influence this switchable site-selectivity control for both Rh(I) and Rh(III) catalytic systems.

References:

[1] (a) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. Acc. Chem. Res. 2012, 45, 814. (b) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. Aldrichim. Acta 2012, 45, 31.

[2] For elegant examples, see: (a) Campeau, L.-C.; Chipper, D. J.; Fagnou, K. J. Am. Chem. Soc. 2008, 130, 3266. (b) Dooley, J. D.; Chidipudi, S. R.; Lam, H. W. J. Am. Chem. Soc. 2013, 135, 10829. (c) Dooley, J. D.; Reddy Chidipudi, S.; Lam, H. W. J. Am. Chem. Soc. 2013, 135, 10829.

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P-147

Mechanistic insight into iron-catalyzed alkylation of amines through ''borrowing hydrogen'' methodology

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Poster Session 1

Recently, the first example of alkylation of amines by alcohols via a molecularly defined iron complex (Knölcher complex, scheme 1) was reported by our research group.[1] Although a ''borrowing hydrogen'' mechanism can be postulated according to the observed reactivity,[1,2] no studies aimed at providing identification of labile intermediates during the catalytic cycle have been performed yet.
Herein, we describe a systematic study on the reactivity of the Knölcher complex towards different alcohols and amines and our attempts to elucidate the elementary steps of the operating mechanism. By monitoring the course of the reaction with several techniques (VT NMR, IR), we aim at shedding light on the nature of transient catalytic species contributing to the understanding of the process and to the design of more active iron catalysts.

References:
[1] Yan T., Feringa B. L., Barta K., Nature Comm. 2014, 5, 1-7.
[2] a) Casey C. P., Guan H., J. Am. Chem. Soc. 2007, 129, 5816–5817; b) Pagnoux-Ozherelyeva A., Pannetier N., Mbaye M. D., Gaillard S., Renaud J.-L., Angew. Chem. Int. Ed. 2012, 51, 4976-4980.

Scheme 1. General scheme for the alkylation of amines with alcohols.

P-148

Dehydrocoupling reactions catalysed by NHC-stabilized Pt(II) complexes

Dr. Joaquin Lopez-Serrano[1], Mr. Pablo Rios[1], Dr. Salvador Conejero[1]
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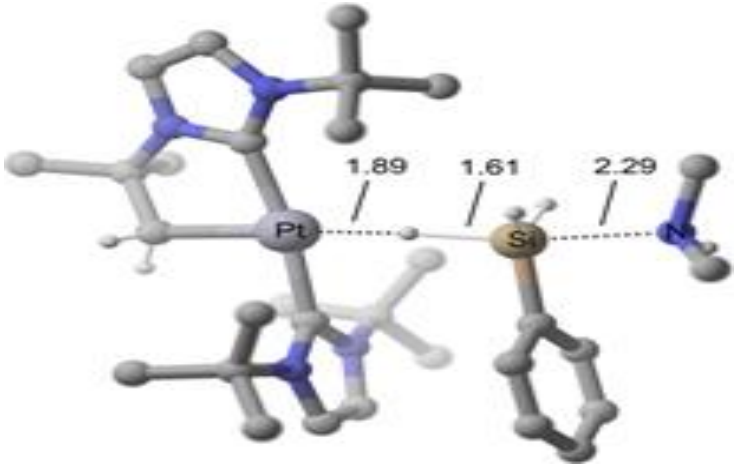
Poster Session 1

Dehydrocoupling of amine boranes (AB) remains an active area of investigation due both to the applications of these species as hydrogen storage materials (19 wt % of H for ammonia borane), as well as for the potential uses of the spent fuel as new polymeric materials. Extensive efforts have been made to understand the mechanism of these processes.[1] These include a recent investigation of our research group in which a role for the solvent in amine-boranes dehydrocoupling with electrophilic Pt(II) complexes is disclosed.[2]

Related dehydrocoupling reactions yield new Si-N bonds from silanes and amines. Silyl amines are used as precursors in the synthesis of bulky bases, as protecting reagents or as silylating reagents.[3] However traditional syntheses of these species require the use of strong bases or halosilanes.
Taking into account the similarity of AB dehydrocoupling with the above process, we have undertaken an investigation on the catalytic dehydrocoupling of silanes and amines with the same platinum framework we used with ammonia boranes. Here we present preliminary experimental and computational results of this investigation.

References:
[1] Topics in Organometallic Chemistry, 2015, 49, 153-220
[2] J. Am. Chem. Soc., 2013, 135, 10910-10913
[3] Nat. Chem. 2013, 5, 817-829



P-149

Development of zinc alkyl/air systems as radical initiators for organic reactions

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[1]*Warsaw University of Technology, Warsaw, Poland,* [2]*Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland*

Poster Session 1

Over the last two decades, homoleptic boron and zinc alkyls in combination with dry air have attracted much attention as they provide a source of radical initiators for various organic reactions. For these RnM/air systems it is commonly assumed that R• radicals are formed in the initial step (cf. eq 1), and are thus considered as the initiating species.[1] The postulated formation of R• radicals has not been in line with some of the recent fundamental studies which have shown that reactions between R_2Zn and O2 can be conducted in a highly controllable manner without any evidence for the liberation of free alkyl radicals.

$R_2Zn + O_2$ --> RZnOO• + R• (eq 1)

Building on our continuous interest and expertise in radicals' chemistry and O2 activation, we will demonstrate comparative experiments on the activity of carbon- and oxygen-centred radical species (derived from a series of zinc alkyl/air reaction systems with a clear mechanistic picture), in a model reaction of radical addition of THF to imines. The results clearly demonstrate that the oxygen-centred radicals are the key species in radical organic reactions mediated by R_nM/air systems and strongly contradict the notion that R• radicals are the initiating species. Finally, the studies not only provide better understanding of how the oxygenated products participate in radical organic reactions but also assists in the development of a new and efficient RZn(L)/air-type initiating system.[3]

References:
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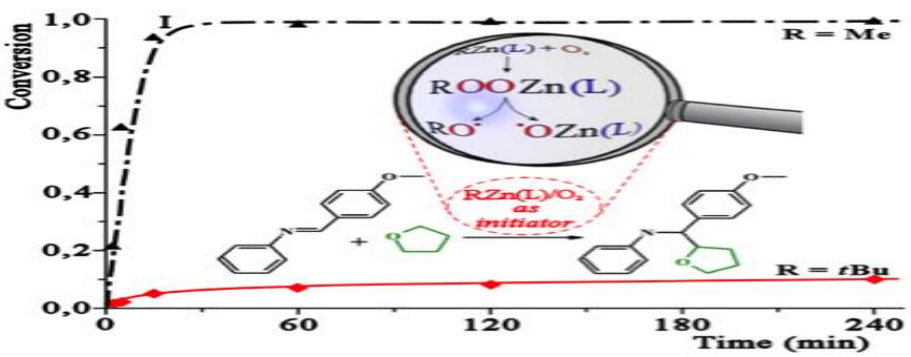

P-151

Pd-catalyzed multiple bond-formations via C(sp3)-H functionalization / carbenoid insertion

MSc Álvaro Gutiérrez Bonet[1], Beatriz De Luis[1], Prof. Rubén Martín [1]
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Poster Session 1

In recent years, the field of C-H functionalization has gained a considerable attention. Despite the advances realized, the means to promote multiple bond-formations via C-H functionalization in the absence of directing groups still represent a formidable quest[1]. This is particularly true when dealing with the functionalization of rather inert unactivated C(sp[3])-H bonds[2]. Herein, we present a new methodology capable of promoting a multiple bond-forming reactions via Pd-catalyzed functionalization of unactivated C(sp[3])-H bonds using carbenes as coupling counterparts[3]. The transformation is distinguished by a wide substrate scope in both coupling partners, thus representing a straightforward entry to indanes possessing two quaternary centers[4].

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3. Hu, F.; Xia, Y.; Ma, M.; Zhang, Y.; Wang, J. Chem. Commun. DOI: 10.1039/C5CC00497G
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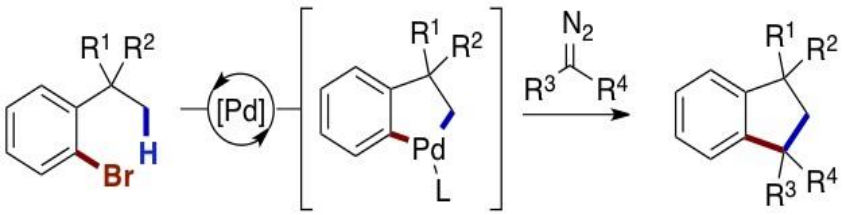

*Functionalization of **inert** C(sp^3)-H bonds.*
*Formation of a **quaternary** centre.*
*Synthesis of elusive **indane** backbones.*

P-152

Adventures in Base-Metal Mediated Csp2-Csp3 Cross-Coupling

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Poster Session 1

Carbon-carbon bond forming reactions based upon palladium catalysed cross-coupling methodologies have revolutionised modern synthetic chemistry.[1] These transformations play pivotal roles in the production of key modern-day commodities including: pharmaceuticals; agrochemicals; and advanced materials. Despite its phenomenal utility, palladium catalysis has a number of undesirable aspects, namely, its associated cost, relative toxicity, low natural abundance and security of supply.
This presentation will focus upon our recent work towards the development of cheap, environmentally benign base-metal (iron and zinc) mediated approaches to Csp2-Csp3 bond formation. Specifically, the investigation of the transmetallation and cross-coupling steps of iron catalysed Suzuki-Miyaura type Csp2-Csp3 cross-coupling.[2] These studies led to an unexpected direct Csp2-Csp3 cross-coupling between diarylzinc reagents and haloalkane electrophiles. This reaction proved highly versatile for coupling benzylic, 1°, 2° or 3° alkyl halides with arylzinc reagents in high yields without the addition of a catalyst.[3] Key factors influencing reactivity, substrate scope and reaction mechanism will be presented and discussed in detail.

References:
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2. J. J. Dunsford & M. J. Ingleson et al. Unpublished work.
3. J. J. Dunsford & M. J. Ingleson et al. Angew. Chem. Int. Ed. 2015, DOI: 10.1002/ange.201411403.

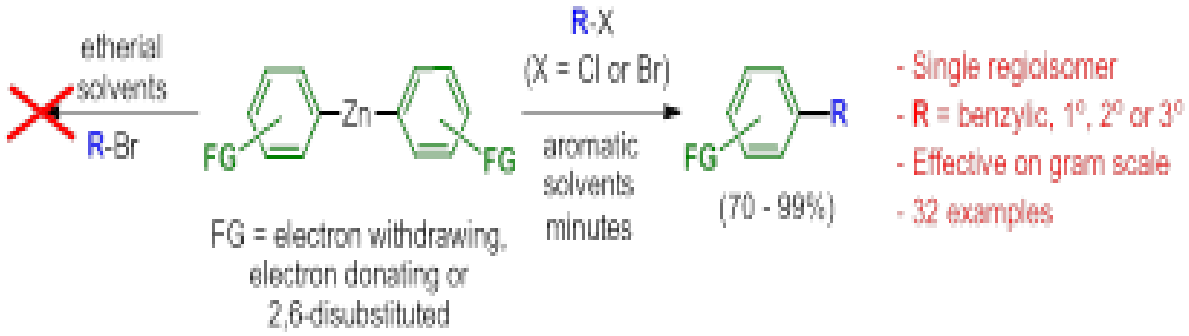

Figure 1. Direct Csp^2-Csp^3 Cross-Coupling of Diarylzinc Reagents and Benzylic, 1°, 2° and 3° Alkyl Halides.

P-156

Asymmetric Synthesis of Axially Chiral P,N-ligands via Dynamic Asymmetric C–P Cross–Coupling Reaction

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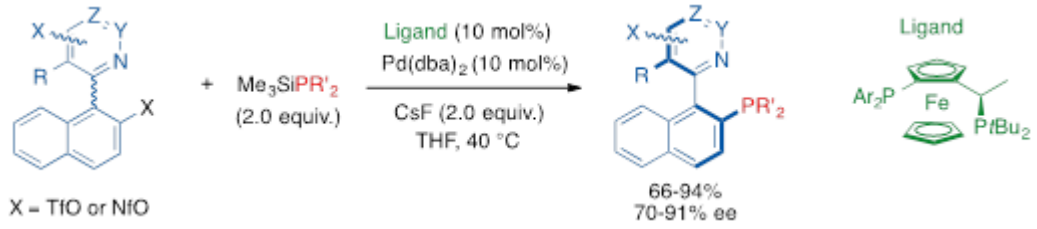
Poster Session 1

Axially chiral P,N-ligands, such as Quinap, have had a considerable impact in asymmetric catalysis.[1] This type of ligands, however, are clearly underexploited for the lack of a general method for the synthesis of analogues, providing the structural variability required to the fine-tuning of their steric and electronic properties. The direct construction of the stereogenic axis by a cross–coupling reaction might appear as the most straightforward approach to these systems. In spite of the great progress achieved during the last years in asymmetric Suzuki-Miyaura cross-couplings, however, the reaction using heterocyclic substrates remains as an unsolved synthetic challenge, presumably due to the interferences caused by the coordination of the heteroatoms in the substrate, the limitations associated with the availability and poor stability of heteroaromatic organometallics and the low configurational stability of the products. Recently, we have developed an alternative methodology for the asymmetric synthesis of axially chiral heterobiaryls consisting of a dynamic asymmetric (DYKAT) Suzuki-Miyaura coupling between racemic triflates and arylboroxines.[2] On this basis, we decided to explore the applicability of this methodology to the asymmetric synthesis of P,N-ligands with axial chirality. The strategy is based on the assumption that the oxidative addition of Pd(0) catalysts generates cationic and configurationally stable intermediates incorporating the basic pyridine N atom as a ligand.



After an intense screening of ligands and phosphine sources, a Pd(0) complex containing a JOSIPHOS-type ligand was identified as the most selective/active catalyst for the dynamic asymmetric (DYKAT) C-P coupling between racemic triflates/nonaflates and diaryl/dialkyl trimethylsilylphosphines, leading to axially chiral P,N-ligands in high yields and ee´s up to 91%.

References:
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2. A. Ros, B. Estepa, P. Ramírez-López, E. Álvarez, R. Fernández, J. M. Lassaletta, J. Am Chem. Soc. 2013, 135, 15730–15733.

P-157

Iron PNP pincer type catalyst for hydrogenation of carboxylic acid derivatives

Dr. Kathrin Junge[1], Dr. Svenja Werkmeister[1], Christoph Bornschein[1], Dr. Elisabetta Alberico[1,2], Dr. Haijun Jiao, Dr. Henrik Junge[1], Prof. Matthias Beller[1]

[1]*Leibniz-Institute for Catalysis, Rostock, Germany,* [2]*Istituto di Chimica Biomolecolare, Sassari, Italy*

Poster Session 1

Recently, we developed a molecular defined iron PNP pincer complex.[1] Now, the first hydrogenation of various nitriles using this iron complex is presented under mild reaction conditions.[2] Next to aryl, alkyl and heterocyclic derivatives also dinitriles such as the industrially important adiponitrile were successfully hydrogenated. Very good functional group tolerance for ester-, ether-, halogen-, acetamido-, amino and ,-unsaturated double bonds is observed and isolated yields between 41-99% are reported.
Additionally, we investigated the hydrogenation of various carboxylic acid esters and lactones. With the iron PNP complex, high efficiency and selectivity was achieved with yields up to 99%.[3] Interestingly, the ester functionality in a dodecapeptide as intermediate for the synthesis of Alisporivir was hydrogenated with outstanding selectivity.
Based on computations, an outer-sphere mechanism is proposed involving simultaneous hydrogen transfer from the iron center and the ligand. This fact is supported by various NMR experiments.

References:
[1] Alberico, E.; Sponholz, P.; Cordes, C.; Nielsen, M.; Drexler, H.-J.; Junge, H.; Beller, M., Angew. Chem. Int. Ed. 2013, 52, 14162-14166.
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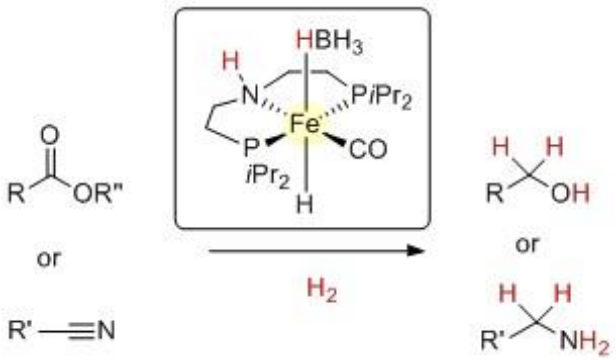
[3] Werkmeister, S.; Junge, K.; Wendt, B.; Alberico, E.; Jiao, H.; Baumann, W.; Junge, H.; Gallou, F.; Beller, M., Angew. Chem. Int. Ed. 2014, 53, 8722-8726.



P-158

GERMYLCOUMARINES – SYNTHESIS, STRUCTURE AND BIOLOGICAL ACTIVITY

Dr. Lubova Ignatovica[1], Dr Victoria Ryabova[1], Dr Vitalijs Romanovs[1], Dr Sergey Belyakov[1], Dr Irina Shestakova[1]

[1]*Latvian Institute of Organic Synthesis, Riga, Latvia*

Poster Session 1

Coumarins are very attractive compounds due to their wide range of valuable biological activities including anticancer, anti-HIV, anti-acetylcholinesterase, antioxidant, antibacterial, and antiviral activities. New biologically active germanium derivatives of coumarin-3-carboxylic esters 1 were synthesized by the following successive reactions:

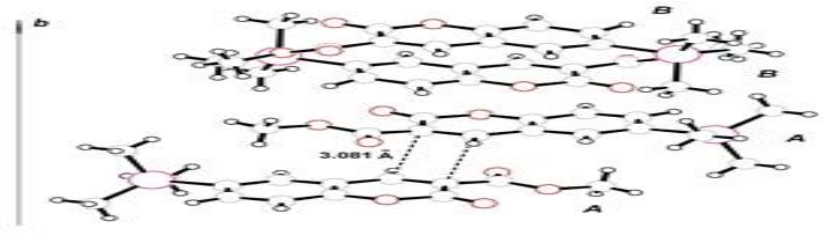
Scheme_omcos 8 jpg (Attachment 2)

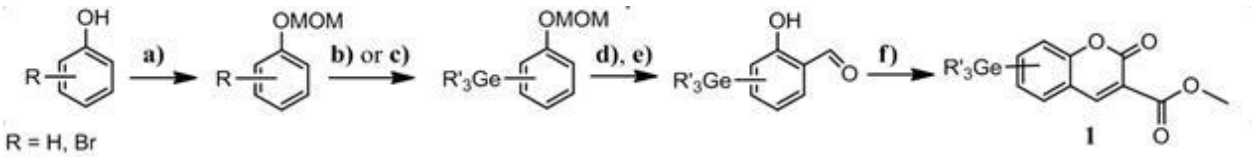
Structure Ge (1) jpg (Attachment 1)

Fig.1. A fragment of the molecular packing in the crystal structure of 1a

Molecular structures for selected derivatives 1 were confirmed by X-ray diffraction measurements. In the asymmetric unit of the crystal structure of 1a (R' = Me in position 6) there are two independent molecules (A and B). In molecules A the ester group is coplanar to the chromen system. In molecules B the dihedral angle between ester and chromen planes amounts 32.1°. The crystal structure is characterized by formation of stacks along monoclinic axis by means of π-π stacking interactions (see Fig. 1). The minimal intermolecular contact in the stacks is 3.081 Å between two molecules A connected by the center of inversion.

The cytotoxic activity and the ability to inhibit matrix metalloproteinases by germanium derivatives of coumarin-3-carboxylic esters 1 were investigated.





a) MOMCl, *i*-Pr_2NEt, CH_2Cl_2, 0°C; **b)** *n*-BuLi, R'_3GeCl, THF, -78°C; **c)** *t*-BuLi, THP, 25°C, R'_3GeCl, -78°C;
d) TMEDA, *n*-BuLi, DMF, Et_2O, 0°C; **e)** 5% CF_3COOH/CH_2Cl_2; **f)** dimethylmalonate, 12,5% piperidine, cat. AcOH, MeOH, reflux

P-159

Synthesis and investigation of a novel and remarkably simple hybrid surfactant-NHC ligand, its gold-complex and application in micellar catalysis

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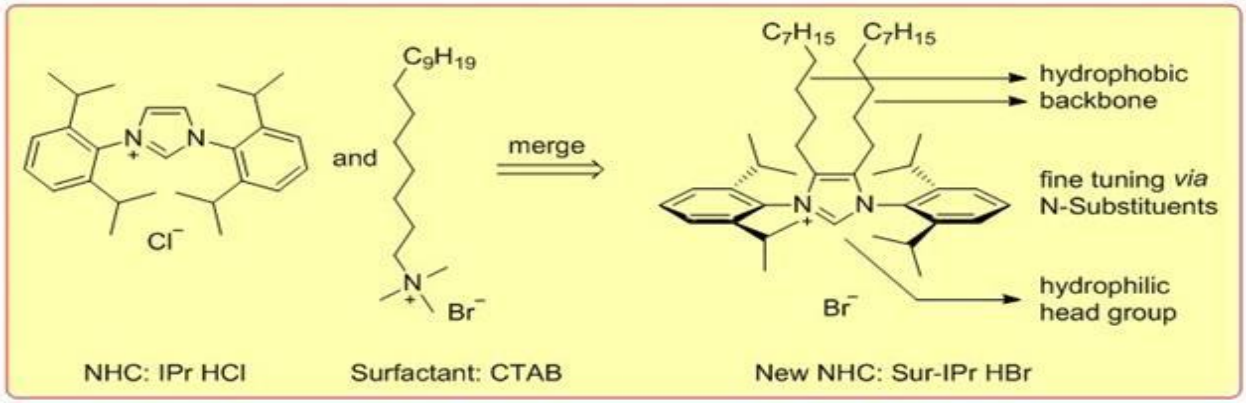
Poster Session 1

Nowadays the majority of reactions in organic chemistry are conducted in organic solvents, often to ensure solubility of the reaction partners and catalysts. Therefore organic solvents count for the biggest part of the waste generated during the reaction and its work up. Hence it is highly desirable to use more environmentally friendly solvents, with water as nature's favorite solvent being a logical and green choice. Different approaches have been established to transfer organic reactions into water as the reaction medium. Especially micellar catalysis has been shown to be an efficient and versatile tool for conducting organic reactions in water. Several reports describe the incorporation of metal catalysts in micelles for micellar catalysis.

The usual strategy for the incorporation of metal catalysts into micelles is the modification of the catalyst's ligand in a way that the ligand can either interact with the micelle, or is solubilized inside the micelle. The vast majority of these ligands are derived from phosphines or amines. Due to our interest in N-heterocyclic carbenes (NHCs) as ligands, we were eager to establish a new class of NHCs, which can act successfully as ligands in micellar catalysis. We therefore envisioned combining the properties of a surfactant with the ones of a NHC; the hybrid-surfactant NHC.

With the derived gold complex, we could successfully hydrate alkynes. So far this reaction has only been reported using mixed solvent systems (e.g. methanol/water or 1,4-dioxane/water), but using our catalyst could be performed under micellar conditions in pure water in moderate to excellent yields.

Film balance and DLS measurements were used to investigate the reaction's mode of action and the nature of the formed micelles.



P-160

Access to dihydrofurans with fully substituted C2 stereocenter by Pd-catalyzedintermolecular asymmetric Heck reaction

Dr. Vincent Bizet[1]

[1]*Departement Of Organic Chemistry, University Of Geneva, Geneva, Switzerland*

Poster Session 1

Until recently the intermolecular asymmetric version of the Heck reaction hasbeen used essentially as a benchmark reaction to validate the design of novelchiral bidentate ligands.1-3Herein we describe a highly selective methodology that gives access to chiral2,3 and 2,5 dihydrofurans with a fully substituted C2 stereocenter. Underidentical experimental conditions, with our homemade (P,N) ligand L1 or thecommercially available (P,P) ligand L2, 2,5 or 2,3-dihydrofurans can be obtainedrespectively with high enantioselectivity, regioselectivity and good yields.4

References:
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2. F. Ozawa, A. Kubo, T. Hayashi, J. Am. Chem. Soc. 1991, 113, 1417-1419.
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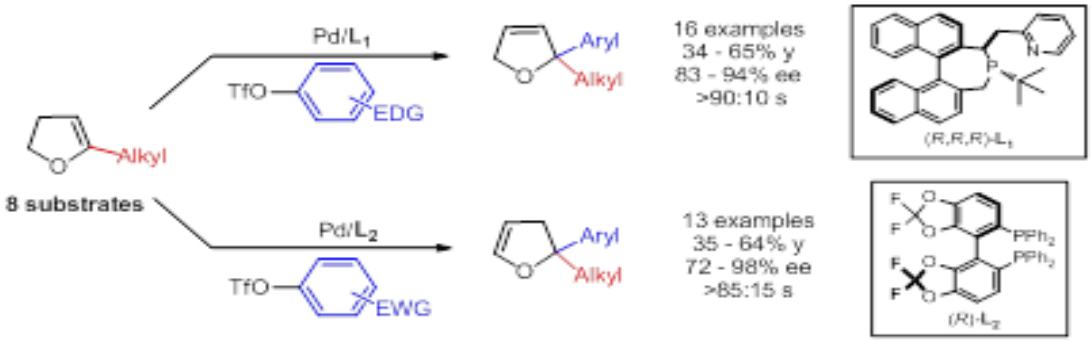

P-161

Asymmetric Transfer Hydrogenation of Ketones Promoted by Osmium(II)-pybox Complexes Containing N-donor ligands

Eire de Julián[1], Josefina Diez[1], Elena Lastra[1], Pilar Gamasa[1]

[1]*Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica Enrique Moles (Unidad Asociada al CSIC), Universidad de Oviedo, Oviedo, Spain*

Poster Session 1

The asymmetric reduction of ketones to enantiomerically-pure secondary alcohols represents a fundamental chemical transformation to access valuable target molecules. In such a context, the asymmetric transfer hydrogenation (ATH) is a highly efficient and practical method for executing this transformation[1].

Recently our research group has reported the synthesis of the complexes trans-[$OsCl^2${$P(OR)^3$}{(S,S)-iPr-pybox}] (R = Me, Et, iPr, Ph). Interestingly, all of these complexes have proven to promote the reaction of TH of several ketones with nearly complete conversion and high enantioselectivity (up to 94%)[2]. Continuing our interest in this area, we now describe the preparation of analogous osmium complexes bearing N-donor ligands such as pyridine (py), isoquinoline (iq) and other substituted pyiridines. We are also studying their behavior as catalysts in transfer hydrogenation processes. (figure 1)

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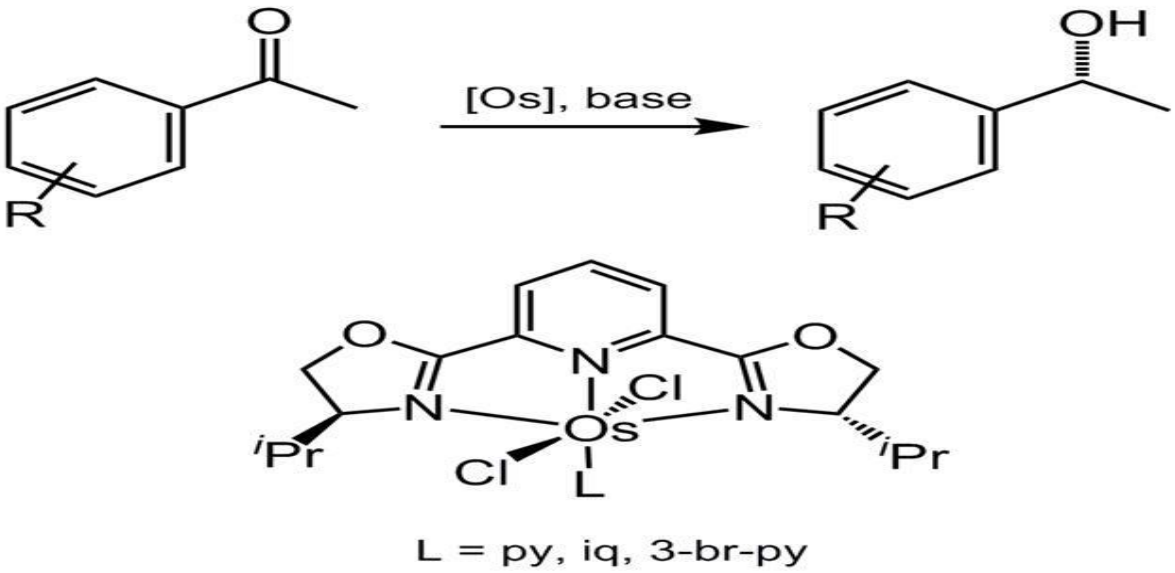

P-162

Combining Gold and Photoredox Catalysis: Visible Light Promoted Functionalization of Alkynes using Diazonium salts as Coupling Partners

Adrian Tlahuext-Aca[1,2], Dr. Matthew N. Hopkinson[1], Basudev Sahoo[1,2], Prof. Dr. Frank Glorius[1]
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Poster Session 1

Homogeneous gold catalysis has received significant attention in the last two decades. Due to their carbophilic π-acidity, gold species catalyze the addition of a variety of nucleophiles to unsaturated molecules, such as alkenes, alkynes and allenes.[1] Although the majority of these gold-catalyzed reactions are based on either Au(I) or Au(III) catalytic cycles, Au(I)/Au(III) redox systems have started to attract increased attention. However, unlike its isoelectronic counterpart Pd(0), Au(I) needs strong external oxidants to access higher oxidation states. Recently, several research groups have described the use of stoichiometric amounts of external oxidants, such as Selectfluor® and hypervalent iodine reagents to overcome this problem.[2] Despite the success of these approaches, novel chemical technologies are still required to avoid the use of stoichiometric oxidants to develop more straightforward and greener catalytic reactions. With this goal in mind, our group developed the first dual gold/photoredox catalytic system, where the Au(I)/Au(III) catalytic cycle was easily accessible without the need of stoichiometric oxidants. We successfully applied this novel methodology for the inter- and intra-oxyarylation of terminal alkenes using diazonium salts as arylating agents.[3] In the present work we sought to expand this concept beyond alkene substrates focused our attention on the functionalization of terminal and internal alkynes. This has resulted in interesting synthetic routes to Songashira-type products and poly-functionalized ketones.

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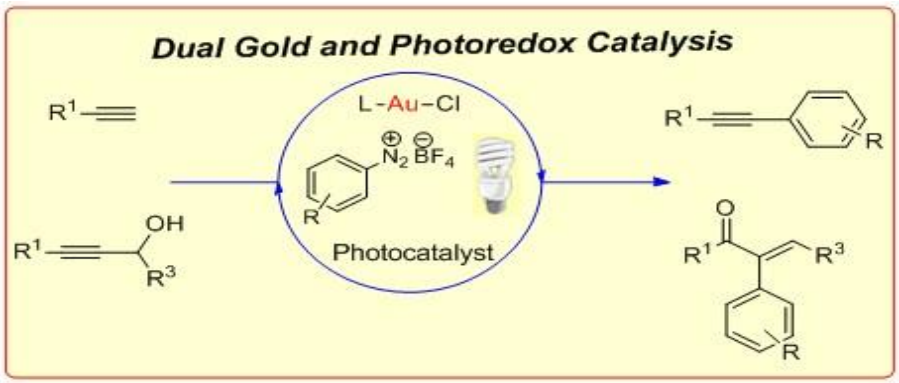

P-163

Cyclooctatetraenes synthesis via palladium-mediated cascade

Ms. Sarah Blouin[1], Dr Gaëlle Blond[1], Dr Jean Suffert[1]
[1]*UMR7200 CNRS/Unistra, Strasbourg, France*

Poster Session 1

Cyclooctatetraenes are a fascinating class of molecules found in Nature[1] and which represent a great potential utility as building blocks for organic synthesis,[2] scaffolds for drug discovery, designed carbohydrate mimics,[3] ligands for metals catalysis (including asymmetric catalysts)[4] and electron transporters in Organic Light Emitting Diodes (OLEDs).[5]
Based on the expertise of our group in the field of palladium-catalyzed cascade reactions,[6] we have developed a versatile methodology leading to octasubstituted cyclooctatetraenes. This step-economical synthesis is a straightforward way to access cyclooctatetraene frameworks starting from original scaffold and creating four new C-C bonds in a one-pot operation.

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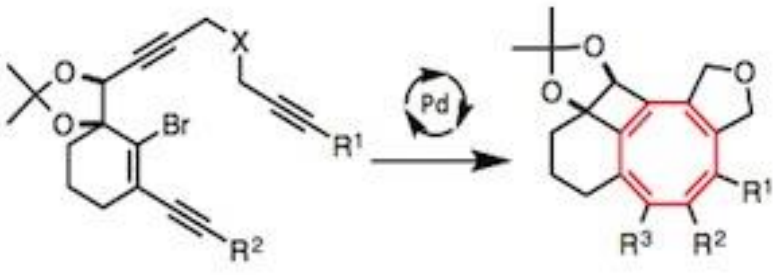

P-164

Developing new synthetic applications for Deep Eutectic Solvents: a green reaction media for Au(I)-catalysed cycloisomerisation of (Z)-enynols and one-pot tandem cycloisomerisation/Diels-Alder reaction.

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Poster Session 1

Due to the depletion of petroleum resources, increasing energy consumption, diminution of raw materials and society demands, Chemistry is facing a number of new challenges to solve the aforementioned concerns. Lately attempts have been made to tackle these problems through a new idea that is called Green Chemistry.[1] This concept contains 12 principles, which state that a chemical reaction should be: i) catalytic; ii) atom economic; iii) safe for the environment; iv) carried out under mild conditions; and v) not involve co-catalysts. Moreover, one of the crucial points in realizing a Green chemical processes involves the choice of a safe, non-toxic, biorenewable, and cheap solvent. However, the use of Green solvents still remains a lasting challenge, even when conventional hazardous volatile organic solvents (VOCs) can cause well-stablished environmental and safety-related problems.[2]
Building new bridges between catalytic reactions and Green Chemistry,[3] by the use of a new class of Green solvents, herein we report the employment of Deep Eutectic Solvents [DESs, comprised of a mixture of a hydrogen bond donor (glycerol, ethylene glycol, urea or water) with a simple halide salt (choline chloride)], as a powerful tool to carry out the Au(I)-catalysed cycloisomerisation of (Z)-enynols into furans, with full atom economy, selectivity, at room temperature and without protecting atmosphere. Furthermore, we also pioneered the use of these Green solvents in one-pot tandem cycloisomerisation/Diels-Alder reaction for the synthesis of 7-oxanorbonadienes, unprecedented in the field of Deep Eutectic Solvents.

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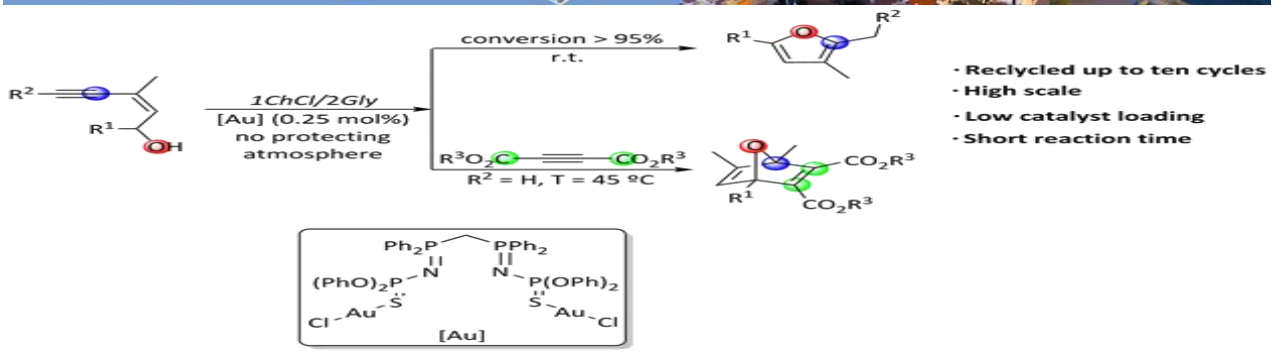

- Reclycled up to ten cycles
- High scale
- Low catalyst loading
- Short reaction time

P-165

HALF-SANDWICH RHODIUM (III) COMPLEXES BEARING HEMILABILE PHOSPHINES. SYNTHESIS AND REACTIVITY STUDIES

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Poster Session 1

Recently our research group has studied the behaviour of ruthenium (II) half-sandwich complexes bearing alkenyl phosphine ligands in cycloaddittion reactions with alkynes [1].
Our interest in this chemistry lead us to extend those studies using rhodium as metal center and a number of rhodium (III) complexes bearing alkenyl phosphines have been synthesized.
In this work we present the synthesis of new dialkynyl half-sandwich complexes of Rh(III) bearing pentamethylcyclopentadienyl as auxiliary ligand and the alkenyl phosphines homoallyldiphenylphosphine (HADPP), allyldiphenylphosphine (ADPP) and the more basic and bulky allyldiisopropylphosphine (ADIP). The reactivity of these complexes towards electrophiles such as CH^3OTf and HBF^4 lead to interesting intramolecular couplings. Theorical studies have been carried out to provide information about the mechanism for these transformations.

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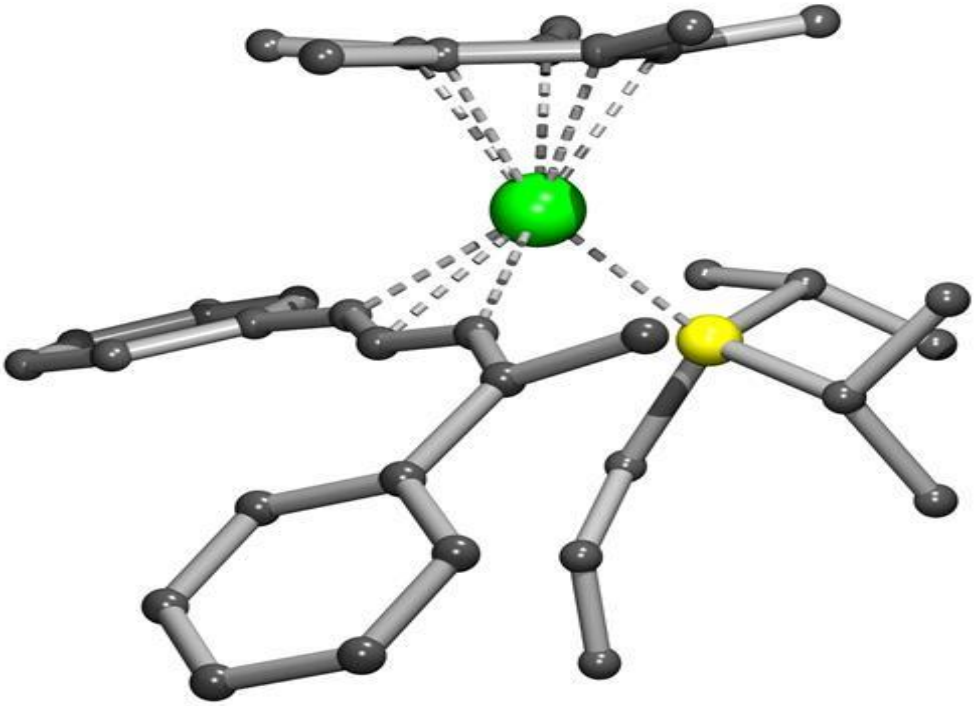

P-166

A Nickel-catalyzed α,β-Coupling of Saturated Ketones

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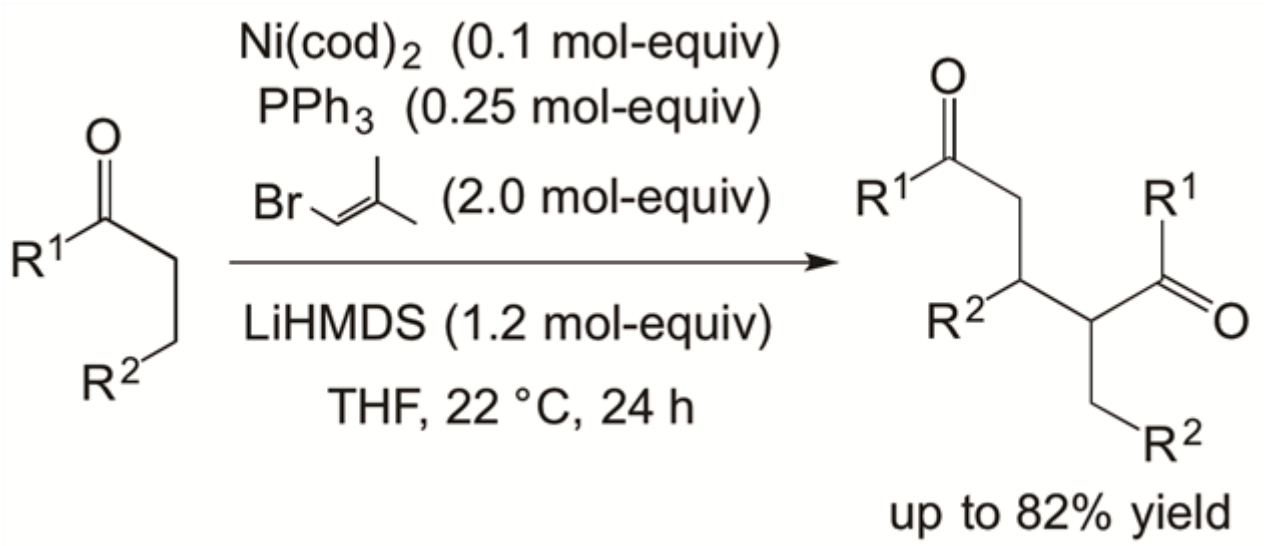
Poster Session 1

An investigation of nickel-catalyzed conditions under which an α,β-coupling of saturated ketones occurs is presented. Studies of reaction conditions reveal that the coupling occurs to produce 1,5-diketones in up to 82% yield using a Ni/PPh3 catalyst with a slight excess of LiHMDS base in the presence of 1-bromo-2-methyl-1-propene at 22 °C, Scheme 1. This reaction occurs mainly with alkyl aryl ketones. While the method does not appear to be general or high yielding, an awareness of the conditions under which it occurs is important to investigators studying enolate coupling conditions under similar conditions.



Scheme 1

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P-167

s-Block geminal dimetallic compounds generated from bis(mesitylsulfonyl)methane

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Poster Session 1

Geminal dimetallic compounds are useful synthons in a number of organic transformations. s-Block metal geminal dianions are particularly useful due to their very high reactivity in the formation of new bonds or as intermediates to transition metal compounds. However, the compounds themselves can be difficult to isolate and characterize as a result of this reactivity. Our group has previously studied the properties of geminal dianions with the simple bis(sulfonyl) ligand $(PhSO_2)_2CH_2$. While the dianions were confirmed to be made their structural characterization was unsuccessful as a result of aggregation and polymer formation. In an attempt to circumvent those problems, we have added steric bulk to the ligand system. Specifically, the ligand $(MesSO_2)_2CH_2$, where Mes = 2, 4, 6-Me3C6H2, has been synthesized and its properties to support a dianion investigated. The monoanionic species $(MesSO_2)_2CHM$ and the dianionic species $(MesSO_2)_2CM_2$ (where M = Li, Na, K, or Mg) were targeted for study, and the results obtained in this system will be outlined.

P-168

Transition Metal Free Trifluoromethylthiolation of Unsaturated Compounds

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Poster Session 1

The trifluoromethylthio motif is an important and interesting functional group for the pharmaceutical and agrochemical industry. Due to its electron-withdrawing nature, the SCF_3-group significantly increases lipophilicity and therefore enhances transmembrane permeation.[1-3] Several approaches for the incorporation of the trifluoromethythio group (SCF_3) have been reported, including the trifluoromethylation of sulfur-containing compounds, halogen-fluorine exchange reactions and coupling of halides or boronic acids. However, these methodologies require the use of prefunctionalized substrates, therefore, reducing the atom economy of the reaction. Direct functionalization of C-H bonds has emerged as a powerful tool for the development of more efficient synthetic protocols.

Several groups have recently reported direct C-H functionalization to form C-SCF_3 bonds, requiring the presence of directing groups. Some of these reports require the use of Cl-SCF_3 as an electrophilic reagent, which is a highly toxic, corrosive and difficult to handle gas. In view of these issues, we have developed a new transition metal-free methodology for the trifluoromethylthiolation of electron-rich heterocycles and/or unsaturated compounds under mild conditions using simple sodium chloride as catalyst.[4] Our procedure enables the efficient and regioselective functionalization of unsaturated molecules using a shelf-stable electrophilic trifluoromethylthiolation reagent 2 and does not require directing groups.[5]

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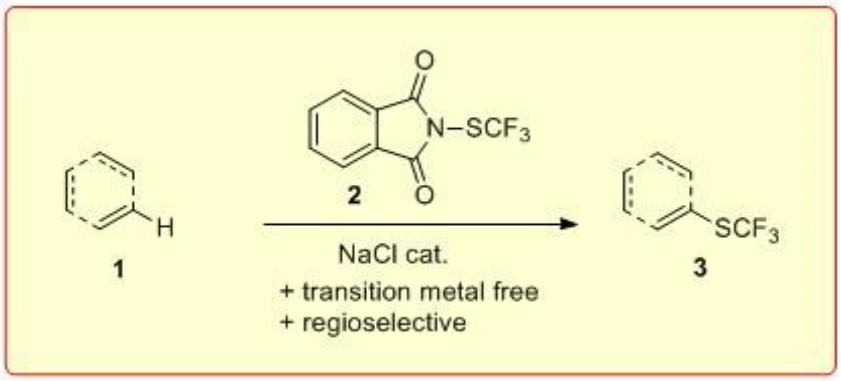

P-169

Pyrrole-based PNP Pincer Complexes with Late Transition Metals

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Poster Session 1

A PNP ligand, PNpyrP ((PNpyrP)H = 2,5-bis((di-iso-propylphosphino)methyl)-pyrrole), which employs a pyrrole unit as a central anionic nitrogen donor, was synthesized. Group 10 metal species ((PNpyrP)MCl, M = Ni, Pd, Pt) were accessible from the pro-ligand and lithium pyrrolide salt, while iridium and ruthenium species were not. Two transmetallation reagents, (PNpyrP)Tl and [(PNpyrP)Ag]2 were synthesized and characterized. These PNP-transfer agents were paramount in the formation of the new iridium and ruthenium complexes, (PNpyrP)Ir(COD) and (PNpyrP)Ru(PPh3)Cl. The stability and reactivity of these species are currently under investigation. Additionally, iridium and ruthenium hydride containing species, (PNpyrP)IrH2 and (PNpyrP)Ru(PPh3)H, have been formed and their ability to perform in transfer hydrogenation reactions is being tested. In the presence of a hydrogen-acceptor (norbornene or tert-butylethylene), the unsaturated iridium complex is capable of activating aromatic, ethereal, or aliphatic C-H bonds at room temperature.

P-170

Visible Light Mediated Photoredox Trifluoromethylation

Dr Adrián Gómez-Suárez[1], Mr Basudev Sahoo[1,2], Dr Mathew N. Hopkinson[1], Dr Jun-Long Li[1], Prof. Frank Glorius[1]

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Poster Session 1

The trifluoromethyl (CF_3) group is a key structural motif in a wide range of pharmaceutical and agrochemical compounds, due to its beneficial effect on the lipophilicity, metabolic stability and membrane permeability of the species.[1] Therefore, many efforts have been devoted to the development of straightforward and mild methodologies for CF_3 incorporation into organic molecules.[1] Recently, visible light mediated photoredox catalysis has emerged as a powerful tool in organic synthesis for the development of extremely mild, sustainable and cost effective transformations.[sup]2, 3[/sup] Therefore, photoredox catalysis has become an attractive alternative for the synthesis of molecules containing CF_3 groups. As a result, the direct trifluoromethylation of alkenes, (hetero)arenes, and several other motifs have been recently reported.[sup]4, 5[/sup] Our group is interested in the discovery of new, straightforward and mild transformations for the synthesis of valuable organic molecules. In the present work, we disclose our latest results in the area of visible light photoredox catalyzed trifluoromethylation of allylic alcohols. Using readily available and easy to synthesize starting materials, in combination with using a commercially available photocatalyst $[Ru(bpy)_3(PF_6)_2]$ and Umemoto's reagent, we have been able to synthesize a wide range of CF_3 containing molecules. In these processes addition of photogenerated CF_3 radical to the alkene moiety is followed by 1,2-migration of either an aryl or alkyl group. In the latter case, a radical-polar crossover mechanism is operating.

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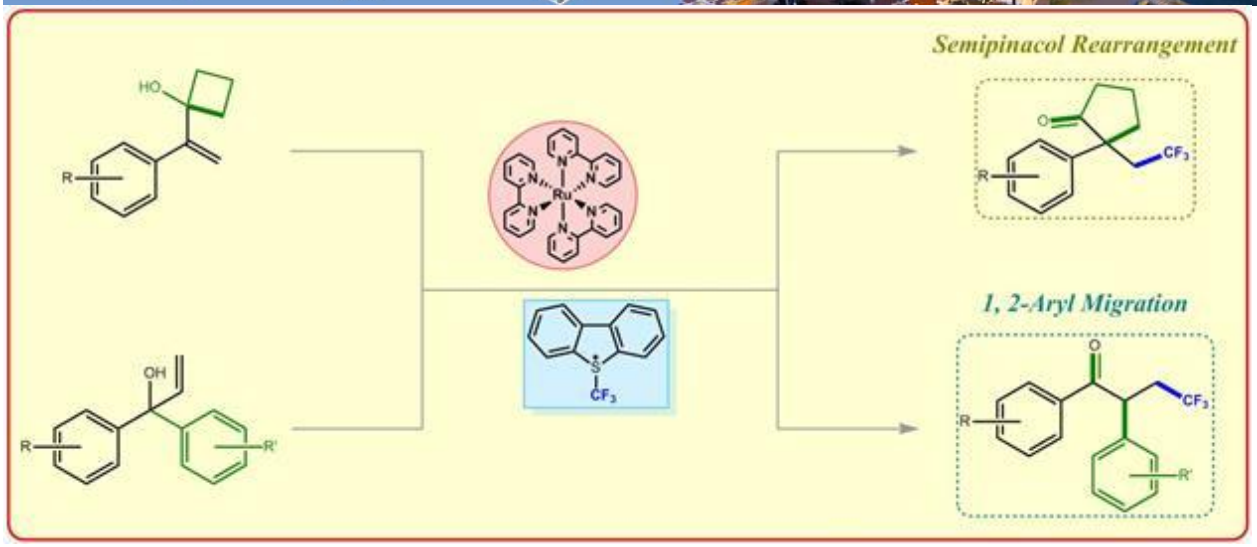

P-171

Co(III)-Catalyzed Directed C–H Coupling with Diazo Compounds: Straightforward Access towards Novel Extended π-Systems

Dr. Ju Hyun Kim[1], Dr. Dongbing Zhao[1], Prof. Dr. Frank Glorius[1]
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Poster Session 1

Carbenoid insertion into C–H bonds is a well-established method to functionalize inert C–H bonds. However, directed C–H bond functionalization involving C–H metalation, metal–carbene formation, and migratory insertion still has limited precedent. In recent years, significant advances have been made in carbenoid insertion of diazo compounds in Rh(III)-catalyzed directed C–H functionalizations. However, although Co is more earth-abundant and inexpensive than Rh, cobalt-catalyzed directed C–H functionalization with carbene precursors has never been reported.

As part of our ongoing recent study on C-H bond functionalization by using the earth-abundant transition metals, we have developed the first highly efficient and scalable Co(III)-catalyzed directed C–H functionalization with carbene precursors. This methodology provides a modular route towards a new class of conjugated polycyclic hydrocarbons with tunable emission wavelengths both in solution and in the solid-state.

P-172

Charged NHC-functionnalized metal nanoparticles as stable catalysts in water

Dr. Angélique Ferry[1], Kira Schaepe[1], Patricia Tegeder[1], Christian Richter[1], Prof. Bart Jan Ravoo[1], Prof. Frank Glorius[1]

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Poster Session 1

Nanoparticles (NPs) have attracted big interest in recent years, especially in the field of catalysis due to their high surface area and the possible metal-metal interactions. However their thermodynamically unstable character limits their applications. In order to stabilize these nanostructures, different ligands can be added. Among them, N-heterocyclic carbenes (NHCs) present the advantage to bind strongly with metals and possess a backbone which can be easily tuned. Nowadays, few examples of NHC-stabilized NPs are described, with limited applications.1

Our group reported the stabilization of metal NPs with NHCs bearing long aliphatic chains at the backbone.2 These sterically stabilized NHC-NPs provide long term stability and chemoselective catalytic activities but are only soluble in organic solvents. In order to investigate a new stabilization mode, suitable to reach stability in water media, we are currently focusing on Pd- and AuNPs functionalized with NHCs bearing anionic functional groups. These charged NHCs act as stabilizers due to electrostatic repulsion and provide NPs which are stable over several months in water. The formation of NPs consists in an exchange ligand process of thioether stabilized NPs.

Various NHCs differing in structural and electrostatic features were tested and led to stable NPs. These NPs showed high catalytic activity in water in hydrogenation reaction.

The ability of cationic NHCs to stabilize metal NPs are under investigation.

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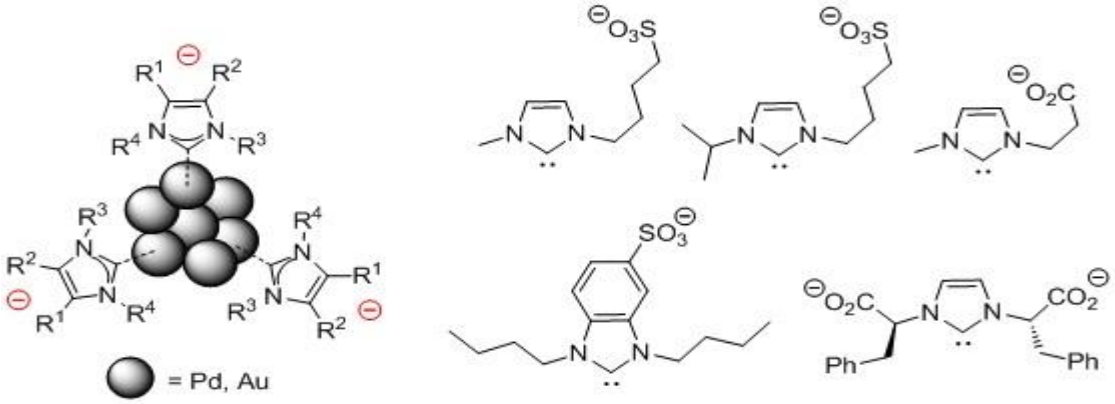

P-173

C–H Bond Activation of N-Acyl Sulfilimines in the Rhodium-catalyzed selective ortho-Olefination

Carl Albrecht Dannenberg[1], Daniel Josef Bell[1], Prof. Dr. Carsten Bolm[1]
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Poster Session 1

Directing group-assisted catalytic C–H bond activation has emerged as a powerful tool in organic synthesis.[1] Previously, our group reported on the selective ortho-olefination of sulfoximines, aza-analogues of sulfones, by C–H functionalization,[2] while Miura and co-workers successfully utilized various phenyl sulfoxides as directing group for ortho-alkenylations.[3]
Sulfoximines are highly potent and visible molecules in medicinal chemistry[4] and crop protection.[5] Since sulfilimines,[6] the aza-analogues of sulfoxides, not only serve as precursors for sulfoximines, but also show bioactivity,[4,5] we envisaged a C–H bond activation utilizing this functionality. The presented method employs N-acyl sulfilimines, which can be prepared by an elegant light-induced ruthenium-catalyzed protocol,[7] and readily available alkenes to obtain the ortho-olefinated products in moderate to good yields.

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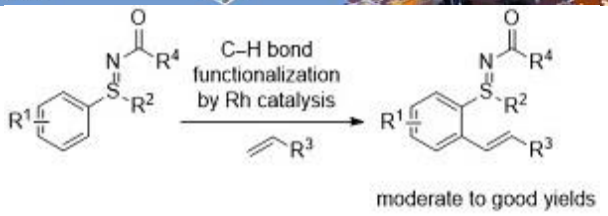
Directed Towards Organic Synthesis
IUPAC International Symposium
Sitges - Barcelona
From June 28th to July 2nd
2015


C–H bond
functionalization
by Rh catalysis
moderate to good yields

P-175

Synthesis Of New Bimetallic Ir(I) Complexes With Pyrene Tags, Immobilization Onto Graphene Surface And Study Of Their Catalytic Properties In Homogeneous And Heterogeneous Catalysis.

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Poster Session 1

We recently showed that NHC-based ligands with polyaromatic systems provide benefits in homogeneous catalysis, which we mainly attributed to π-stacking interactions between the polyaromatic ligands and the substrates.[1-3] We also proved that ligands with pyrene tags could be useful for the immobilization of metal complexes by non-covalent interaction onto chemically derived graphenes (CDGs), such as graphene oxide (GO) and reduced graphene oxide (rGO).[4,5] The resulting immobilized complexes were excellent catalysts that could be effectively re-cycled many times without measurable loss of activity.
In this new work, we report the preparation of a series of mono- and di-metallic rhodium and iridium complexes supported by N-heterocyclic carbene ligands with pyrene pendant groups. The catalytic activity of the complexes has been tested in the reduction of ketones by transfer hydrogenation, and in the β-alkylation of alcohols with primary alcohols. The pyrene-tagged complexes were supported onto rGO, and the resulting materials were effective catalysts in the alkylation of secondary alcohols. Furthermore, the heterogeneous catalysts could be recycled up to 8 times without loss of activity.

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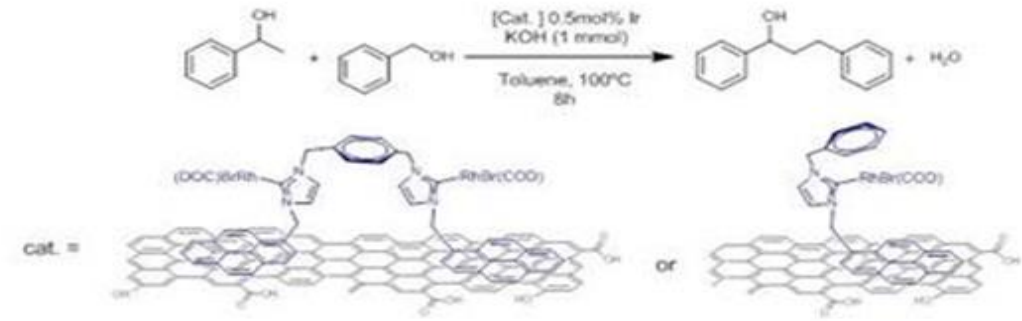

P-078

Rhodium-Catalysed Bis-Hydroformylation of 1,3-Butadiene to Adipic Aldehyde

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Poster Session 1

Hydroformylation (the “oxo reaction”) is one of the largest homogeneous transition-metal-catalysed processes operated industrially.[1][sup],[/sup][2] While a plethora of methods has been developed for the hydroformylation of monoalkenes the selective dihydroformylation of conjugated dienes is still underdeveloped.[1][sup],[/sup][3] For instance, the simplest diene, 1,3-butadiene, typically obtained from large industrial steam-cracking units, can yield up to 14 different aldehydes and their reaction products. Among those products, is 1,6-hexanedial (adipic aldehyde), a potentially important industrial building block.[4] Therefore, we investigated the rhodium-catalysed dihydroformylation of 1,3-butadiene to yield selectively adipic aldehyde.

Broad screening of reaction conditions and new ligand structures revealed, that the selectivity for the desired linear dihydroformylation product, adipic aldehyde, mainly depends on the ligand structure and is essentially less dependent on all other reaction parameters. The optimum reaction parameters and ligand structures have so far resulted in a maximum selectivity of 50% for adipic aldehyde.[5]

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(1) Arpe, H.-J. Industrial Organic Chemistry; 5th ed.; Wiley-VCH: Weinheim, Germany, 2010.
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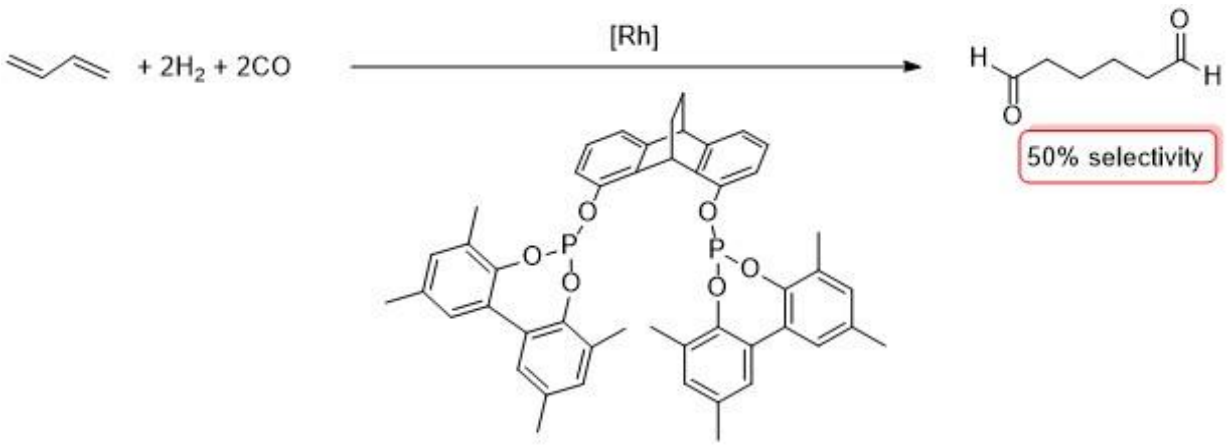

P-176

New Ru(II)-CNN Pincer N-Heterocyclic Carbene Complexes: Synthesis and Applications in Hydrogen-Transfer Reactions.

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Poster Session 1

Ruthenium complexes featuring pincer ligands are an attractive class of homogeneous catalytic systems, especially due to their outstanding performance. [1] Among their numerous catalytic applications, they have resulted very efficient catalysts in hydrogen-transfer reactions, which are very interesting transformations, due to their simplicity and potential use at ambient pressure.

Pincer ligands can present different topologies and sets of donor atoms. In particular, those containing more electron donating N-heterocyclic carbene moieties generally show higher catalytic activity and stability due to their stable metal-carbon bond. Therefore, the seek of new pincer ligands having different donor functionalities may bring better catalytic activities.

Herein the synthesis of a new pincer-type ligand derived from its imidazolium salt precursor L Bold along with their coordinating abilities towards ruthenium(II) precursors will be presented.

Dimeric or monometallic complexes can be obtained depending on reaction conditions.

Finally we carried out the study of the catalytic activity based on the reduction of various ketones to the corresponding alcohols with iPrOH as hydrogen source and KOH as base. [2]

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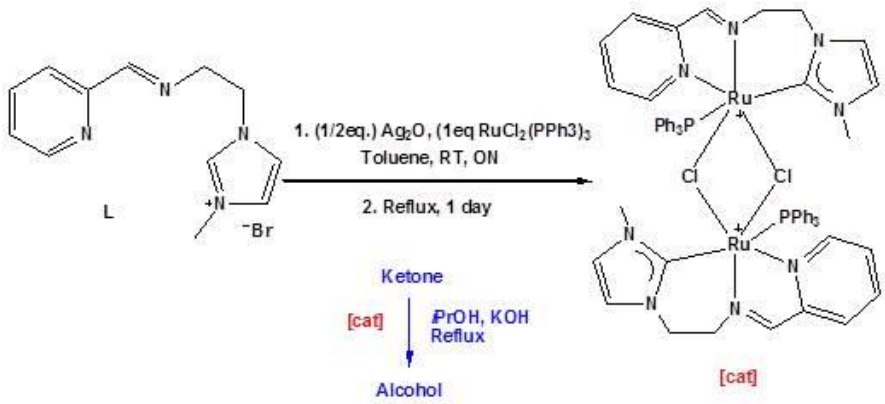


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P-177

Asymmetric Synthesis of Phosphonate-containing γ-(Alkyl)butenolides with two Stereogenic Centers

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Poster Session 1

Organophosphorus compounds are widely spread in nature, and various bioactive products containing C-P bonds are known.[1] Especially, α-hydroxy phosphonic acids, which are bioisosteric to α-carboxylic acids,[2] are of high interest. Other structural prominent motifs are butenolides. Due to their biological properties, e.g. anti-inflammation,[3] they are popular targets in organic synthesis. Furthermore, they can be applied as nucleophiles in vinylogous Michael additions.[4] Combining the valuable features of both compound classes, we herein report the successful development of a vinylogous Mukaiyama Michael addition towards phosphonate-containing γ-(alkyl)butenolides.[5] Catalyzed by a copper(II)-tBu-BOX system a range of nucleophiles and electrophiles undergo this addition in a highly diastereoselective and enantioselective manner.

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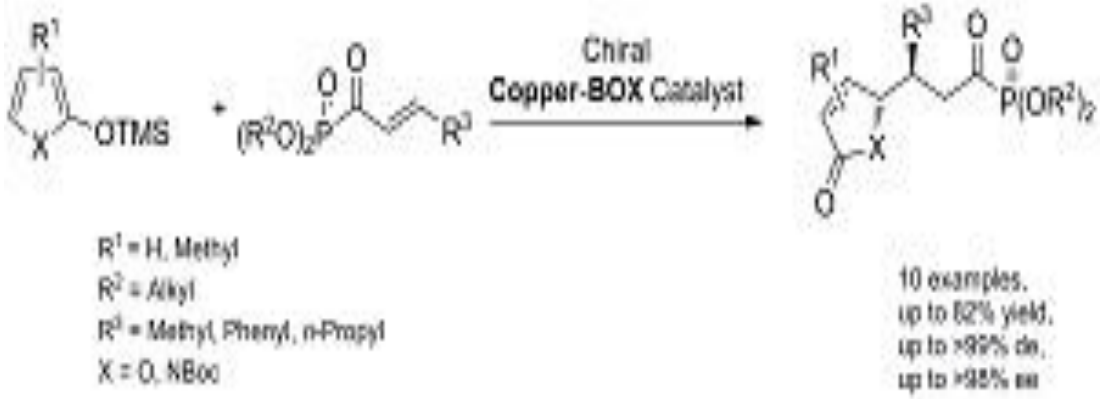

P-178

Rhodium-Catalyzed Intramolecular Dehydrogenative Aryl-Aryl Coupling using Air as Terminal Oxidant

Hannah Baars[1], Yuto Unoh[2], Dr. Koji Hirano[2], Prof. Dr. Tetsuya Satoh[2], Prof. Dr. Carsten Bolm[1], Prof. Dr. Masahiro Miura[2]

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Poster Session 1

Fluorene represents an important scaffold for the construction of organic electronic and optoelectronic materials. Among the simple and straightforward synthetic methods of fluorene derivatives is the dehydrogenative cyclization of 1,1-diphenylalkanes. We recently reported such a transformation under rhodium catalysis.[sup](1)[/sup] Thus, di- and triphenylmethylamines were found to undergo intramolecular dehydrogenative aryl-aryl couplings through amino-directed C-H bond cleavage. However, a stoichiometric copper(II) salt was needed as the oxidant for obtaining reasonable conversions. A highly desirable alternative to overcome this problem is the use of molecular oxygen as terminal oxidant.

Consequently, we explored a new catalyst system, conducting the coupling under air in the presence of $[RhCl(cod)_2]$ as the catalyst, copper(II) acetate as the cocatalyst, and pivalic acid as the promoter.[sup](2)[/sup]

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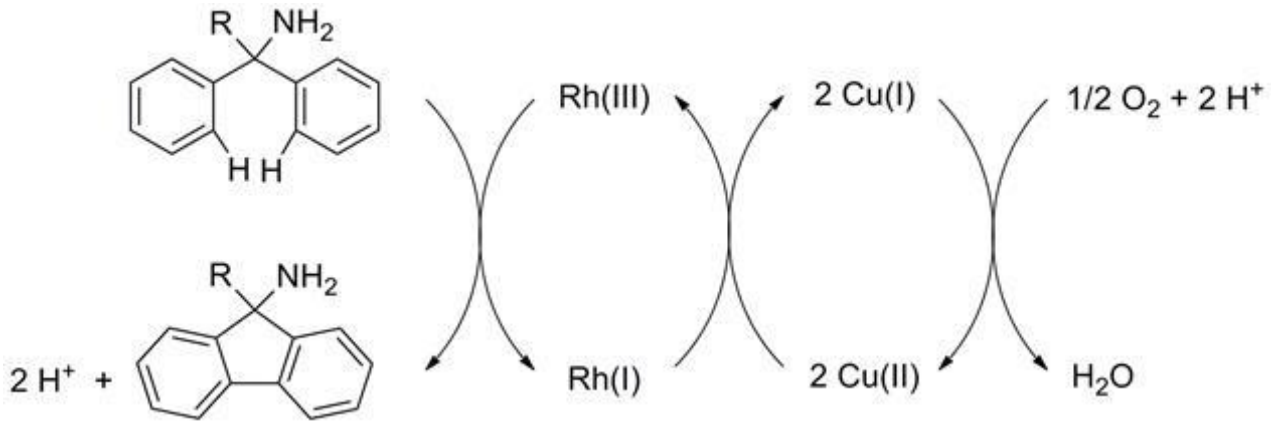

P-179

Acylsilanes in Rhodium(III)-Catalyzed Directed Aromatic C-H Alkenylations and Siloxycarbene Reactions with C-C Double Bonds

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Poster Session 1

Thermally or photochemically induced 1,2-silicon-to-oxygen migration, also known as the Brook rearrangement, is a unique property of acylsilanes, which leads to the formation of siloxycarbenes. While many reports exist detailing the insertion of carbenes into C-H or C-C bonds applying diazocarbonyl compounds as carbene precursor, the application of siloxycarbenes has remained virtually unexplored.[1] Recently, our group reported the insertion of acylsilanes into C-C triple bonds utilizing alkynyl-tethered aroylsilanes to yield chromone derivatives.[2] To further study siloxycarbene insertion into C-C double bonds, a new synthetic method was developed yielding previously inaccessible aromatic acylsilanes containing an ortho-tethered C-C double bond. The appropriate substrates were obtained by a rhodium-catalyzed oxidative Heck-type olefination involving the acylsilane moiety as a directing group. It was subsequently demonstrated that the ortho-olefinated acylsilanes underwent a smooth intramolecular cyclization process, when exposed to visible-light irradiation, to afford valuable indanone derivatives in quantitative yields.[3]

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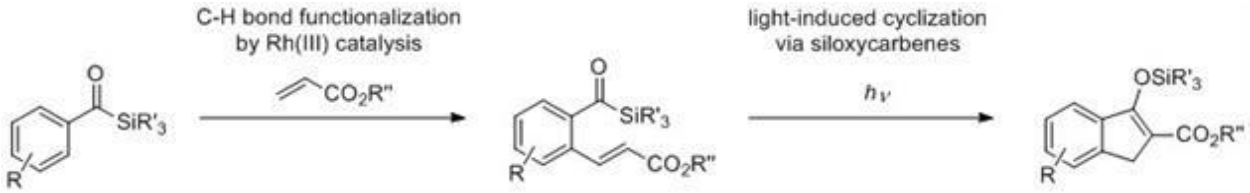

P-180

Exploring the Reactivity of N-Alkynylated Sulfoximines: [2+2]-Cycloadditions

Ramona Pirwerdjan[1], Dr. Daniel L. Priebbenow[1], Peter Becker[1], Philip Lamers[1], Prof. Dr. Carsten Bolm*[1]
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Poster Session 1

In the last decades, sulfoximines have been given considerable interest for their application in organic synthesis, medicinal chemistry and agrochemistry. Therein, the development of synthetic strategies to include the sulfoximine moiety into organic molecules is of particular importance in our research group.[1] In 2013, our group became interested in the development of synthetic strategies to prepare N-alkynylated sulfoximines leading to copper-catalyzed coupling protocols.[2] Compared to the reactivity of ynamides, N-alkynylated sulfoximines depict an interesting substrate for further transformations leading to valuable sulfoximine-containing products.[3] With N-alkynylated sulfoximines in hand, we then investigated their reactivity in cycloaddition reactions. We found that N-alkynylated sulfoximines easily undergo [2+2]-cycloadditions when reacted with ketenes resulting in sulfoximine-functionalized cyclobutenones in excellent yields.[4]

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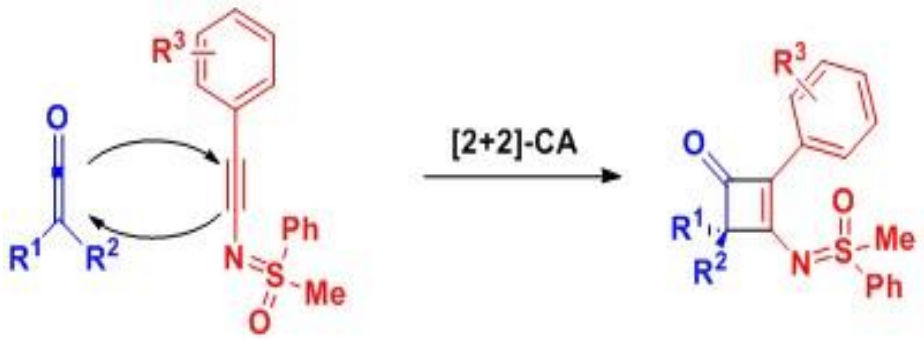

P-181

Synthesis and Catalytic Activity of New N-Heterocyclic Carbene (NHC) Palladium Complexes Containing Fluoride Ligand

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Poster Session 1

Transition metal complexes containing fluoride ligand now enjoy a great interest of researchers because of their relevance in C-F bond activations and formation. Moreover, some fluoride complexes of platinum group metals exhibit good catalytic properties. Surprisingly little is known about palladium fluoride complexes, despite the role of palladium in modern organic synthesis and catalysis [1].
In the communication we report on the synthesis and catalytic activity of new N-heterocyclic carbene palladium complexes containing fluoride ligands. Synthesized complexes exhibit attractive catalytic performance in selected coupling reactions including Suzuki, Kumada, Heck and copper free Sonogashira coupling. Catalytic properties of new palladium fluorides have been compared with those exhibited by selected commercially available palladium catalysts.

Acknowledgement. The research was co-financed by the National Research and Development Center (NCBiR) under Project ORGANOMET No: PBS2/A5/40/2014

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P-182

Development of new catalytic systems for allylic substitution reactions

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Poster Session 1

The formation of chiral C-C and C-X bonds is the most fundamental process in the synthesis of complex molecules from simple ones. Of all the C-C and C-X bond forming strategies, asymmetric Pd-catalyzed allylic substitution is the one that has received most attention for decades, mainly because of the mild reaction conditions required, the high functional group tolerance and the versatility of the alkene functionality adjacent to the chiral center for stereoselective functionalization. Most of the successful catalysts reported to date for Pd-allylic substitution make use of either C2-symmetrical scaffolds, to restrict the number of diastereomeric transition states, or ligands containing different donor atoms, which can electronically discriminate the two allylic terminal carbon atoms.[1] Our group has contributed in this field with an improved generation of ligands. We have therefore shown that the presence of biaryl-phosphite moieties in ligand design is highly advantageous by overcoming the most common limitations of this process, such as low reaction rates and high substrate specificity.[2]
In this poster, I will present the results using a novel Pd-catalyst that can create new C-C, C-N and C-O bonds, in several substrate types with high activities and enantioselectivities. The potential application of allylic substitution using functionalized malonates will be demonstrated by the practical synthesis of the carbo- and heterocyclic compounds.

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P-183

Reactivity of complexes bearing. Hemilabile phosphines towards diazoalkanes

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Poster Session 1

Ruthenium diazoalkane complexes, such as $[Ru(\eta^5\text{-}C_5H_5)\{N_2C(Ar^1)(Ar^2)\}(PPh_3)(L)][BPh_4]$ (L= $P(OMe)_3$, $P(OEt)_3$), have been recently synthesized and found to react with ethylene to provide unexpected 3H-pyrazole derivatives $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}N\text{-}(N{=}NC(Ar^1)(Ar^2)CH_2CH_2)\}(PPh_3)(L)][BPh_4]$ through a [3+2] dipolar cycloaddition. Moreover, the reaction of these diazoalkanes towards alkenes and alkynes has been reported (1, 2).

On the other hand, our group has been involved in the synthesis of Ru(II) semisandwich complexes containing hemilabile phosphines such as $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3\text{-}P,C,C\text{-}(R_2PCH_2CH{=}CH_2)\}(L)][PF_6]$ (R = Ph, iPr, L= PPh_3, $P(OEt)_3$) (3). Herein the reactivity of this type of complexes towards diazoalkanes is presented. Thus, the [3+2] dipolar cycloaddition between the hemilabile phosphine-containing complex and the dialzoalkane allows to prepare the complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^2\text{-}P,N\text{-}(N{=}NCH(R)CH_2CHCH_2PPh_2)\}(L)][PF_6]$ (see example in Figure 1).

We have also obtained analogous Ru(II) complexes $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3\text{-}P,C,C\text{-}(R_2PCH_2CH{=}CH_2)\}][BPh_4]$ ($C_{10}H_{14}$ = p-cymene) (4), whose reactivity towards diazoalkanes has also been tested.

In addition, studies using other different metallic fragments, like rhodium and iridium, will be carried out.

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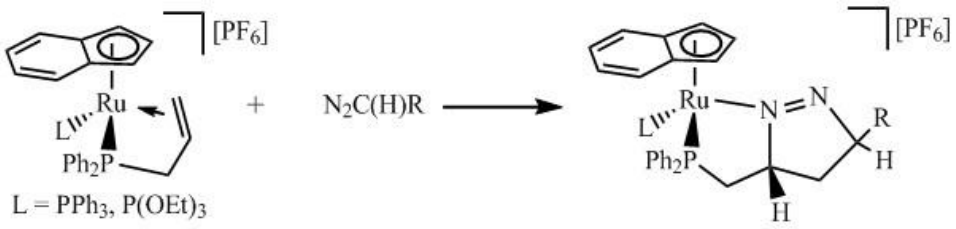

P-184

Design and Application of Bis(phosphite) Ligands with a Distal Regulation Site for Asymmetric Catalysis

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Poster Session 1

The design and development of new strategies to obtain efficient ligands is an important topic, due to the widespread application of these ligands in enantioselective catalysis.[1] Our research group has synthesized a family of bis(phosphite) ligands with a regulation site.[2] These ligands contain two different structural features: a catalytic site containing the phosphite fragments and a regulation site (polyethyleneoxy group) (Scheme 1). The activity of these ligands is controlled by a regulation agent (RA) that interacts with the polyether chain through supramolecular interactions.[2b] The binding of the RA to the regulation site induces small changes in the geometry of the active site and modify the catalytic activity.[2b] These ligands and different regulation agents have been evaluated in rhodium-catalyzed hydrogenation and hydroformylation reactions with excellent levels of activity and enantioselectivity.[2c] (Scheme 1).

P-193

A Novel Approach to BIMs by using Bartoli Indolization

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Poster Session 1

We wish to report a one-pot synthesis of bisindolylmethanes (BIMs) from nitrobenzene and vinylmagnesium bromide through the Bartoli indolization. Remarkably, the acid used to quench the Bartoli indolization markedly affected its results (scheme 1). For example, quenching the reaction of nitrobenzene 1 and vinylmagnesium bromide with concentrated HCl produced BIM 5 through intermediates 2 and 3, by caputuring acetaldehyde (7) as a C-2 unit derived from intermediate 6, in contrast to the formation of 7-chloroindole (4) by quenching with aqueous NH4Cl. Based on these results, we expected that a one-pot reaction of nitrobenzene 8 and vinylmagnesium bromide containing an additional aldehyde should provide various BIMs 9 (scheme 2). This one pot-protocol is applicable to the synthesis of 9. Furthermore, the synthesis of indole alkaloids have been achieved, where the tandem Bartoli indolization using nitrobenzenes, vinylmagenesium bromide, and aldehyde is a key reaction.

P-195

Metal Free, Catalytic Trans-Hydroboration Of Internal And Terminal Alkynes By (NHC)-Borenium Species

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Poster Session 1

The use boranes in cis-hydroboration of alkynes is well known (1), and the metal catalysed trans-hydroboration of terminal (2a,b) and internal alkynes (3) has been reported, although the latter has limitations. Work within our group has shown that 3 coordinate borocations (termed borenium cations) can activate alkynes resulting in novel halo- and carbo-boration reactions. (4a,b) Herein, we report that borenium species trans-hydroborate terminal and internal alkynes in the presence of a hydride donor. Using low catalytic loadings of B(C6F5)3, both internal and terminal alkynes are rapidly hydroborated using BBN(H)(NHC) adducts in good to excellent yields, with high selectivity and tolerant of a range of functional groups.

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P-197

Silylcyanocuprates: Potential Reactive Intermediates in Silylboration Reactions

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[1]*Technische Universität Braunschweig, Institut Für Analytische Und Anorganische Chemie, Braunschweig, Germany*

Poster Session 1

The copper(I) catalysed silyl transfer reactions based on silylboranes (e.g. pinB-SiMe2Ph) have gained increased attention during the last years.1 While depending on the substrate (e.g. aldehydes ,-unsaturated carbonyls) the reaction may follow different pathways. All these reaction pathways include a CuI–silyl species as a central intermediate as demonstrated using a NHC-Copper(I) complex as catalyst model.1-3 Oestreich and co-workers introduced a surprisingly simple yet very effective precatalyst system comprising of CuCN and NaOMe.1,3 However, for this system no experimental investigations regarding the copper complexes formed and the species involved in the catalytic processes have been reported.3,4 In this contribution we will present our recent insights in this copper(I) cyanide based catalyst system. Studying the model system CuCN + (18 C 6)KOtBu we isolated and characterised, structurally as well as spectroscopically, a number of catalytically presumably relevant of alkoxido- and silylcyanocuprates (Scheme).

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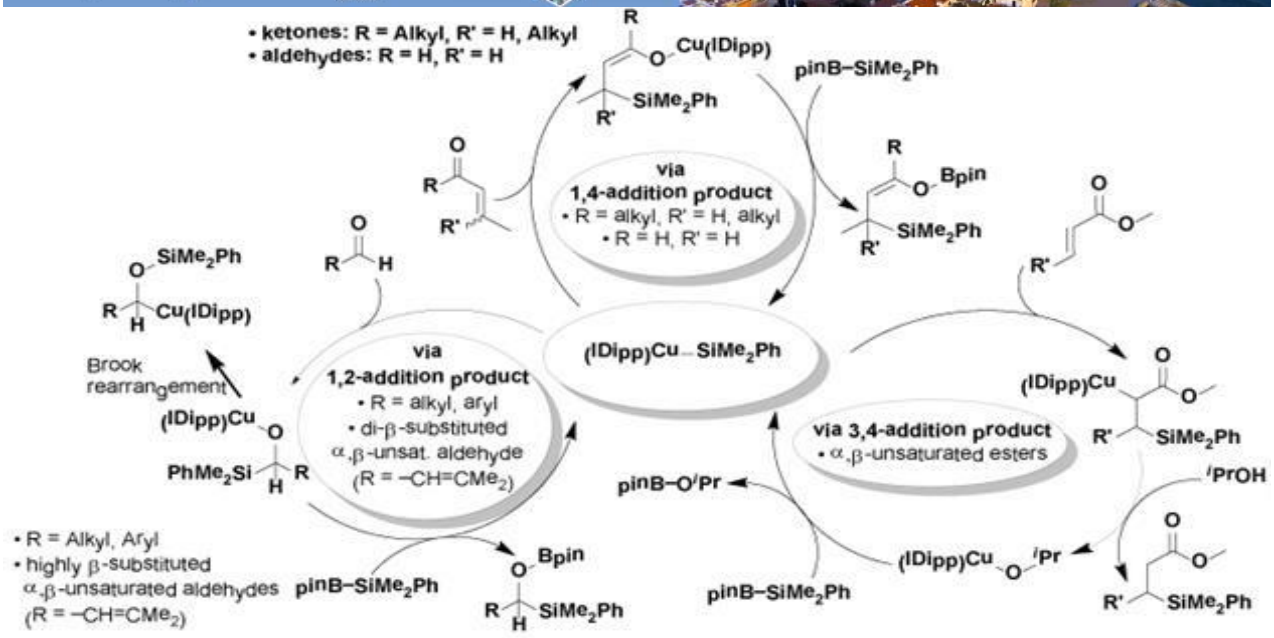
• ketones: R = Alkyl, R' = H, Alkyl
• aldehydes: R = H, R' = H
Cu(IDipp)
SiMe2Ph
pinB–SiMe2Ph
Bpin
via
1,4-addition product
• R = alkyl, R' = H, alkyl
• R = H, R' = H
(IDipp)Cu–SiMe2Ph
via
1,2-addition product
• R = alkyl, aryl
• di-β-substituted
α,β-unsat. aldehyde
(R = –CH=CMe2)
Brook
rearrangement
(IDipp)Cu
PhMe2Si
via 3,4-addition product
• α,β-unsaturated esters
(IDipp)Cu
iPr
iPrOH
pinB–OiPr
• R = Alkyl, Aryl
• highly β-substituted
α,β-unsaturated aldehydes
(R = –CH=CMe2)
pinB–SiMe2Ph
pinB–SiMe2Ph

P-198

Copper-catalysed trifluoromethyaltion of N,N-Disubstituted hydrazones

Mr. Alexis Prieto[1]
[1]*ICBMS, Villeurbanne, France*

Poster Session 1

The trifluoromethyl (CF3) group has gained tremendous importance in various areas of medicinal and agrochemical chemistries owing to its unique functional properties. We recently developed a very mild procedure for the trifluoromethylation of aldehyde N,N-dialkylhydrazones using the Togni hypervalent iodine reagent (1) under copper chloride-catalysis. However, a significant drawback of the method lay in the low efficiencies obtained so far for aliphatic aldehyde hydrazones, the substrate scope being primarily limited to (hetero) aromatic derivatives. Access to trifluoromethylated aliphatic aldehyde hydrazones would greatly improve the synthetic utility of the methodology for instance as a mean of accessing variety of valuable fluorinated heterocyclic compounds. We report herein the successful extension of the substrate scope of our hydrazone trifluoromethylation process to include aliphatic derivatives, thereby demonstrating the general utility of the method. Trifluoro-methylated N-arylhydrazones have been shown to be suitable starting products in the synthesis of 2-trifluoromethylindole derivatives.

P-199

Mono- and Bimetallic Au-Cu dendrimer micelle encapsulated nanoparticles as catalysts in the solvent-free oxidation of styrene.

Dr. Rehana Malgas-Enus[1]
[1]*Stellenbosch University, Stellenbosch, South Africa*

Poster Session 1

Abstract text: Dendrimers are highly branched, monodisperse macromolecules consisting of a core that has subsequently been reacted with monomeric units to form the macromolecule.1,2 The functionalization of the dendrimer's peripheral groups with alkyl chains results in an inverse micelle being formed i.e. the hydrophilic dendrimer is converted to a hydrophobic dendrimer micelle which is soluble in organic solvents.3 Consequently encapsulation of metal salts is solubility driven and subsequent reduction results in nanoparticles which are retained in the dendrimer micelle largely due to steric effects rather than through coordination with functional groups. Here we report on the synthesis and characterization of dendrimer micelles with varying alkyl chain lengths (C15, C10, C5), which were used as templates and stabilizers for the synthesis of dendrimer encapsulated nanoparticles (DEN's). Both mono- and bimetallic DEN's were prepared and it was found that the length of the peripheral alkyl chain of the dendrimer micelle had a direct influence on the average nanoparticle size obtained. These DENs were evaluated as catalysts in the solventless oxidation of styrene. It was found that the bimetallic nanoparticles showed a higher conversion towards styrene oxidation products than the monometallic nanoparticles at optimal reaction conditions. Greater conversion was seen for longer dendrimer micelle chain nanoreactors (DAB-PPI G3 C15) due to the stabilisation that it provided compared to the shorter micelle chain length (DAB-PPI G3 C5) catalytic systems.

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P-200

Synthesis of Novel â-Diketonate Derivatives Ligands and Their Pd (II), Cu (II) Complexes for Using In Supercritical CO2 Deposition

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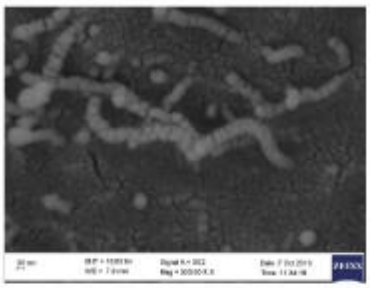
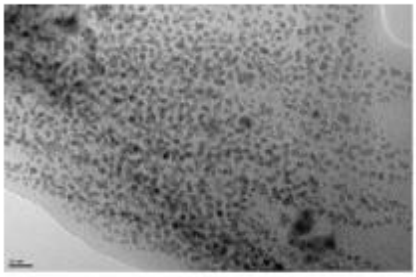
Poster Session 1

Previous researches indicate that, limited numbers of metal complexes are known as a precursor for supercritical deposition. According to this, we were synthesized novel fluorinated â-diketonate derivatives of Cu(II) and Pd (II) complexes and characterized by elemental analysis, FT-IR, 1H, 13C, and 19F NMR. The solubility's of precursors in scCO2 were measured by using high pressure sapphire windowed view cell. Solubility's of fluorinated â-diketonate precursors is 100 times greater than non-fluorinated. Solubility data's have been showed the usability of metal complexes as a precursor for deposition in scCO2. Deposition on Multi-walled Carbon Nanotube by using scCO2 as reaction media has been studied under temperature of 363 K and pressure of 26.5 MPa. Surface analyses of MW-CNT's have been investigated by Transmission Electron Microscopy (TEM), Scattering Electron Microscopy with EDX (SEM-EDX), and X-ray Diffraction (XRD). Results have been showed that metal nanoparticles distributed homogenously on to MW-CNT with size range of 2-20 nm.

a)  b) 

P-201

Nickel-catalyzed cyanation of carbon--carbon multiple bonds

Prof. Shigeru Arai[1]
[1]*Chiba University, Adana, Turkey*

Poster Session 1

Because the utility of a cyano group, its catalytic introduction to non-activated C-C multiple bonds has been major challenge in synthetic chemistry. We focused on Ni-catalyzed hydrocyanation and achieved high and unprecedented regioselectivity in cyclization reactions and cyclopropane cleavage using various functionalized allenes. These protocols offer a new application of cyanation chemistry and the synthesis of biologically important compounds is currently undergoing. Details will be presented.

P-202

Regioselective Double Stille Coupling Reaction of Stannolanes

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Poster Session 1

The Stille coupling reaction is regarded as a powerful tool in organic synthesis. We have recently succeeded to prepare tin-containing five-membered heterocyclic compounds, stannolane, in one-step radical cascade reaction with 1,6-enyne compounds.1 The stannolane is regarded as a potential donor for double Stille coupling reaction, and we have recently developed an efficient double coupling reaction with aryl dibromide.2 In this presentation, we will show regioselecive intra- and intermolecular double coupling reactions with varuous aryl halides and dihalides. Treatment of stannolane with 1-bromo-2-iodoarene in the presence of catalytic amounts of Pd(tBu3P)2 provided desired benzoisoindoles in good yields. The presence of catalytic amounts of DABCO progressed successful reaction to give the coupling products in good yields. The regioslelectivity reached approximately 10:1 to 20:1. The coupling progressed selectively in a manner of the combination of sp2-tin site with iodo-substituted carbon and sp3-tin side with bromo-substituted carbon. Use of o-bromoaryl-substituted stannolanes achieved intra- and inter molecular double coupling with iodoarenes to give indanopyrrolidines in good yields. Use of D2O instead of iodoarene introduced D atom at Z-position of the exomethylene unit stereoselectively.

P-203

DFT-derived mechanism of the ruthenium catalyzed hydrogenation of CO2 to methanol

Dr. Markus Hölscher[1]
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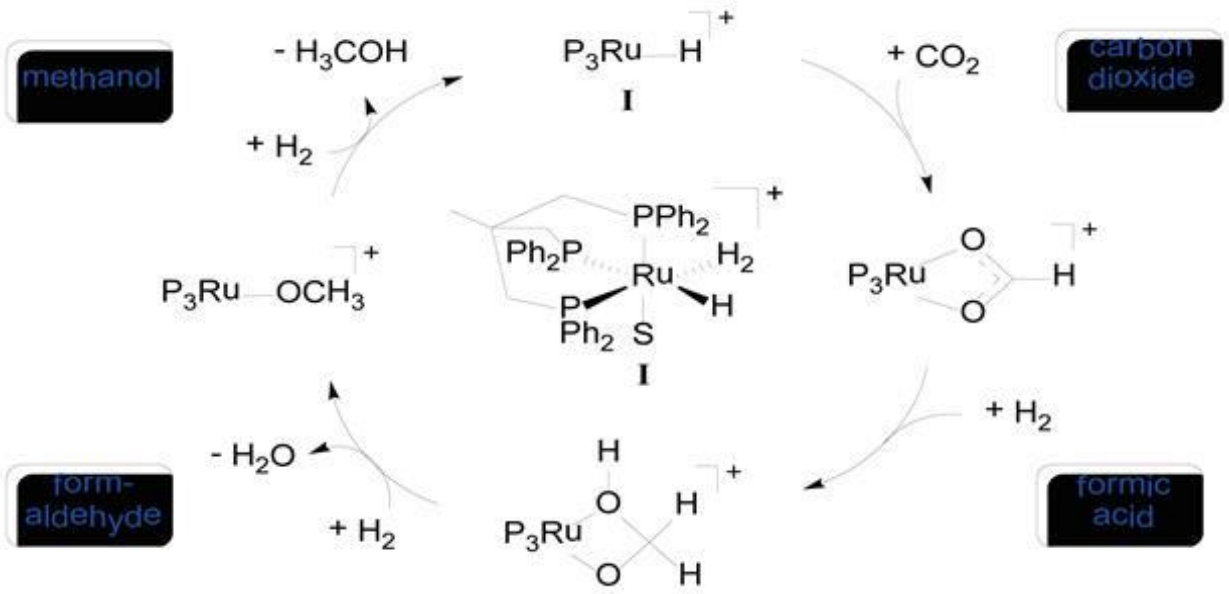
Poster Session 1

Chemical transformations of CO2 to compounds useful as fuels such as methanol are highly interesting since CO2 is a nontoxic and abundant compound available at low cost. Sustainable, CO2-based chemical transformations to methanol can open entry points for alternative fuel supplies. We have recently reported on the hydrogenation of CO2 to methanol with defined molecular ruthenium triphos catalysts (Figure 1).[1] Here we report the full details of the catalytic cycle as derived by state of the art DFT calculations and we correlate the computed results with the experimental observations.



P-204

N-t-Butanesulfinyl Glycosylamines: Synthesis and Exploitation for the Preparation of Novel Glycoside Mimics in the Iminosugar Series

Mr. Cyril Nicolas[1]
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Poster Session 1

Glycosylamines are convenient precursors of a diversity of natural products and analogues of biological interest. In particular they have been used as latent imine equivalents in reactions with various organometallic nucleophiles.[1] Both N-benzyl and N-benzyloxycarbonyl glycosylamine derivatives have been prepared, the former being rather labile and their reactions with organometallic species often sluggish; the latter are more stable, but reacts only with silylated nucleophiles, with frequent side-reactions such as substitution at the anomeric position. Considering the advantages of Ellman's t-butanesulfinyl imines as convenient electrophiles for the stereocontrolled addition of various groups to form amines,[2] we have embarked in an investigation of the synthesis and reactivity of yet little known t-butanesulfinyl glycosylamines. We will report, in this poster, our results on the preparation of such glycosylamines, their reactivity towards various nucleophiles to give open-chain amines, with details on the stereochemical effects at play in this process, and the transformation of the intermediate into imino-C-glycosyl compounds of biological interest.[3]

Acknowledgments: Project funded by Labex SynOrg (ANR-11-LABX-0029) [1] Compain, P.; Chagnault, V.; Martin, O.R. Tetrahedron: Asymmetry 2009, 20, 672-711. [2] Robak, M.T.; Herbage, M.A., Ellman, J. Chem. Rev., 2010, 110, 3600-3740 [3] Iminosugars, from Synthesis to Therapeutic Applications Compain, P.; Martin, O.R., Eds, Wiley-VCH, Weinheim, 2007.

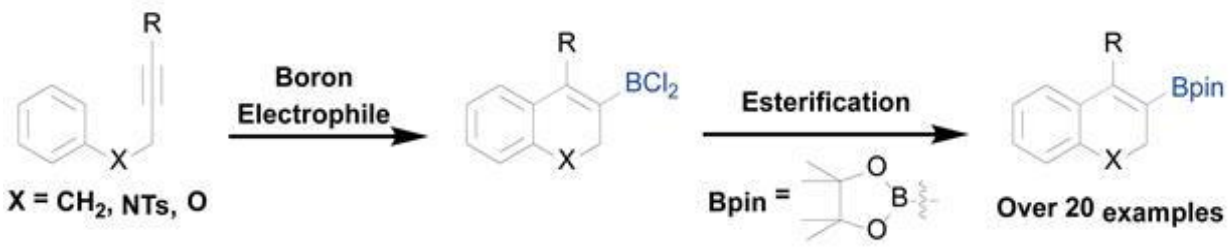
P-205

Electrophilic Cyclisation Using Boron Lewis Acids

Mr. Andrew Warner[1]
[1]*University Of Manchester, Manchester, UK*

Poster Session 1

The electrophilic cyclisation of internal alkynes has been previously investigated using a wide array of electrophiles, for example, aromatic electrophiles generated from iodonium reagents. However, related cyclisations using boron electrophiles are extremely limited, yet they offer an attractive route to cyclic systems possessing a boronic ester moiety. Such cyclic systems include the dihydronaphthalene framework, which can be found in many biologically active compounds including the anti-cancer drug, Nafoxidine. Boronic esters have been exploited by synthetic chemists for decades as they provide synthetically important intermediates that can be used to build and functionalise complex molecules.



P-206

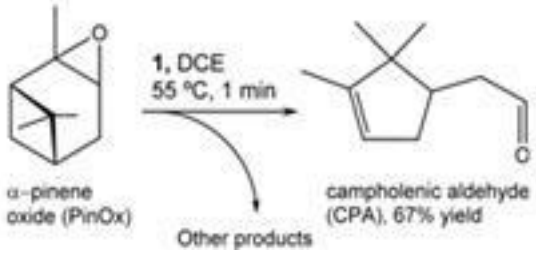
Isomerisation of pinene oxide in the presence of an indenyl molybdenum carbonyl complex

Prof. Carla Gamelas[1]

[1]*Escola Superior de Tecnologia de Setúbal - Instituto Politécnico de Setúbal; Instituto de Tecnologia Química e Biológica - Universidade Nova de Lisboa, Lisboa, Portugal*

Poster Session 1

The complex ((eta5-Ind)Mo(CO)2(-Cl))2 (1) has been tested for the catalytic isomerisation of alfa-pinene oxide (PinOx) to campholenic aldehyde (CPA, see Scheme). Complete conversion of PinOx was achieved within 1 min at 55 C or 30 min at 35 C using 1,2-dichloroethane as solvent, giving CPA in 68% yield.1 Other products included trans-carveol, iso-pinocamphone and trans-pinocarveol. The stability of 1 under the reaction conditions was investigated by FT-IR spectroscopy and ESI-MS to characterise recovered solids. In the presence of air/moisture 1 undergoes oxidative decarbonylation upon dissolution to give oxomolybdenum species that are proposed to include a tetranuclear oxomolybdenum(V) complex. Conversely, ESI-MS studies of 1 dissolved in dry CH3CN show mononuclear species of the type [IndMo(CO)2(CH3CN)n]+. The crystal structure of [(eta3-Ind)Mo(CO)2Cl(CH3CN)2] (2) (obtained after dissolution of 1 in CH3CN) is reported.



P-207

X-Ray Characterization of an Electron Donor–Acceptor Complex that Drives the Photochemical Alkylation of Indoles

Ms. Ana Bahamonde[1]

[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 1

A photochemical strategy for the direct alkylation of indoles is described.1 The reaction, which occurs at ambient temperature, is driven by the photochemical activity of electron donor–acceptor (EDA) complexes,2 generated upon association of substituted indoles with electron-accepting benzyl and phenacyl bromides. The most significant results of our studies are the successful isolation and full characterization by X-ray single-crystal spectroscopic analysis of a visible-light-absorbing EDA complex, and the demonstration that its photochemical activity drives the alkylation process. Furthermore, the determination of the quantum yield (ɸ) of the process provides additional insights on the reaction mechanism. As depicted in Figure 1, the electron-rich indole 1 and the electron-accepting bromide 2 readily associate to form the photoactive (EDA) complex I. Upon irradiation with light, the alkylation product 3 is formed with high yield (CFL = compact fluorescence lamp).

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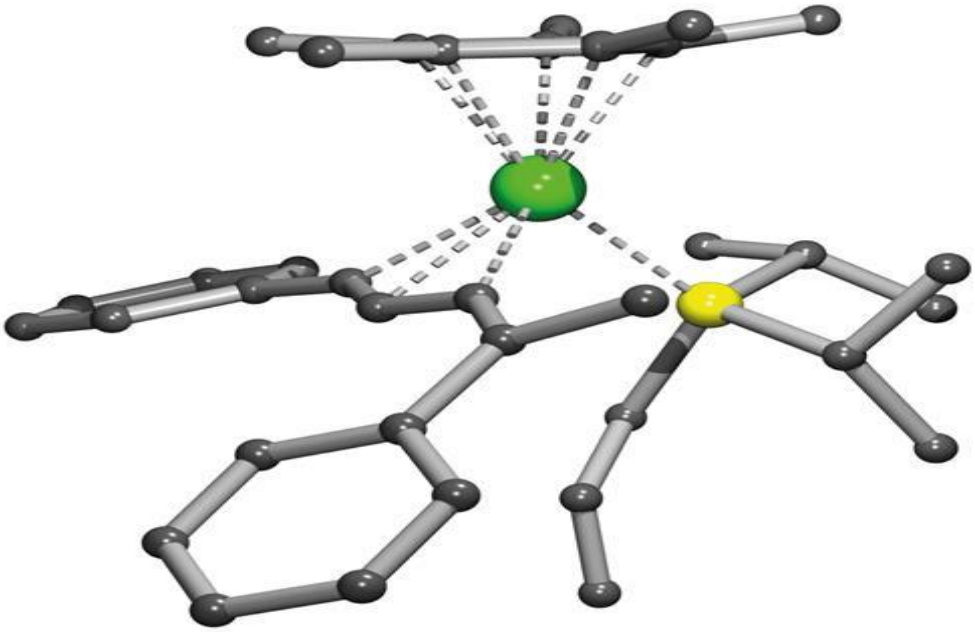

P-208

Regio- and Stereoselective Functionalization of Electron-Rich Alkynes

Prof. Jianwei Sun[1]

[1]*Hong Kong University Of Science And Technology, Hong Kong, China*

Poster Session 1

Alkyne functionalization is a long-standing topic in organic synthesis. In the past few decades, various functionalization reactions such as hydrosilylation, hydroboration, hydroamination, and silylboration for the transformation of alkynes to stereodefined alkenes have been developed. An important challenge of these reactions is the control of both regioselectivity and stereoselectivity, particularly for unsymmetrical internal alkynes. Moreover, regarding electronic properties of the alkyne substrates, electron-normal and deficient alkynes have been well-studied. In contrast, electron-rich alkynes (e.g., ynol ethers, ynamines/ynamides, thioalkynes) have been much less explored. Here we would like present our recent progress on highly stereo- and regioselective functionalization of internal electron-rich alkynes for the synthesis of various highly substituted/functionalized and stereodefined alkenes (Scheme 1), which are highly versatile species in organic synthesis. Detailed scope and mechanistic discussion as well as representative product transformations will also be presented.

Scheme 1: Functionalization of E-Rich Alkynes

P-209

Hiyama coupling made easy

Mr. Juan Del Pozo Del Valle[1]
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Poster Session 1

Palladium-catalyzed cross-coupling reactions have emerged as efficient synthetic tools for the construction of carbon− carbon bonds. Particularly, organic molecules containing bulky groups have shown great potential in drug discovery and medicinal chemistry.1 They are often introduced into pharmaceuticals to enhance lipophilicity and/or improve the drug's metabolic stability. Hiyama reaction is particularly attractive due to the low cost, low toxicity, and high chemical stability of the silicon compounds used as cross-coupling partners. However, much fewer examples its use in synthesis can be found in the literature than that of the homologous Suzuki or Negishi reactions. The reason for this is the lack of robust procedures when the coupling gets taught. As far as we know, there is no precedent in the literature of the use of diorthosubstituted-aryl silanes or siloxanes in the Hiyama coupling, due to the very low reactivity of these nucleophiles. In this communication, we report their use in an unprecedented copper-promoted Hiyama coupling that allows for the synthesis of hindered biaryls in nearly quantitative yields. The coupling is highly versatile, accepting both electron withdrawing and electron donating substituents, and also sensitive moieties such as aldehydes. Mechanistic insights are also given to unveil the nature of this interesting novel reaction. Scheme 1

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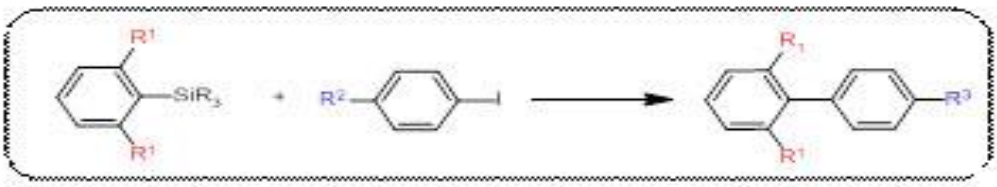

P-210

Palladium-catalyzed Isomerizations of Highly Substituted Allylic, Homoallylic and Alkenyl Alcohols

Mr. Luqing Lin[1]
[1]*Department of Organic Chemistry, University Of Geneva, Geneva, Switzerland*

Poster Session 1

Metal-catalyzed directed isomerizations of functionalized olefins are particularly attractive because, upon migration of a C=C bond, the substrates undergo refunctionalization in an overall redox neutral operation with no chemical waste generated.1 Herein we report the palladium-catalyzed isomerization of highly substituted allylic alcohols and alkenyl alcohols by means of a single catalytic system.2 The operationally simple reaction protocol is applicable to a broad range of substrates, displays a wide functional group tolerance and the products are usually isolated in high chemical yield.

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P-211

Pd(II) organometallic complexes: towards the achievement of liquid crystal materials

Mr. Cristián Cuerva[1]
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Poster Session 1

Dicatenar pyridine-functionalized pyrazole ligands [HpzR(n,n)py] were used as building blocks to synthesize columnar discotic metallomesogens through their coordination to PdX2 (X = Cl, Br, I) metallic fragments.1 As shown in Fig. 1a, the formation of hydrogen bonds between half-disc shaped molecules achieves head-to-tail dimers in the solid state, which are arranged in columns. In agreement with this fact, chloride and bromide Pd(II) complexes exhibit the characteristic broken fan-like textures of columnar mesophases in a wide temperature range. By contrast, iodide derivatives do not show liquid crystal properties, probably due to the high size of the halide atom. On the other hand, the effectiveness of the allyl palladium fragment to induce mesomorphism as well as the introduction of certain electronegative substituents like Br can be suggested to improve the liquid crystalline behaviour. On this basis, new Pd-complexes of the type [Pd(ƞ3-C3H5)(pyBrpzR(n))][BF4] have been obtained. As it was expected, those ionic complexes present lower melting and clearing temperatures than the previously described [Pd(ƞ3-C3H5)(pypzR(n))][BF4].2 On the other hand, Pd(II) derivatives containing the new ligand (pypzR(n)py) only were found to be liquid crystal species in presence of the [Pd(ƞ3-C3H5)]+ fragment (Fig. 1b).

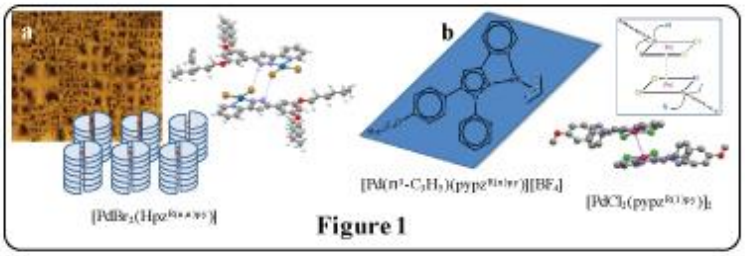


Figure 1

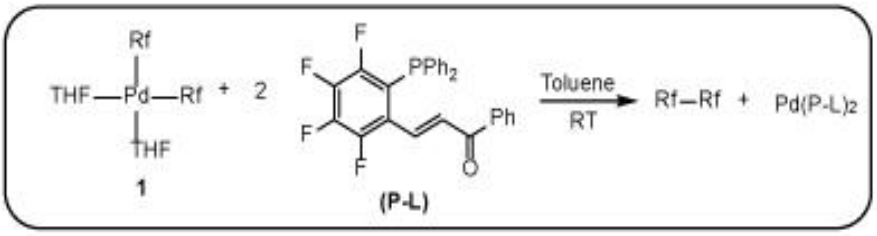
P-212

A new ligand for difficult C–C couplings

Ms. Estefania Gioria[1]
[1]*IU CINQUIMA – University of Valladolid, Valladolid, Spain*

Poster Session 1

In this work we focus on the reductive elimination step of polyflourinated aryl groups prompted by a hybrid phosphine-olefin ligand (P-L). This ligand was synthetized and studied previously in our group showing very good results in Negishi aryl-alkyl cross-coupling reactions. Polyfluorinated groups are very interesting substrates, due to the increase in solubility, lipophilicity and other properties that F atoms lend to these skeletons, and their broad applications in different fields such as pesticides, pharmaceuticals, liquid crystals and other materials. However the introduction of these polyfluorinated groups via cross-coupling reactions is not a simple issue, especially due to the extremely high activation energy of the reductive elimination involving these groups. The barrier to reductive elimination has been experimentally measured using this hybrid ligand in the process shown in Scheme 1, and others, such as Buchwald-type ligands (tBuXphos and tBuBrettphos) or Xantphos, which are also known to be very efficient in difficult cross-coupling catalysis. Reductive elimination promoted by P-L proved to be not only the fastest but the one that provides the mayor conversion to Rf-Rf coupling product. Additionally, a computational investigation of the process was carried out, which explains the mechanistic base for the good performance of the phosphine-olefin ligand in promoting reductive elimination on PdII complexes.



P-214

A Study of Cobalt Metal Organic Framework Material as Adsorbent for Lead ions removal in Aqueous Solution

Mr. David Shooto[1]
[1]*Vaal University Of Technology, Vanderbijlpark, South Africa*

Poster Session 1

Cobalt-Metal-Organic Frameworks (Co-MOFs) were synthesized and their morphological features studied using thermalgravimetrc analysis, Raman spectroscopy, energy dispersive spectroscopy (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction spectroscopy and Fourier transformed infrared spectroscopy. Equilibrium and thermodynamic batch adsorption experiments were carried out to determine concentration, time and temperature effects respectively. The morphological images showed Co-MOFs of irregular sized highly crystalline regions. It also showed the presence of C, O, Co and OH which may create charges and functionalities on the surface of the Co-MOF for adsorption. The adsorption studies recorded a rapid uptake of Pb2+ by the Co-MOFs. The equilibrium, kinetic and thermodynamic studies suggested relatively low temperature (low energy) favoured sorption which was exothermic with a physi-sorption mechanism.

P-215

New Carbocyclic and N–heterocyclic Phosphine Ligands: Application in Homogenous Catalysis

Dr. Anahit Pews-Davtyan[1]
[1]*Leibniz Institute for Catalysis (LIKAT), Rostock, Germany*

Poster Session 1

Palladium phosphine complexes represent powerful catalytic systems for numerous C–C bond formation reactions in contemporary organic chemistry. Among the different coupling reactions, carbonylations allow for a straightforward synthesis of all kinds of carboxylic acid derivatives. As a result significant efforts have been dedicated to the development of new phosphine ligands for carbonylation catalysts, which are widely used both in academic laboratories and for industrially relevant processes. Based on our long lasting interest in the development and application of novel phosphorus ligands, we became interested in the synthesis of new carbocyclic and N–heterocyclic analogues of "state–of–the–art" ligand bis(di–tert–butylphosphinomethyl) benzene (Figure 1).[1] Figure 1 The new carbocyclic and N–heterocyclic phosphorus ligands have been synthesized in moderate to very good yields. The ligands are constructed on benzene, tetralin, lutidine, pyrazine, quinoxaline and maleimide backbone. Substituents at phosphorus with different electronic and steric properties have been introduced, which enable "fine tuning" of the resulting homogeneous palladium catalysts. The novel ligands have been tested in a benchmark reaction, the palladium–catalyzed alkoxycarbonylation of 1–octane and show potential for further applications. In our presentation we will discuss all results in more detail.

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Figure 1

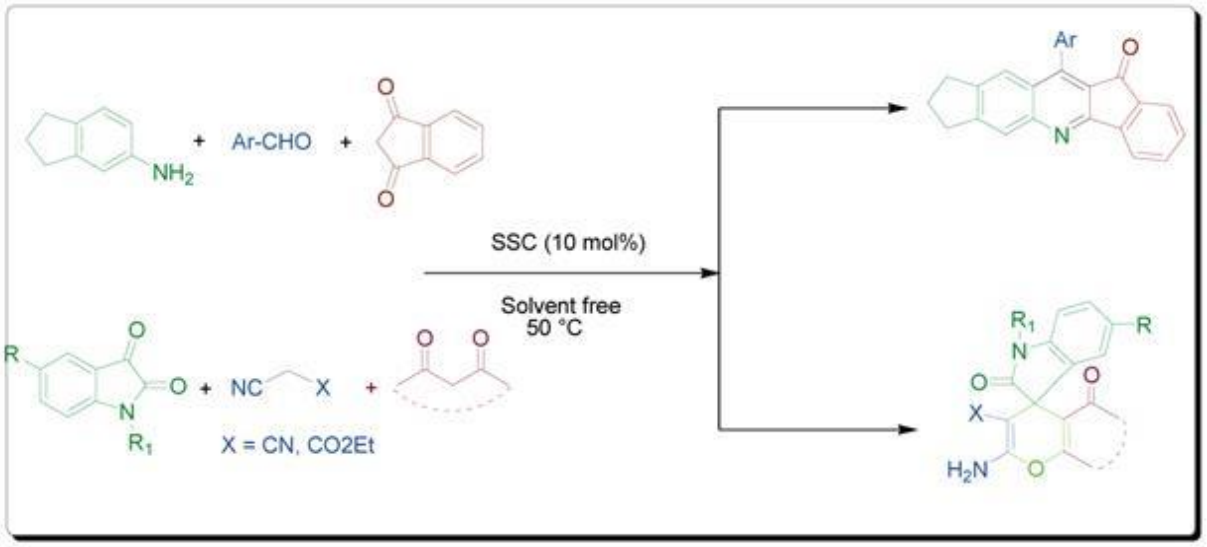
P-216

Silica sodium carbonate (SSC): efficient catalyst for the one-pot synthesis of indeno[1,2-b]quinolin and spiro[chromene-4,3'-indoline]-3-carbonitriles under solvent-free condition

Mr. Vijay Shinde[1], Sang Dong Lee, Yeon Tae Jeong
[1]*Pukyong National University, Busan, South korea*

Poster Session 1

A new silica sodium carbonate assisted convenient and efficient strategy for the synthesis of indeno[1,2-b]quinolin and spiro[chromene-4,3'-indoline]-3-carbonitriles derivatives in solvent-free media is describe. The reactions can be performed at low catalyst loadings with excellent functional group tolerance. The catalyst can be easily recovered and reused for the next reaction for at least three runs without any significant impact on the yields of the products. The easy recovery of the catalyst and high yield of the products make the protocol attractive, sustainable, and economic.



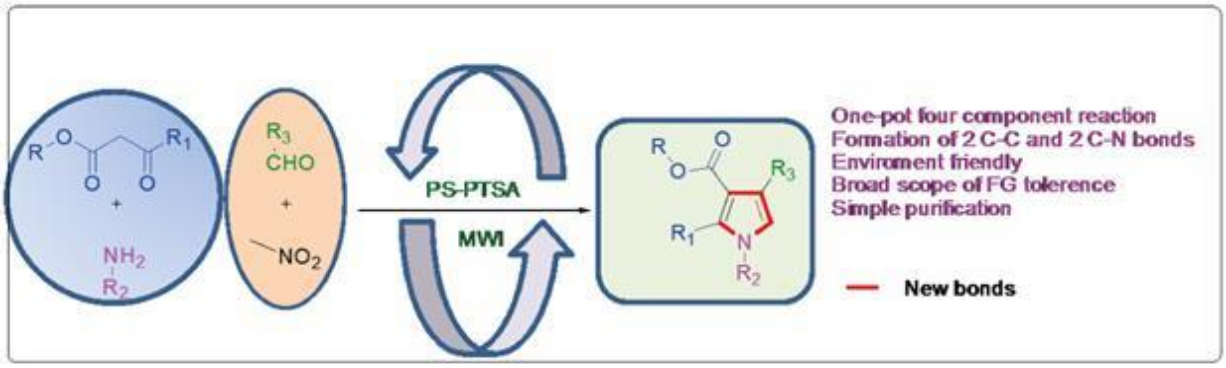
P-217

P-toluenesulfonic acid doped Polystyrene (PS-PTSA): solvent-free microwave assisted cross-coupling-cyclization-oxidation to build one-pot diversely functionalized pyrrole

Mr. Sang Dong Lee
[1]*Pukyong National University, Busan, South Korea*

Poster Session 1

A solvent-free environmentally benign approach for the synthesis of diversified pyrrole derivatives has been described by the one-pot multicomponent reaction of aldehydes, nitroalkane, amine and enolizable active C─H reactant using polystyrene supported p-toluenesulfonic acid (PS-PTSA) under microwave irradiation. In comparison to the conventional methods, this efficient green protocol provides remarkable advantages such as good to excellent yields, shorter reaction, low cost, easy work-up procedureand bypass for use of hazardous organic solvent.



P-218

Rh(III)-Catalyzed Ortho Alkenylation of Aryl Dithioacetals

Masahiro Miuraa1, Koji Hiranoa1, Mr. Yuto Unoh[1,2], Tetsuya Satoha[1,2]
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Poster Session 1

Dithioacetals such as dithianes are recognized as useful protecting groups for carbonyl moieties in organic synthesis field. Most frequently, they are utilized as umpolung acyl anionic synthons taking advantages of the acidic nature of their α C-H bond. In contrast to these conventional usage, their utilization as directing groups for transition-metal catalyzed C-H bond functionalization is less explored.[1] During our continuous studies on Rh(III)-catalyzed C-H functionalization, we have found a dithioacetal-directed regioselective direct alkenylation.[2] Thus, the oxidative coupling of 2-aryl dithianes and dithiolanes with alkenes proceeded smoothly in the presence of a Cp*Rh(III) catalyst and an appropriate oxidant to produce the corresponding ortho alkenylated products. For example, treatment of 2-phenyl-1,3-dithiane with t-Bu acrylate in the presence of [Cp*Rh(MeCN)3(SbF6)] and Cu(OAc)2•H2O in THF at 60 °C provided the ortho-alkenylated product in 86% yield. The dithiane protecting group can be removed easily after the coupling event. The details of substrate scope, effect of substituents, and proposed mechanism will be shown in this presentation.

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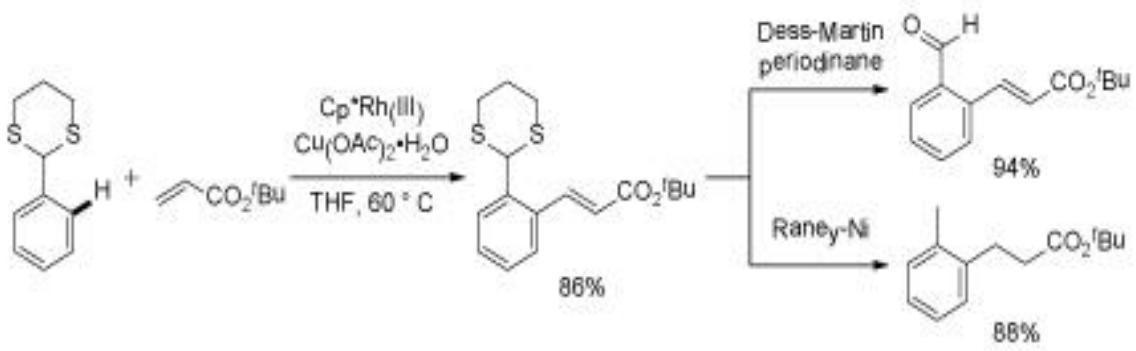

P-219

Oxidative Homocoupling of Terminal Alkynes by Allyl Palladium Complexes

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Poster Session 1

Conjugated acetylenes are present in many drugs, natural and bioactive products and also play an important role as precursors of some molecular organic materials. Although the first acetylenic coupling reaction was described by Glaser in 1869, the development of new efficient and environmental friendly synthetic methods remains a challenge. In the last years, the use of palladium has improved the selectivity and reliability of acetylenic couplings. This work describes the synthesis of 1,3 diynes by oxidative homocoupling of terminal alkynes catalyzed by an allylic palladium complex in the absence of copper.

Results: Conjugated acetylenes have been obtained with moderated to excellent yields from the homocoupling of terminal alkynes with diverse functional groups. The conditions employed (water/acetone mixture as solvent, sodium acetate as base and air as the oxidant, without additional ligands) lead to a cleaner chemical process in comparison with others previously reported. The choice of an allylic Pd complex as catalyst is crucial since only traces of dialkyne are obtained using other common Pd catalytic precursors. The allyl fragment plays only the role of auxiliary ligand and the allyl-alkynyl coupling is not observed. The slow reductive elimination of allyl-R in [Pd(allyl)RL], when R = alkynyl has been reported before

P-220

Rhodium nanoflowers as recyclable catalyst for the hydrosilylation of internal alkynes

Prof. Roser Pleixats[1]
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Poster Session 1

The transition-metal catalyzed hydrosilylation of alkynes represents a straightforward and convenient route for the preparation of vinylsilanes. The process is fully atom-efficient and the resulting organosilicon species are versatile building blocks in synthesis. We have recently reported the hydrosilylation of internal alkynes using tris-imidazolium salt-stabilized Pd nanoparticles.1 We present here morphology and size controllable rhodium nanoparticles stabilized by a nitrogen-rich PEG-tagged derivative. The flower-like Rh NPs obtained by the reduction of RhCl3 with NaBH4 in water at room temperature proved to be effective catalysts for the stereoselective hydrosilylation of challenging internal alkynes and diynes, affording the (E)-vinylsilanes in quantitative yields for a wide range of substrates (Scheme).2 The insolubility of the nanocatalyst in diethyl ether allows its easy separation and recycling.

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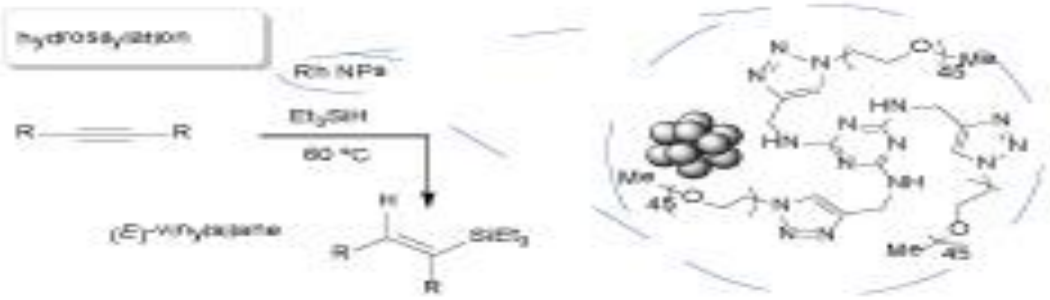


P-221

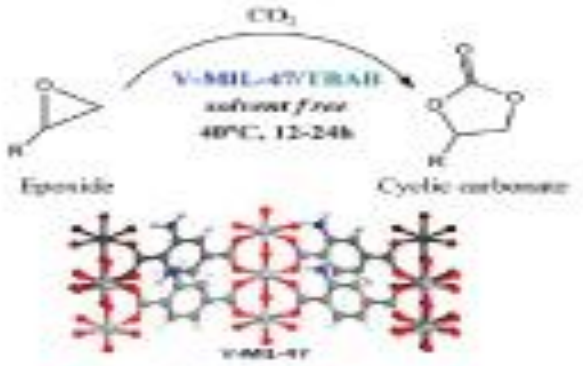
VANADIUM BASED METAL ORGANIC FRAMEWORKS FOR THE SYNTHESIS OF CYCLIC CARBONATES FROM CO2 AND EPOXIDES

Prof. Dae-Won Park[1]

[1]*Pusan National University, Busan, South Korea*

Poster Session 1

Vanadium is one of the less explored elements for its catalytic activity towards the cycloaddition of CO2 with epoxides to yield five membered cyclic carbonates1 (Scheme 1). Considering the wide range of clusters and complexes that can be formed with vanadium nodes, a large number of metal organic frameworks with potential catalytic abilities could be synthesized2. In this work, we examined the catalytic potential of two series of Vanadium based MIL metal organic frameworks; the ones with a) V-O-V infinite chains (V-MIL-47, V-MIL-48, V-MIL-68) and b) oxido centered V trimers (V-MIL-100, V-MIL101) along with tertiary butyl ammonium bromide (TBAB) co-catalyst. Among these, the highly porous V-MIL-47 was found most efficient which catalyzed the cycloaddition reaction of propylene oxide with CO2 to propylene carbonate with high selectivity (>99%) and in high yields (>85%) at temperatures as low as 40oC in 12-24 h reaction time. Density functional theory (DFT) was applied to find out the reaction pathways behind the catalysis.



Scheme 1

P-223

Synergistic Steric Effects in the Development of a Pd-Catalyzed Alkyne Carbohalogenation Reaction

Ms. Christine Le[1]
[1]*University of Toronto, Toronto, Canada*

Poster Session 1

Aryl and vinyl halides are versatile building blocks in organic synthesis due to their applicability towards a vast range of transition metal-catalyzed cross-couplings. In contrast to oxidative addition, the reductive elimination of carbon–halogen bonds from Pd(II) complexes to yield organohalide products is an unfavourable process when conventional ligands, such as triarylphosphines, are employed. Our group has previously reported the application of bulky, electron-rich Pd catalysts in the carboiodination reaction of alkenes to form alkyl iodides. We now report that by exploiting the synergistic steric effects between substrate and catalyst, an intramolecular Pd-catalyzed alkyne carbohalogenation can be realized, providing access to vinyl halides in a stereoselective manner.[1] The success of this transformation strongly depends on the steric properties of the substrate, which promotes C(sp)2–halogen reductive elimination in concert with the bulky catalyst employed. Mechanistic studies reveal that oxidative addition is a reversible process, thereby preventing catalyst deactivation and, more interestingly, enabling a thermodynamically-driven isomerization of the vinyl halide product at elevated temperatures. This atom-economical reaction represents the first Pd(0)-catalyzed stereodivergent addition of an aryl–halide across an alkyne.

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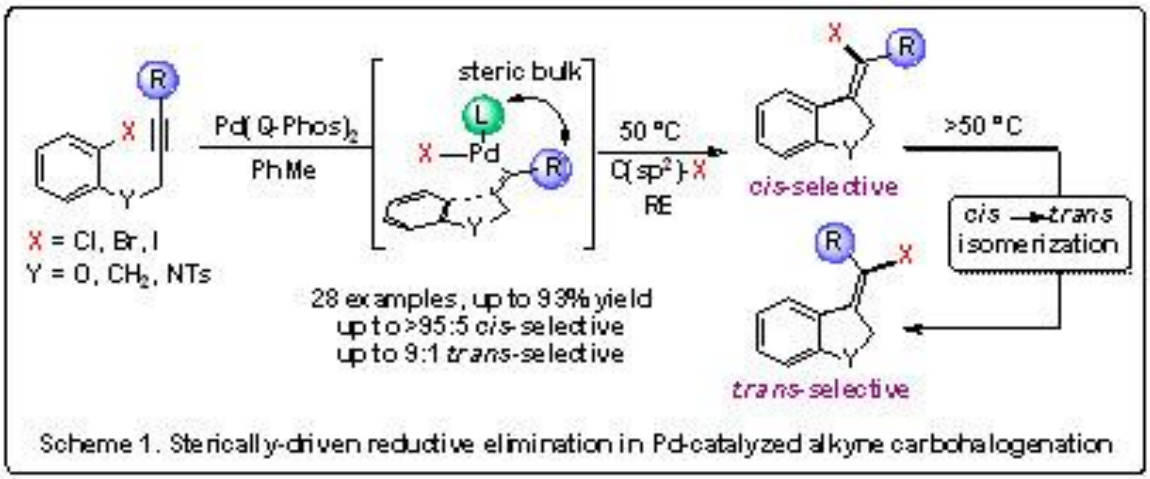


Scheme 1. Sterically-driven reductive elimination in Pd-catalyzed alkyne carbohalogenation

P-224

BIS(1,2,3-TRIAZOL-5-YLIDENE)CARBAZOLIDE RHODIUM(I) COMPLEXES AND THEIR APPLICATION IN THE CATALYSIS OF ALKYNE DIMERISATION

Dr. Daniela Bezuidenhout[1]
[1]*University of Pretoria, Pretoria, South Africa*

Poster Session 1

The synthesis of a novel tridentate bis(1,2,3-triazolylidene)carbazolide pincer ligand [1], and its coordination to various late transition metals, specifically Rh(I), are presented. The tridentate biscarbene pincer ligand has proven to stabilize very reactive late transition metal complexes through the chelate effect, in combination with the rigid carbazole backbone and bulky wingtip functionalities for steric stabilization, together with the electron donating central amido and two strong σ-donor flanking triazolylidene moieties. In addition, the Rh(I)-dioxo-adduct complex displays activity as a highly selective catalyst in the head-to-tail dimerization of terminal alkynes [2], catalyzing the exclusive formation of the gem-enyne from substrate 1-pentyne.

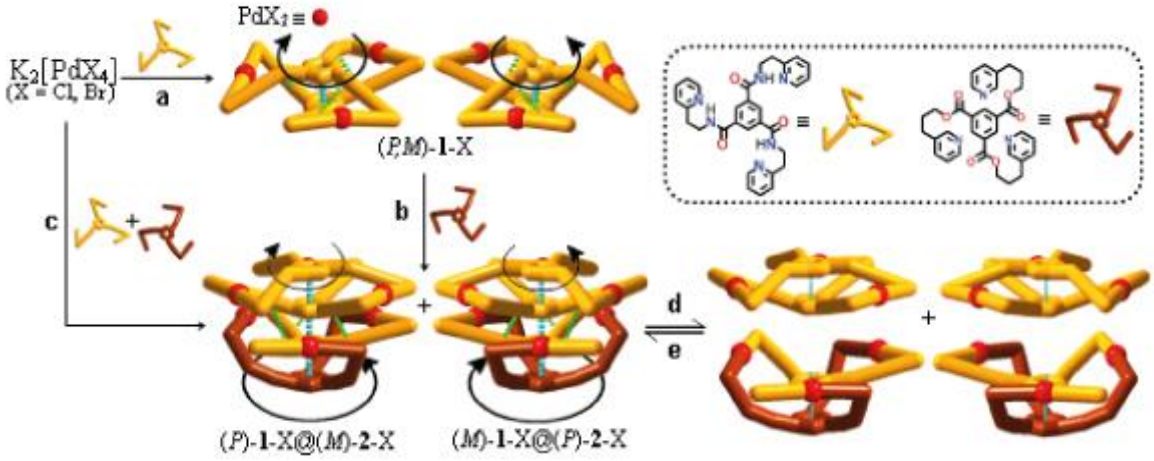
P-225

Molecular host-guest system of conglomerate helical metallacyclophanes

Ms. Haeri Lee[1]
[1]*Pusan National University, Busan, South Korea*

Poster Session 1

We employed a self-assembly approach that incorporates the three methods described above to construct racemic helical metallacyclophanes, (P,M)-[Pd3X6(L1)2], by the reaction of K2[PdX4] (X=Cl, Br) with the C3-symmetric tridentate ligand L1 as a programmed discrete helical component. A subsequent partial substitution reaction of (P,M)-[Pd3X6(L1)2] with another C3-symmetric tridentate ligand L2, or direct self-assembly of K2[PdX4] with both L1 and L2, produced unprecedented conglomerate crystals forming a ball-joint-type host–guest system, (P)-[Pd3X6(L1)2]@(M)-[Pd3X6(L1)(L2)] and (M)-[Pd3X6(L1)2]@(P)-[Pd3X6(L1)(L2)] (X=Cl, Br; L1=N,N¡¯,N¡¯¡¯-tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide[1]; L2=N,N¡¯,N¡¯¡¯-tris-(3-pyridinylpropyl)-1,3,5-benzenetricarboxylate; P=right-handed helix; M=left-handed helix). The synthesis of this host– guest system is an effective method for obtaining useful aggregates. Herein, we present a very effective strategy for the synthesis of such a system. Its crystal structures, the driving aggregative force behind it, and the reversible equilibrium between the aggregate and its dissociated species in solution are also discussed. Furthermore, the catalytic activities for the C-C coupling reaction under mild conditions were investigated.



P-320

Phosphite-thioether ligands for asymmetric Ir-catalyzed hydrogenation of minimally functionalized olefins

Ms Carlota Borràs[1], Dr Oscar Pàmies[1], Prof Montserrat Diéguez[1]
[1]*Universitat Rovira i Virgili, Tarragona, Spain*

Poster Session 1

Because of its high efficiency, atom economy and operational simplicity, the metal-catalyzed asymmetric hydrogenation using molecular hydrogen of properly selected prochiral olefins can be a sustainable and direct synthetic tool for preparing enantiopure compounds. The asymmetric hydrogenation of minimally functionalized olefins is less developed than asymmetric Rh-catalyzed hydrogenation because they have no adjacent polar group to direct the reaction.1 Iridium complexes with chiral P,N-ligands have become one of the most efficient catalyst for the hydrogenation of minimally functionalized olefins. However, another new class of non-N-donor heterodonor ligands have been successfully applied in this reaction such P,O-ligands2 and P-S-ligand3. By introducing a thioether moiety in the ligand design: (i) the S atom becomes stereogenic center when coordinated to the metal, which moves the chirality closer to the metal, and (ii) the thioether group is more stable than the oxazoline moiety.
Here, we show a successful application of thioether-phosphite ligands, in the reduction of unfunctionalized olefins.
Excellent enantioselectivities (ee's up to 99%) have been obtained for a wide range of substrates, including challenging terminal disubstituted substrates, under standard conditions.

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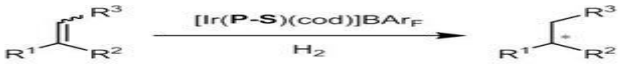

Scheme 1. Ir-catalyzed asymmetric hydrogenation of unfunctionalized olefins

P-226

Pd(0)-Catalyzed Enantioselective Synthesis α-Alkynyl and Azido Ketones

Ms. Maria Victoria Vita[1]
[1]*Epfl, ,*

Poster Session 1

The asymmetric synthesis of α-functionalized ketones represent one of the most used strategy to increase complexity in organic molecules. In particular the decoration of the alpha position of a carbonyl with versatile functionalities such as alkynyl and azido group is highly desirable. However, due to the inherent nucleophilicity of both alkynes and azides, methods based on the umpolung of the reactivity had to be developed for these transformations. We present herein our unified approach to access them by an electrophilic alkynylation/azidation-enantioselective palladium-catalyzed allylic decarboxylation sequence. Our catalytic system is based on a palladium catalyst bearing chiral biphosphine ligands developed by Trost and co-workers. The required racemic starting materials were easily synthetized by the α-alkynylation/α-azidation of allyl β-keto esters using cyclic hypervalent iodine reagents (ethynyl- or azido- benziodoxol (on)e). The products obtained were demonstrated to be versatile building blocks for the synthesis of fused or spiro polycyclic ring systems based on metal-catalyzed cycloisomerization reactions and ring-closing metathesis.

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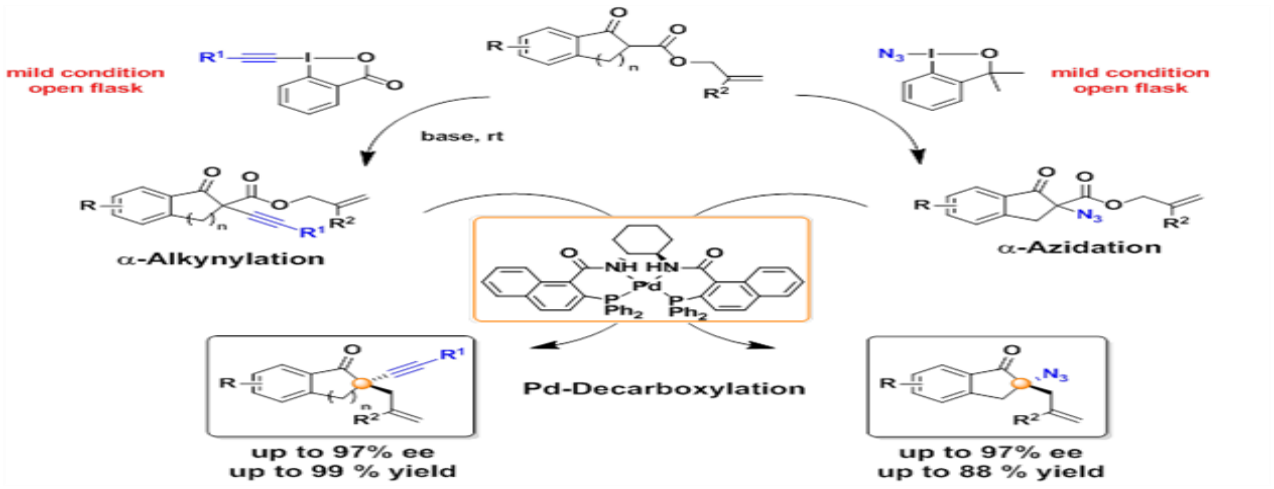

P-227

Oxidant-Free Au(I)-Catalyzed Halide Exchange and Ar-O Bond Forming Reactions

Jordi Serra, Christopher J. Whiteoak, Ferran Acuña-Parés, Marc Font, Josep-Maria Luis, Julio Lloret-Fillol, Xavi Ribas

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Poster Session 1

Homogeneous Au catalysis in cross-coupling transformation has attracted much attention lately owing to its π Lewis acid character to activate insaturations,[1] or based on its Au(I)/Au(III) redox properties. As a result of the high oxidation potential of the Au(I)/Au(III) couple,[2] usually a harsh external oxidant is used to bring Au(I) into Au(III) species,[3] which undergo further reactivity including 2 electron reductive elimination steps. In this study, we present an unusual external oxidant-free Au(I)-catalyzed exchange (including the challenging fluorination) and Ar-O bond forming reactions within a family of model aryl halide macrocyclic substrates. Catalyst requirements include a strong binding ligand to avoid Au(I) decomposition into colloidal Au(0), with enhanced catalytic properties for N-heterocyclic carbenes compared to phosphine based ligands. Of potential interest, the halide exchange and Ar-O coupling reactivity could be also transferred from our macrocyclic aryl halide model substrates to more useful compounds bearing only one directing group, providing some hints on the reaction mechanism.

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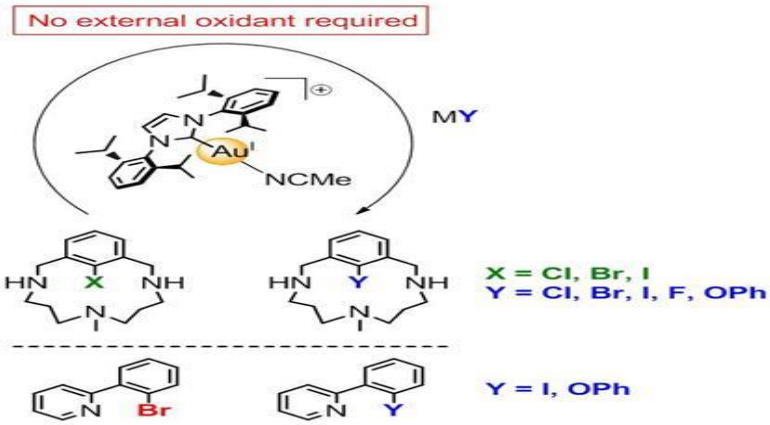


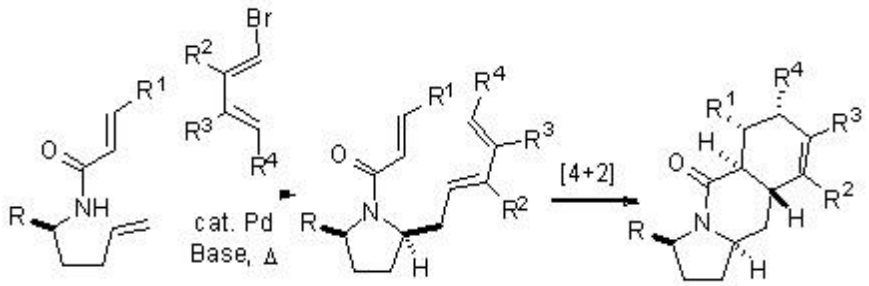
P-295

Pd-catalyzed Alkene Difunctionalization Reactions for the Synthesis of Nitrogen Heterocycles and Functionalized Indanes

D. R. White[1], Prof. J. P. Wolfe[1]
[1]*University of Michigan, Ann Arbor, USA*

Poster Session 1

Our group has shown that in the presence of a palladium-phosphine catalyst, a number of heterocyclic architectures can be synthesized via carboamination reactions. Simple starting materials consisting of a nucleophile tethered to a pendant alkene and an alkenyl or aryl halide allows a library of compounds to be synthesized through simple variation of the electrophile. To this end, we wondered if a cascade process could be exploited by coupling the Pd-catalyzed carboamination reaction with a Diels-Alder cyclization for the rapid formation of polycyclic heterocycles with a high degree of stereocontrol. Strategic placement of an additional pendent alkene on the nucleophile and reaction with aromatic or linear bromodienes successfully afforded polycyclic heterocycles in a one-pot sequence. In general, we were able to achieve moderate to good yields (30-77%) with up to >20:1 diastereoselectivity. This methodology successfully generates 4 bonds, 3 rings, and 3-5 stereocenters depending on the substitution of the diene and dienophile. In addition to the cascade process, new reaction development has led to the discovery of an efficient and stereoselective route to the synthesis of functionalized indanes. This work provides a complementary method to accessing stereo-defined indanes but through the use of palladium alkene difunctionalization reaction of a triflate appended to a pendant alkene and an exogenous nucleophile (N, O, and C nucleophiles). The intermolecular process allows a wide scope through variation of the exogenous nucleophile. So far, we have been able to achieve excellent yields with a number of nucleophiles (up to >95% yield) and exceptional asymmetric induction (up to 96% ee).



P-228

Self-assembled coordination complexes incorporating the ligand tetrathiafulvalene-pyridine

Prof xunwen xiao, Prof Jianghua Fang
[1]*Ningbo University of Technology, Ningbo, China*

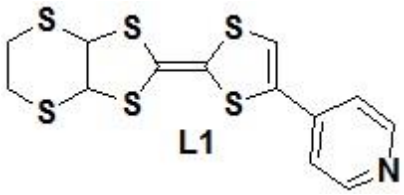
Poster Session 1

Crystal engineering of supramolecular architectures formed by metal-ion directed self-assembly have attracted attention, especially on the electrical conducting nano/micro crystals, since they can be utilized as electrical wires and molecular modules in the next-generation flexible organic nanoelectronics. As a famous donor molecule, tetrahiafulvalene is a π-conjugated system that has been exploited as electrically conducting materials. And we reported EDT-TTF-4-py, L1, could form microstructures by the coordinative self-assembly method. Here, we reported some coordination complexes based on the L1.

a. When we used the ligands as ZnX2 and L1, we obtained new coordination complexes formulated as (L1)2•ZnX2 due to the remarkable coordinating properties of the ligand L1 to the Zn2+ ion. The crystal structures of the TTF coordination hybrids are found to be dependent on the halide of ZnX2. Unexpectedly, the neutral hybrid (L1)2•ZnBr2•CH2Cl2 showed a high conductivity at room temperature whereas the (L1)2•ZnCl2 is an insulator. The □''-type stacking motif and abundant short S…S contact result the complex 2 is highly conductive at room temperature and show semiconducting behavior.

b. Taking advantage of the ability of L1 to coordinate transition metals, we prepared two coordination complexes formulated as (L1)2M(hfac)2 (M = Cu2+ 3, Mn2+ 4), The magnetic measurement revealed a very weak antiferromagnetic interaction between the d spins of M(hfac)2 ion in the microcrystal of 3 and 4.

The results indicate that coordinative self-assembly method is an easy procedure to implement, to afford micro- or nanometer-sized materials.



L1

P-229

Direct Transformation of Benzylic Alcohols via Palladium Catalysis in the Absence of Bases

Dr. Zhi-Chao Cao[1], Prof. Zhang-Jie Shi[1]
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Poster Session 1

The cross-coupling reaction has been a powerful tool to furnish C-C and C-X bonds since 1970s. However, the use of irritative organohalides and their equivalents in conventional cross-couplings limits their practical applications. In recent decades, C-O electrophiles have emerged as powerful and environmentally benign alternatives in the area of cross-coupling reactions, various kinds of phenol and alcohol derivatives, such as carbonates, carboxylates and ethers, have been successfully used in the C-C and C-X bonds formation. Despite the recent great progress, direct catalytic transformation of alcohols to furnish various products are still appealed. Herein, we report a reliable and straightforward method to transform benzylic alcohols to diarylmethanes and organoboron compounds via Pd catalysis under mild conditions. This methodology was featured as high functional group tolerance, broad substrate scope and simple conditions.

P-230

A tandem 3-cr approach for the synthesis of highly functional carbamates from CO2

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Poster Session 1

The use of (bio)renewable reagents and precursors in organic synthesis is currently of crucial importance to increase the sustainability of chemical synthesis.1 In this regard, carbon dioxide (CO2) has emerged as an interesting example of an alternative carbon feed stock that can help to (partially) phase out the use of fossil fuel based synthesis. However, powerful catalytic strategies are warranted for CO2 conversion as it represents a highly stable entity. Our group has previously reported on Al(III) aminotriphenolate complexes showing excellent catalytic activity for the formation of cyclic organic carbonates from CO2 and oxiranes/oxetanes with ample scope.2 Here we present a highly efficient catalytic synthesis of hydroxy-carbamates from CO2 based on a Al(III) aminotriphenolate catalyzed one-pot 3-CR between a cyclic ether, an amine and CO2. The in situ formation of a range of cyclic carbonate intermediates allows for subsequent aminolysis giving rise to the carbamate target. The scope of the reaction involves the use of challenging internal epoxides and oxetanes, and allows for the isolation of highly functional carbamates in good selectivity and yields. The method allows for the presence of various functional groups that permit the post-modification of these versatile synthons, as illustrated by the synthesis of Carisoprodol, a drug known as a muscle relaxant (Scheme 1).

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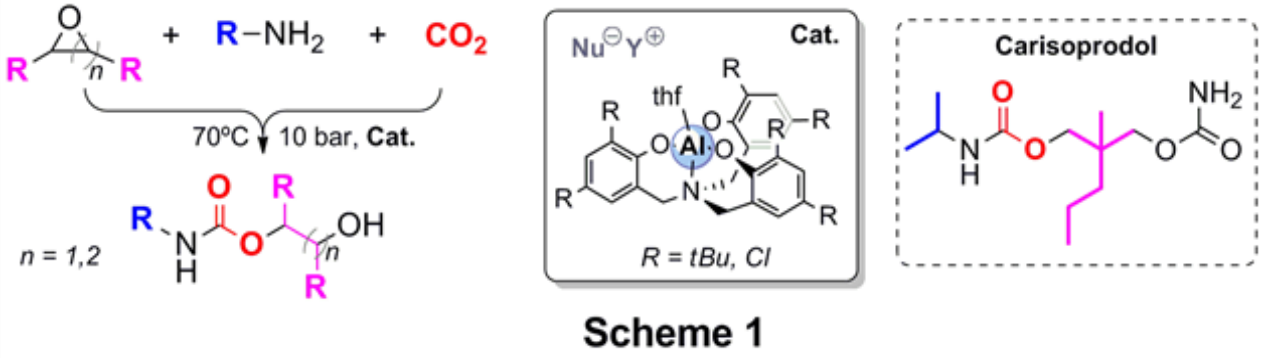

Scheme 1

P-231

Behaviour of Well-Defined Cu(III)-Aryl Complexes in Presence of Carbon Dioxide

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Poster Session 1

The amount of waste produced by our modern society, in particular small molecule gases, is continuously increasing and represents a major issue that we have to face. One solution is to re-use these molecules as reagents and to incorporate them in new valuable organic molecules. Among them, CO_2, a by-product of fuel combustion and commonly regarded as mainly responsible for the greenhouse effect,[1] could be considered as a source of C1-synthons. In this regard, the involving of some transition metal complexes has already been reported to achieve such incorporation.[2] For example, palladium(II)-aryl organometallic complexes have been shown to insert CO_2 in the carboxylation of aryl bromides.[2]

Thus, based on the background of our group on well-defined Cu(III)-aryl complexes,[3] we will report here our preliminary results concerning the behaviour of these complexes in presence of CO_2. Experiments regarding a putative interaction with CO_2 as well as the possibility to form phenylcarbamates will be discussed.

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P-232

REGIO- AND STEREOSELECTIVE DIMERIZATION OF TERMINAL ALKYNES IN THE PRESENCE OF ACTIVATED PEPPSI-TYPE PALLADIUM COMPLEXES

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Poster Session 1

Dimerization of terminal alkynes is a practical and atom-economic approach toward conjugated enynes, important building blocks which has applications in synthetic organic chemistry, materials science, and medicinal chemistry [1]. Recently, many examples processes carried out in the presence of transition metal complexes have been described [2]. However, the highly selective synthesis of conjugated enynes by dimerization is still a challenging process. Depending on the type of catalyst and the nature of substituent at the triple bond, the reaction may produce different products, or a mixture thereof.
The objective of the research described here was to find the optimal conditions of the regio- and stereoselective dimerization of terminal acetylenes (Scheme 1) in the presence of commercially available (PEPPSI)-type palladium precatalysts. A number of chemical activators has been tested to find optimum catalytic activity. Highly regio- and stereoselective procedures of the synthesis of conjugated enynes have been developed by using KOtBu, TBAF, K2CO3, Cs2CO3 as co-catalysts. New conjugated enynes were isolated and characterized. Mechanism of activation of PEPPSI type precursor with TBAF has been studied in more detail. Moreover, mechanism of acetylene dimerization has been discussed on the basis of literature reports and our findings. Financial support from the National Science Centre (Poland), (UMO-2013/11/N/ST5/01612) is gratefully acknowledged.

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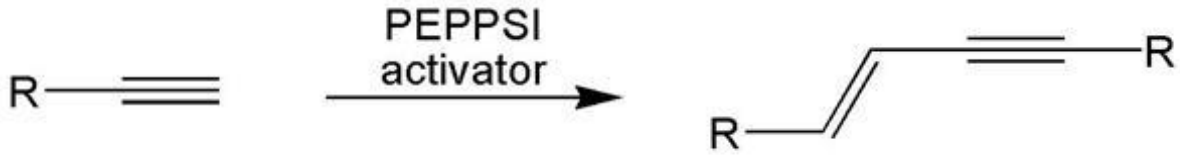

R = C_6H_5, C_6H_4Me-4, C_6H_4Me-2, C_6H_4OMe-4, $C_6H_3(OMe)_2$-2,4, 1-naphthyl, $SiEt_3$

P-233

Rh(I)-Catalyzed Novel Ring-Closing Reaction of Allene-Alkynes

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Poster Session 1

The transition-metal-catalyzed ring-closing reactions provide a powerful step- and atom-economical methodology for the construction of various polycyclic compounds. We have recently reported the novel method for the construction of the bicyclo[m.4.0](m=5,6,7) skeletons based on the Rh(I)-catalyzed intramolecular cycloaddition of the alkyne-allenylcycloalkane (cyclopropane, cyclobutane, cyclopentane).[1] In these reactions, the plausible rhodabicyclo[4.3.0] intermediate might be formed, which would subsequently assist the C-C cleavage of inactive cyclobutane or cyclopentane. We now developed another type of ring-closing reaction of the benzylallene-alkynes 1 and allene-alkyne-alkenes 3 (Figure 1).

1. Rh(I)-catalyzed cycloisomerization of benzylallene-alkynes[2]
The efficient Rh(I)-catalyzed cycloisomerization of benzylallene-alkynes 1 produced the tricyclo[9.4.0.0^{3},^{8}]pentadecapentaene skeleton 2 through a Csp^{2}-H bond activation in good yields. It was proposed based on deuteration and competition experiments that the reaction would involve the consecutive oxidative addition of the acetylenic C-H bond to Rh(I), an ene-type cyclization to the vinylidenecarbene–Rh intermediate, and an electrophilic aromatic substitution with the vinylidenecarbene species.

2. Rh(I)-catalyzed intramolecular [2+2+2] cycloaddition of allene-alkyne-alkenes[3]
Treatment of the allene-alkyne-alkenes 3 with $[RhCl(CO)_2]_2$ effected the intramolecular [2+2+2] type ring-closing reaction to produce various tri- and tetracyclic derivatives 4 containing a cyclopropane ring. The reaction is highly stereoselective as well as stereospecific with good to excellent yields.

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1. Rh^{I}-catalyzed cycloisomerization of benzylallene-alkynes **1**[2]

2. Rh^{I}-catalyzed intramolecular [2+2+2] cycloaddition of allene-alkyne-alkenes **3**

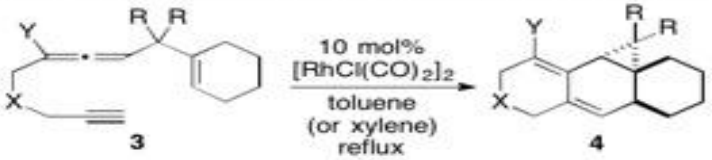

Figure 1. Rh(I)-catalyzed ring-closing reaction of allene-alkynes.

P-234

Straightforward Synthesis of HOMSi Reagents by C–H Silylation with Hydrosilanes

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Poster Session 1

Catalytic transformation of a C–H bond to a new C–C bond has presently drawn much attention in view of atom-economy and step economy. However, such reaction requires the presence of a directing group commonly. On the other hand, direct C–H borylation[1] and silylation[2] takes place regioselectively at various arenes without such a directing group. We have disclosed that R-(2-HydrOxyMethyl)phenyldimethylSilane (R-HOMSi) reagents are conveniently used for the cross-coupling reaction and the silicon residue is readily recovered and reconverted to R-HOMSi or H-HOMSi.[3] Herein, we report the straightforward synthesis of R-HOMSi by the Ir-catalyzed C–H silylation of arenes and alkenes with H-HOMSi. For example, benzothiophene reacts with THP-protected H-HOMSi in the presence of $[Ir(OMe)cod]_2$, Me_4phen (3,4,7,8-tetramethyl-1,10-phenathroline), and norbornene as a hydrogen acceptor in $(i\text{-}Pr)_2O$ to give THP-protected benzothienyl-HOMSi reagent in 89% yield. Various heteroarenes and terminal alkenes are applied to this silylation to give the corresponding heteroaryl-HOMSi and (E)-alkenyl-HOMSi reagents.

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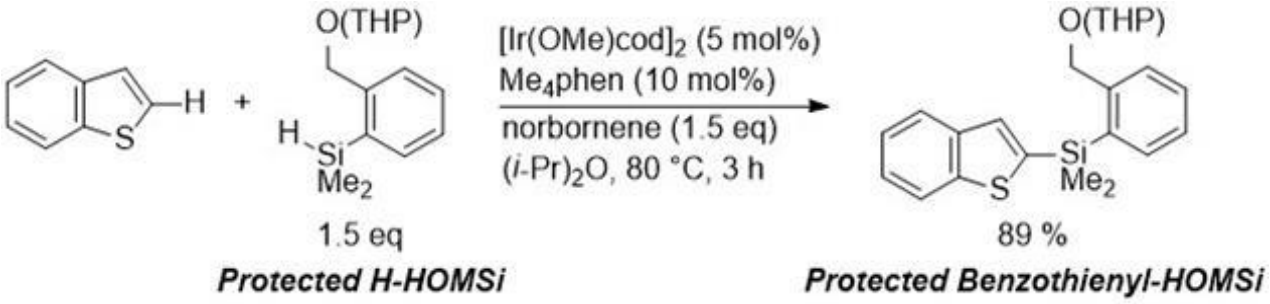

P-318

Palladium-catalyzed Direct Arylation of Arenes Using Aryl sulfides

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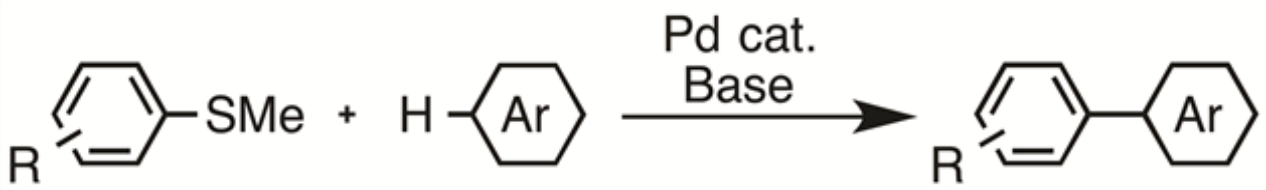
Poster Session 1

Aryl sulfides are an important class of organosulfur compounds. Thus, coupling reactions using aryl sulfides as electrophiles are receiving attentions. However, catalytic reactions of organosulfur compounds are difficult due to catalyst poisoning. Even though Wang reported a catalytic C–H direct arylation of azoles with aryl sulfides very recently, the scope is limited. We have developed palladium-catalyzed direct arylation of polyfluoroarenes or heteroarenes using aryl sulfides as electrophiles. Our success lies in the employment of a palladium-NHC complex as a catalyst and zinc amide as a base. This reaction can be applied to varieties of arenes and aryl sulfides in high yields. When this reaction is combined with specific reactions of organosulfur compounds, such as an SNAr reaction or extended Pummerer reactions, we have invented several new transformations.



P-235

Direct detection of aryl-Cu(III)-L intermediate species in Ullmann-type arylation of O- and N-nucleophiles

Marta Soler[1], Imma Güell[1], Mireia Rovira[1], Ferran Acuña-Parés[1], Ming-Zheng Wang[1], Marc Font[1], Alicia Casitas[1], Julio Lloret-Fillol[1,3], Josep M Luis[1], Laura Gómez[1], Erik Andris[2], Jana Roithová[2], Xavi Ribas[1]

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Poster Session 1

The mechanistic understanding of copper-catalyzed Ullmann-type cross coupling reactions has been under discussion, especially during the past decade.[sup]1,2[/sup] One main proposal relies on a two-electron redox mechanism involving a Cu(I)/Cu(III) catalytic cycle.[3] Additionally, the synthesis of well-defined, stable and soluble Cu(I) complexes has also been used as a proof of their utility as efficient catalysts in copper-catalyzed C-heteroatom bond formation reactions.[sup]4,5[/sup] Therefore, the nature and concentration of the auxiliary ligand used in Ullmann-type condensation reactions have a big impact in the equilibrium between different Cu(I) complexes present in solution as well as in the formation of the active catalysts.[6] Finding inspiration on the macrocyclic model systems that can stabilize the aryl-Cu(III)-X species,[7] we have used a newly designed tridentate auxiliary ligand to perform mild arylation of phenols, amines and amides using different iodobenzene derivatives. Remarkably, the key aryl-Cu(III) intermediate species [(Pyr(NHMe)(NMe))Cu(III)-(aryl)]+ have been trapped by cryospray high-resolution mass-spectrometry (cryospray-HRMS). The exact mass of the trapped intermediates ensures their correct identification and the time-dependent peak intensity nicely correlates with the yield of the cross coupling catalysis. The results clearly point out that the Cu(I)/Cu(III) mechanism can be favored by a proper design of the auxiliary ligand used.

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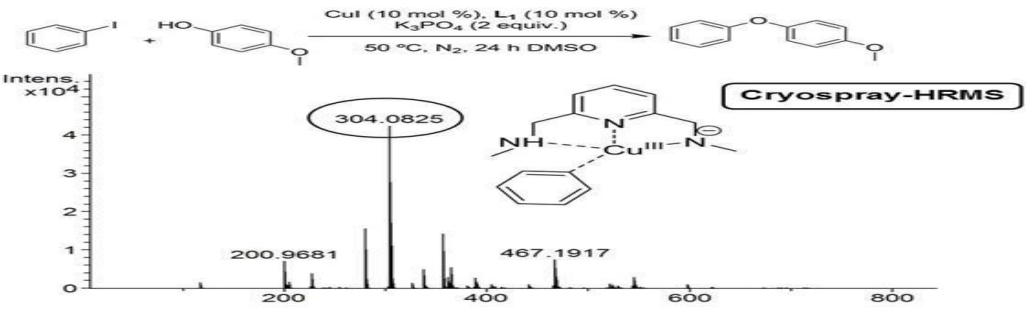
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Cryospray-HRMS
Intens.
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304.0825
200.9681
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NH
Cu^III
N
0
1
2
3
4
200
400
600
800

P-236

Homo and Heteroleptic Trinuclear Cylinder-like Assemblies Based on Tris-Mesoionic and Tris-N-Heterocylic carbene ligands with AgI, AuI

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Poster Session 1

The development of self-assembly architectures with very small cavities has become a very intense field of research, due to their ability of hosting molecules and unique optical, sensing and catalytic properties.[1]
A new generation of ready available homoleptic self-assemblies based on N-heterocyclic carbenes (NHC) ligands of AgI, AuI and CuI have only very recently emerged.[2] Heteroleptic NHCs and triazolylidene (MICs) metal complexes can be prepared via ligand dissociation. Acid or metal-initiated ligand migration have generated species that can serve as latent catalysts activated selectively, or they could be used for drug delivery.[3] Therefore, the design of new latent catalysts derived from self-assemblies is highly desirable. Herein, the synthesis of the first homo and heteroleptic cylinder-like assemblies based on tris-MIC and tris-NHC bridged ligands with AgI (Figure 1) and AuI obtained by ligand transfer and preliminary catalytic studies will be described.

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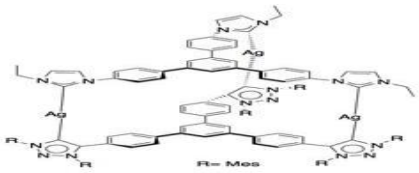

Figure 1

P-237

Postmodification of the Electronic Properties by Addition of π-Stacking Additives in NHC Complexes with Extended Polyaromatic Systems

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Poster Session 1

The use of N-heterocyclic carbene (NHC) ligands with extended polyaromatic systems has given rise to families of metal complexes whose electronic properties are influenced by π-stacking additives. In this sense, we recently proved that the presence of a π-stacking additive such as pyrene, had an important influence in both catalytic performance and electronic properties of a series of polyaromatic-based NHC complexes.[1,2] For these reasons, we decided to prepare higher extended aromatic NHC-based ligands, which may help us undergo a detailed study in the influence of π-stacking interactions on their donor properties. Figure 1 depicts the synthesis of the three carbonyl complexes under study (5, 6 and 7). We observed that their CO IR-stretching frequencies decrease or increase depending on the addition of pyrene or hexafluorobenzene, respectively. Hence, the electronic nature of these NHCs with the polyaromatic backbones can be fine-tuned by the addition of the suitable additive. To shed light to these results, the interaction between the additives and the NHC ligands was studied by DFT calculations and [1]H NMR.

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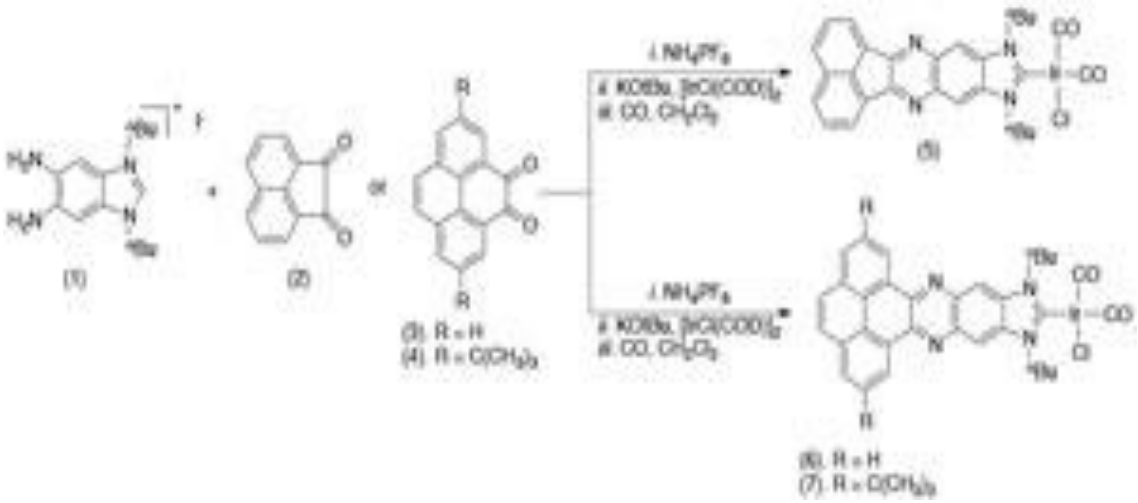
We gratefully acknowledge financial support from MEC of Spain (CTQ2011-24055/BQU) and UJI (P1.1B2011-22). We also would like to thank the Santiago Grisolía (H.V.) and Ramón y Cajal (M.P.) programs.



P-238

Rhodium-Catalyzed Oxygenative [2 + 2] Cycloaddition of Terminal Alkynes and Imines for the Synthesis of β−Lactams

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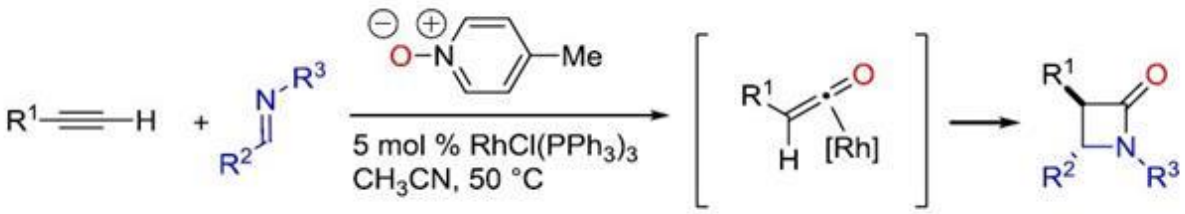
Poster Session 1

Transition metal vinylidene complexes exhibit interesting reactivities due to the electrophilic nature of the α-carbon and have been used as catalytic intermediates in a variety of reactions of terminal alkynes. We recently described a rhodium-catalyzed oxygenative addition reaction that furnishes carboxylic acid derivatives from terminal alkynes and various nucleophiles. In continuing efforts to extend the alkyne-to-ketene chemistry, we discovered that the ketene can undergo a Staudinger reaction with imines to give β-lactam products. The new method taking advantage of catalytic generation of a ketene species directly from a terminal alkyne provides a novel and efficient entry to the Staudinger synthesis of β-lactams under mild conditions.



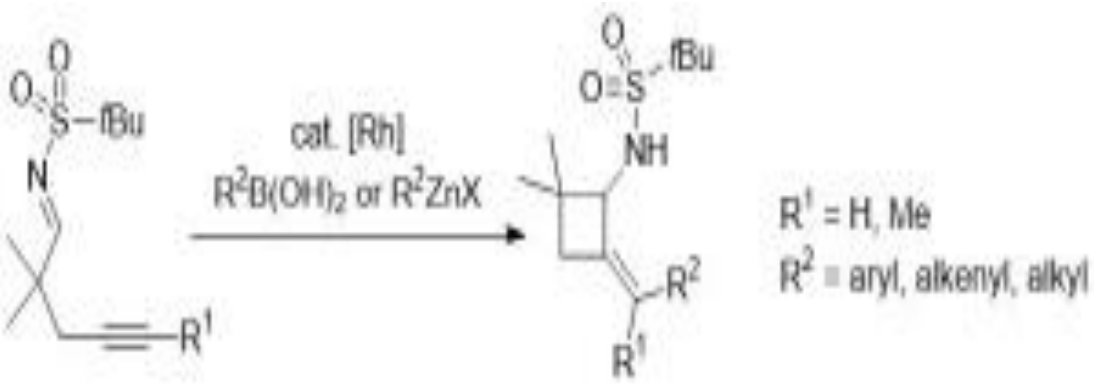
P-239

Rhodium-Catalyzed Tandem Addition–Cyclization of Alkynylimines

Kyoungmin Choi[1], Jung Min Joo[2], Chulbom Lee[1]
[1]*Seoul National University, Seoul, South Korea,* [2]*Pusan National University, Busan, South Korea*

Poster Session 1

In this poster, rhodium-catalyzed tandem addition–cyclization of alkynylimines is described. In this process employing a single rhodium catalyst, alkyne-tethered N-sulfinyl and sulfonylimines react with aryl/alkenylboronic acids and aryl/alkyl zinc reagents to give 2-alkylidene-substituted cyclobutyl and cyclopentyl amine products. The reaction occurs through a tandem sequence involving 1,2-carbometalation of the alkyne and 4- and 5-exo-cyclization of the resulting alkenyl rhodium with the imine. This method allows for the catalytic alkyne addition/cyclization process to include imine substrates, providing expeditious access to complex cyclobutyl and cyclopentyl amines with potential stereocontrol.



P-240

Reactivity of a nickel(II) bis-amide complex with HmCPBA: formation of anickel(IV) oxidizing species

Teresa Corona[1], Florian Felix Pfaff[2], Ferran Acuña-Parés[1], Ray Kallol[2], Anna Company[1]
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Poster Session 1

The study of high-valent nickel complexes in particular and the redox chemistryof nickel in general has attracted the attention of the bioinorganic chemistrycommunity to provide models of nickel-containing enzymes that catalyze redoxprocesses.[1] Moreover, high-valent nickel species have been frequentlypostulated as key reaction intermediates both in the catalytic cycle ofoxidation reactions and in coupling reactions.[2]Focusing in oxidation reactions, there are some nickel(III)-oxygen species whosereactivity has been studied in detail and also they have been characterized bydifferent technics, such as, EPR and UV-vis spectroscopies.[3,4] However, thereare only a few examples of nickel(IV)-oxygen complexes in the literature. Forinstance, theoretical evidence for the formation of a transient[NiIV(OH)(cyclam)]2+ competent to epoxidize olefins has been gathered for thereaction of the corresponding nickel(II) precursor with H2O2 in acidic media.[5]In this field, nickel(III)-oxygen and nickel(IV)-oxygen species are supposed tobe formed after homolytic or heterolytic O-O bond cleavage due to thecoordination of a nickel(II) precursor with the oxidant (HmCPBA, peracetic acid,…).Herein, we report the formation of a highly reactive intermediatenickel(IV)-oxygen/nickel(III)-oxyl species (2) that has been spectroscopicallytrapped by reaction of [NiII(L)] (1) with HmCPBA (Scheme 1). Compound 2 is onlydetectable at low temperatures and it is much more reactive towards organicsubstrates (C-H bonds, C-C double bonds and sulfides) than the previouslyreported well-defined Ni-oxygen species. Remarkably, this species is formed byheterolytic O-O bond cleavage as supported by experimental and computationalmethods.

P-241

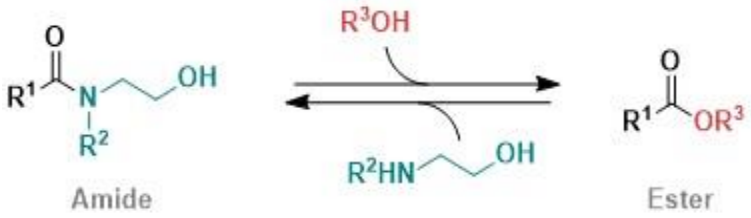
Zinc and Manganese Catalyzed Formation and Cleavage of N-β-hydroxyethylamides

Mr. Yuji Nishii[1], Ms. Sarah Fernandez[2], Ms. Shoko Akiyama[1], Dr. Yusuke Kita[1], Dr. Paul Knochel[2], Dr. Kazushi Mashima[1]

[1]Osaka University, Toyonaka, Japan, [2]Ludwig-Maximilians-Universität, Germany

Poster Session 1

Amides are ubiquitous in nature as well as of vital motifs in various important synthetic molecules. Recently, amides have been used as versatile directing groups for transition metal catalyzed C-H bond functionalization1 and lithium/magnesium mediated C-H functionalization2; however, due to stable amide bond, harsh conditions including strong acids or bases at high temperature were required to cleave the amide bond. Accordingly, it is in high demand to catalytically convert amides into other functional groups under mild conditions. In this context, our interest has been focused on amide alcoholysis because the resulting esters can be easily transformed to various functional groups, and we already reported that the zinc triflate became a catalyst for selective esterification of N-β-hydroxyethylamides via N,O-acyl rearrangement3. In addition, a peptide bond at serine residues was selectively cleaved. Herein, we report that N-β-hydroxyethylamides are used as removal directing groups for C-H functionalization: tertiary N-β-hydroxyethylamides bearing various alkyl- and aryl-substituent on the amide nitrogen atom were readily prepared by the zinc catalyzed N-acylation of aminoalcohols with methyl esters and N-β-hydroxyethylamides upon treated with 1-propanol were easily converted to the corresponding propyl esters under mild conditions.



P-242

Towards the Synthesis of Incednam, the Aglycon of Incednine

Mr Haraldur Gunnar Gudmundsson[1], Dr Diane S. W. Lim[1], Dr Edward A. Anderson[1]
[1]*University of Oxford, Oxford, UK*

Poster Session 1

Efforts towards the total synthesis of incednam (1), the aglycon of incednine (2), is described. Incednine, a bioactive polyketide natural product isolated from a Streptomyces sp. culture broth, has been shown to serve as a potent modulator of the anti-apoptotic oncoproteins Bcl-2 and Bcl-xL overexpressing human lung cancer cells.[1] The synthesis of incednam commenced with the preparation of three key building blocks; the C1-C5 fragment 3, the C6-C13 fragment 4 and the C14-C23 fragment 5. Key to our strategy is the stereocontrol afforded by cyclic vinylsilane 4 which controls the C12-C13 Z-alkene geometry, and incorporates both hydroxyl-bearing stereocenters without the need to protect the allylic alcohol.[2] Construction of the C5-C6 bond has been successfully achieved via the Suzuki-Miyaura cross-coupling reaction between fragments 3 and 4. Separately, the C13-C14 bond has been achieved via the palladium catalysed Hiyama cross-coupling reaction of fragments 4 and 5. We are currently working towards converging both cross-coupling strategies before constructing the 24-membered macrocycle via macrolactamisation.

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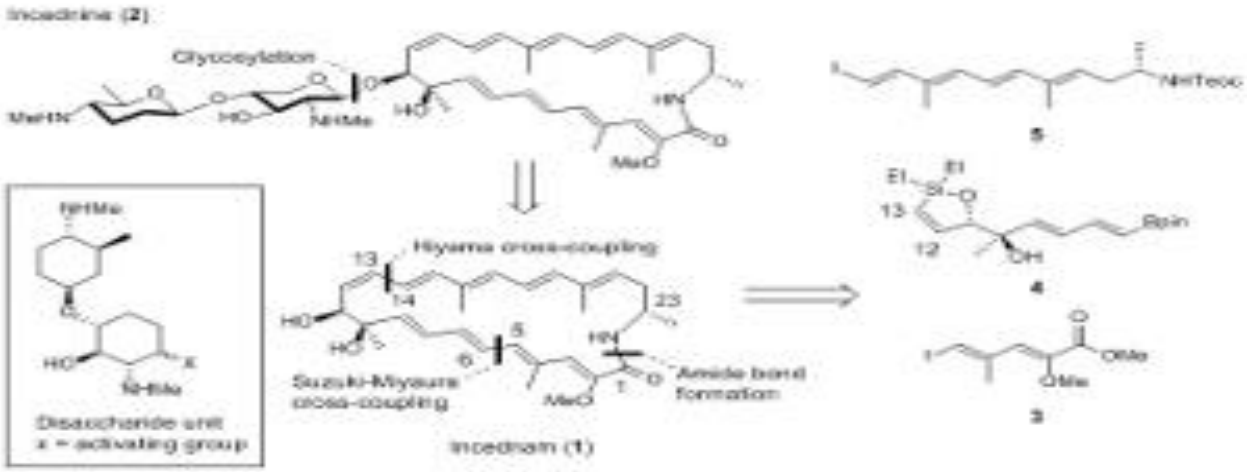

P-243

Salt Formation Strategy for Asymmetric Hydrogenation of N-Heteroaromatic Compounds

Mr. Atsuhiro Iimuro[1], Mr. Kenta Yamaji[1], Mr. Kosuke Higashida[1], Mr. Shoji Hida[1], Dr. Sathaiah Kandula[1], Dr. Yusuke Kita[1], Prof. Kazushi Mashima[1]

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Poster Session 1

Chiral cyclic amines are highly important molecular skeletons abundant in natural alkaloids as well as biologically active compounds. Catalytic asymmetric hydrogenation of N-heteroaromatic compounds has been considered as one of the most straightforward synthetic methods for obtaining chiral cyclic amines; however, due to their aromatic nature, catalytic asymmetric hydrogenation of isoquinolines and pyridines has been regarded as difficult tasks so far. In the course of our investigation, we found that the salt formation of isoquinolines facilitated asymmetric hydrogenation of isoquinolinium salts with high enantioselectivity.[1] This strategy was also applied to asymmetric hydrogenation of pyridinium salts.[2] In these reactions, multi-substituted substrates were smoothly hydrogenated to afford the corresponding chiral cyclic amines with high diastereoselectivity. Based on mechanistic investigations of asymmetric hydrogenation of isoquinolinium salts, we have proposed a conceptually new outer-sphere transition state for hydride attack involving chloride coordination to an iridium center and a hydrogen bond between the chloride ligand and N-H proton of the substrate salt to form a six-membered ring.[3]

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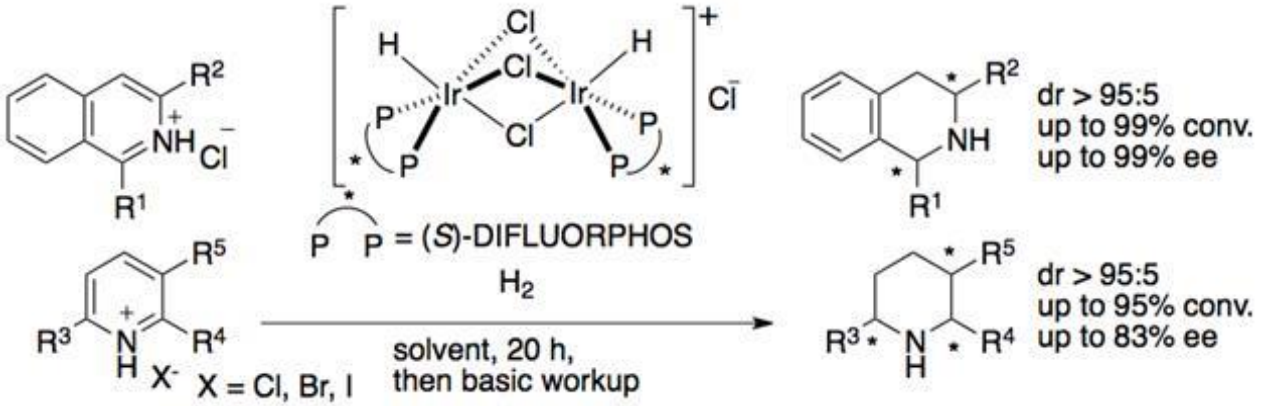

P-244

Effective synthetic protocol for chiral 4-substituted tetrahydroquinazoline by asymmetric hydrogenation

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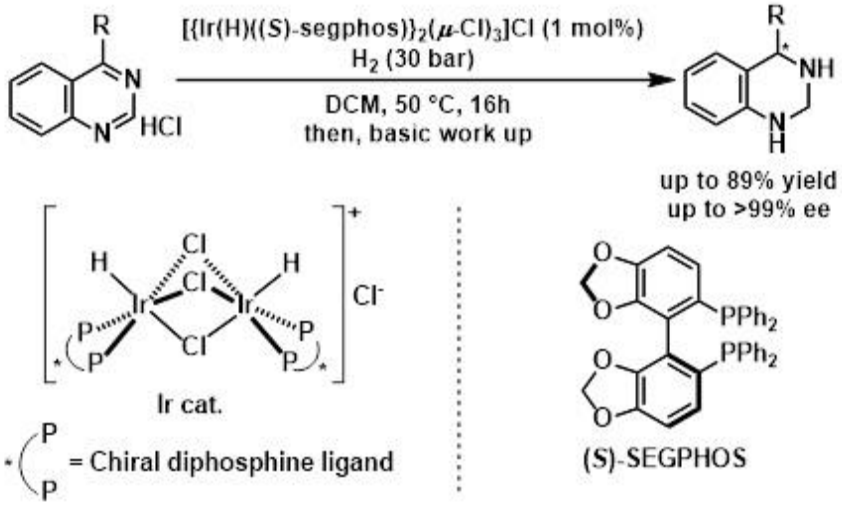
Poster Session 1

Chiral cyclic amines are one of the most abundant skeletons in nature and biologically active compounds, and various synthetic protocols for producing chiral cyclic amines have been developed so far. As our continuous interest in developing an effective synthetic route to prepare these bioactive cyclic amines, we have focused our efforts on asymmetric hydrogenation of substituted N-heteroaromatic compounds since asymmetric hydrogenation is atom economical reaction and suitable reaction for industrial application. Despite its advantageous merits, there are some problems such as the high stability of N-heteroaromatic compounds and the deactivation of the catalysts. We already found that dinuclear halide-bridged iridium complexes bearing chiral diphosphine ligands served as catalysts for the asymmetric hydrogenation of the HCl salts of isoquinolines[1] and pyridines.[2] In this contribution, we report asymmetric hydrogenation of the HCl salt of quinazolines.[3] When 4-phenylquinazolinium chloride was hydrogenated under optimal conditions, the yield and enantiomeric excess of the corresponding product were 89% and 99% ee, whereas the asymmetric hydrogenation of 4-phenylquinazoline produced the product in only 4% yield. Various 4-substituted quinazolinium chlorides were hydrogenated to give the corresponding tetrahydroquinazolines with high yield and excellent enantiomeric excess (Scheme 1).

References: (1) Kita, Y.; Yamaji, K.; Higashida, K.; Sathaiah, K.; Iimuro, A.; Mashima, K. Chem. Eur. J. 2015, 21, 1915. (2) Kita, Y.; Iimuro, A.; Hida, S.; Mashima, K. Chem. Lett. 2014, 43, 284. (3) Kita, Y.; Higashida, K.; Yamaji, K.; Iimuro, A.; Mashima, K. Chem. Commun. 2015, 51, 4380.

Scheme 1. Asymmetric Hydrogenation of Quinazolinium chloride.



P-245

RHODIUM AND IRIDIUM (I) COMPLEXES CONTAINING (N-DONOR-FUNCTIONALISED 1,2,3-TRIAZOL-5-YLIDENE) LIGANDS, SYNTHESIS AND CATALYTIC APPLICATIONS

Mr Ian Strydom[1], Dr. Daniela Bezuidenhout[1], Dr. Gregorio Guisado-Barrios[2], Prof. Eduardo Peris[2]
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Poster Session 1

1,2,3-triazol-5-ylidene ligands have been investigated to a lesser extent than other N-Heterocyclic carbenes ligands, particularly due to their more recent discovery [1]. However, due to their mesoionic nature, they have shown unique catalytic possibilities and potential for ligand cooperativity [2]. Rh and Ir metal complexes with 1,2,3-triazolylidene ligands are rare, and very few donor functionalised complexes have been reported [3]. Herein, the synthesis of a series of novel neutral and cationic N-donor functionalised 1,2,3-triazol-5-ylidene based Rh and Ir (I) complexes (figure 1) along with some preliminary results of their catalytic activity in transfer hydrogenation reactions are reported.

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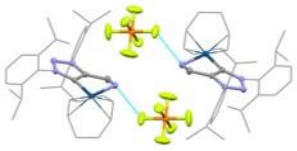

Figure 1: X-ray structure of (N-donor functionalised 1,2,3- triazol-5-ylidene) Ir(I) complex.

P-246

Nickel Catalyzed Insertion of Alkynes and Electron Deficient Olefins into Unactivated sp^3 C–H Bonds

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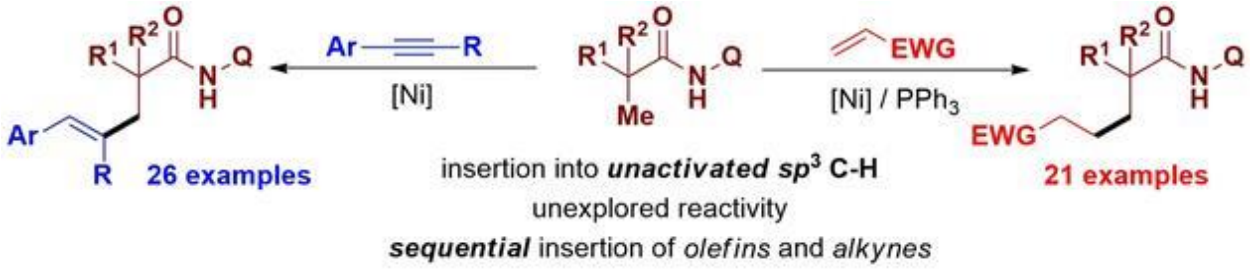
Poster Session 1

Insertion of unsaturated systems such as alkynes and olefins into C-H bonds is one of the most thoroughly studied transformations in transition metal chemistry. Over the last three decades, a wide variety of catalysts based on Rh, Ir, Pd, Ru, Ni, Co, Mn, Fe etc. have been developed for these fundamental C-C bond-forming reactions. However, majority of these transformations have been accomplished through the activation of an aromatic sp^2 C–H bond regardless of the transition metal catalysis. A related reaction with aliphatic C-H bond on the other hand, is much less studied. Only a limited number of reports are available on insertion at sp^3 C–H with activated benzyl, allyl and C–H bonds next to heteroatom at the core of substrate design. Consequently, insertion of alkyne and olefin into unactivated sp^3 C–H bond remained unprecedented in literature. We addressed this fundamental setback of insertion reactions with pivalic acid derivatives as the model system. A strongly chelating directing group, 8-amino quinoline proved beneficial while an air stable and inexpensive nickel salt has been employed as the active catalyst. A number of symmetrical and unsymmetrical alkynes and electron deficient olefins with different functional groups such as -OMe, -F, -Cl, -Br, $-CO_2Me$, $-NO_2$, $-CF_3$ have been included in this study. More interestingly, rational design of substrates helped us to shed light into the electronic dependence of the insertion step. In a few words, this new method represents the first alkyne/olefin insertion at unactivated sp^3 C–H and is expected to inspire related developments in near future.



P-247

Annulation of Alkynyl Aryl Ethers with Bicyclic Alkenes via Palladium-catalyzed ortho-C–H Activation

Graduated Student Tatsuro Kodama[1], Prof. Tamejiro Hiyama[2], Assistant Prof. Yasunori Minami[2]
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Poster Session 1

Transition metal-catalyzed C–H bond functionalization is a useful synthetic transformation in terms of step economy and atom economy. Recently, we have disclosed that the annulation of alkynyl aryl ethers with alkynes proceeds via ortho-C–H activation in the presence of a palladium catalyst to give 6-membered oxacycles.[1a] This method is applied to the intramolecular hydrobenzylation of alkynyl ortho-tolyl ethers and hydroarylation of 2-alkynyloxy biphenyls.[1b.1c]

The important structural factor for the reaction is the alkynyloxy group (–OC≡C–R) that acts as not only a directing group but also a dihydrogen acceptor. Herein we report that the reaction of alkynyl aryl ethers with norbornene (2a) and its analogues takes place in the presence of a zero-valent palladium catalyst to give 2-methylenechromane derivatives through ortho-C–H activation. For example, 4-methoxyphenyl triisopropylsilyl (TIPS)ethynyl ether (1a) reacted with 2a in the presence of Pd(PCy3)2 and Zn in toluene at 120 °C and gave the corresponding exo-cycloadduct 3aa in 51% yield (Eq. 1). Norbornadiene (2b) also underwent the reaction to give the corresponding a 1 : 1 adduct.

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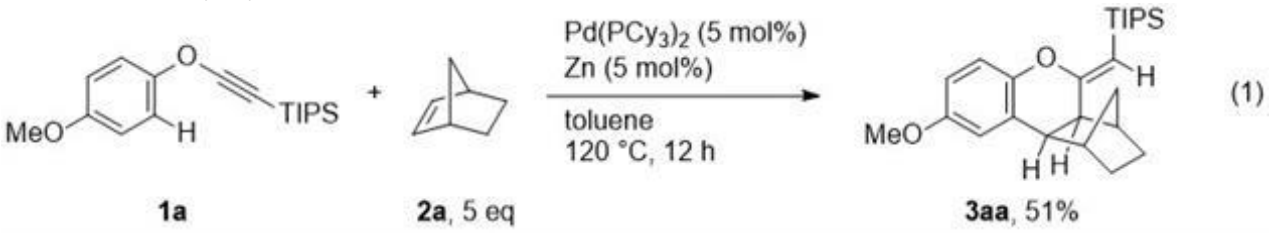

1a **2a**, 5 eq **3aa**, 51%

P-248

DFT study of Cp*Co[sup]III[/sup] catalyzed C-H allylation with allylic alcohols

Dr. Ken Sakata[1,2], Mr. Yudai Suzuki[3], Mr. Bo Sun[3], Dr. Tatsuhiko Yoshino[3,4], Dr. Shigeki Matsunaga[2,3,4], Dr. Motomu Kanai[3]

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Poster Session 1

Transition metal-catalyzed direct C-H bond functionalization has been much attention because of a useful synthetic methodology. We have developed the C-H bond functionalization catalyzed by cationic Cp*Co(III) complexes, and demonstrated a unique synthetic utility of a Cp*Co(III) catalyst in comparison with related Cp*Rh(III) catalysts (J. Am. Chem. Soc. 2014, 136, 5424). Recently, we have found that a cationic Cp*Co(III)-catalyst promoted dehydrative direct C-H allylation of indoles with allyl alcohol. Experimental results showed the C2 selectivity and γ-selectivity, which indicated that the reaction proceeded via directing group-assisted C-H metalation rather than Friedel-Crafts-type pathway via either an allylic cationic intermediate or a π-allyl metal intermediate. To clarify the reaction mechanism of the catalytic reaction system, we performed B3LYP-D3//B3LYP level DFT calculations for the model reaction between N-pyrimidin-2-yl indole and allyl alcohol catalyzed by [CpCo(III)(OAc)]+.

The reaction is initiated by the C-H bond metalation. In our previous study, we proposed that the C-H bond metalation proceeds via concerted metalation-deprotonation (CMD) assisted by the acetate ion. Next, the Co-C bond inserts to the C=C bond in allyl alcohol. The calculations showed that the Co-C bond insertion is more favorable in comparison with the SN2' substitution. Then, the β-hydroxide elimination occurs. We found that the β-hydroxide elimination is more favorable to the β-hydride elimination. The difference in reactivities between CpCo(III) complex and related CpRh(III) complex is discussed.

P-249

Synthesis and applications of spin-labelled DNA

Mr Marius M. Haugland[1], Dr Afaf H. El-Sagheer[1], Dr Janet E. Lovett[2], Prof Tom Brown[1], Dr Edward A. Anderson[1]

[1]*University of Oxford, Oxford, UK* , [2]*University of St Andrews, St Andrews, UK*

Poster Session 1

Spin labelling has recently emerged as an increasingly important method for studying biomolecules such as proteins, saccharides and nucleic acids.[1] This technique relies on using electron paramagnetic resonance (EPR) spectroscopy to investigate paramagnetic 'spin' labels which have been incorporated in a site-specific fashion into biomolecules.

In order to obtain accurate and reliable EPR data, it is crucial to construct highly rigid labelled systems. This can easily be achieved using the well-known Cu(I) catalysed azide-alkyne [3+2] cycloaddition ('click' reaction)[2], which has enjoyed high popularity as a tool for labelling biomolecules. Late-stage divergence in choice of label, as well as the rigidity of the resulting triazole moiety makes 'click' chemistry particularly suitable for spin labelling. This prompted the utilisation of 2'-ethynyl-2'-deoxynucleoside derivatives 1–3 as reporter groups for spin labelling of DNA.

Alkynyl nucleosides 1–3 were incorporated into terminal and internal positions of DNA strands by automated oligonucleotide synthesis, and spin labels were installed in a site-specific manner via 'click' reaction with azide nitroxyl radicals such as 4. 'Click' functionalization of these C-branched nucleosides incorporates the shortest possible linker, maintaining the lowest possible number of flexible, rotatable bonds between the nucleoside, triazole and spin label. It was necessary to avoid the use of ascorbic acid for in situ generation of catalytic Cu(I), as this reagent also reduces nitroxyl radicals to the corresponding hydroxylamines.

The spin-labelled DNA strands were investigated by EPR spectroscopy. After forming doubly labelled duplexes, distances were measured by the double electron-electron resonance (DEER) experiment and found to be in proximity to computational values.

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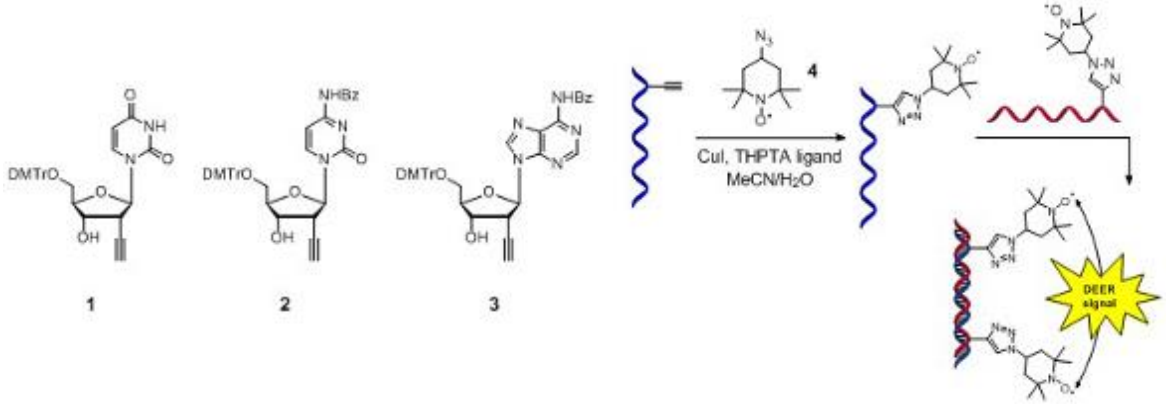
DMTrO
OH
NHBz
1
2
3
4
CuI, THPTA ligand
MeCN/H2O
DEER
signal

P-250

Theoretical Study on the Thiocyanide Formation of 3-mercaptopyruvate Metal Complexes

Prof. Jen-Shiang K. Yu[1], Mr. Tung-Lin Wu[1]
[1]*National Chiao Tung University, Hsinchu City, Taiwan*

Poster Session 1

In this study, computational design of efficient detoxification metal drugs to rescue for the cyanide poisoning by molecular simulation is attempted. Two molecules of 3-mercaptopyruvate (3-MP) are expected to chelate one metallic divalent cationic center (M[sup]2+[/sup], M= Cu and Zn) to form stable four-coordinate complexes. Geometry optimization of the model complex (1), bis[2-(2-thienyl)-glyoxylato-O,O'] copper(II), is performed using various density functionals including BP86, B3LYP, TPSS, and PBE. The structure of (1) may be further reduced into (2) and optimized at identical levels. The geometries of the ligand coordinations remain almost identical compared to the structure of 3-MP calculated at high level CCSD theory. Transition state (TS) of (2) in the reaction of cyanide detoxification process is proposed; in this TS, the thiol group (-SH) tends to shift to cyanide and produce the thiocyanic acid. Subsequently, the thiocyanic acid approaches the oxygen atom of the carboxyl group and transfers the proton to oxygen, forming thiocyanide which is less toxic and can be metabolized easily in urea. Energy profile of the dithiolation reaction is also constructed.

References:
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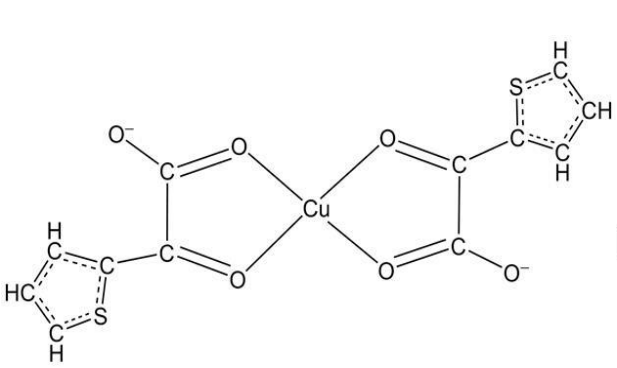
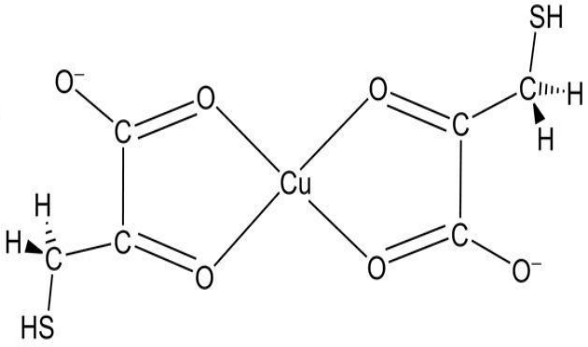


(1)



(2)

P-251

Asymmetric Synthesis and Thermal Rearrangement of Imino-substituted Spiropentanes

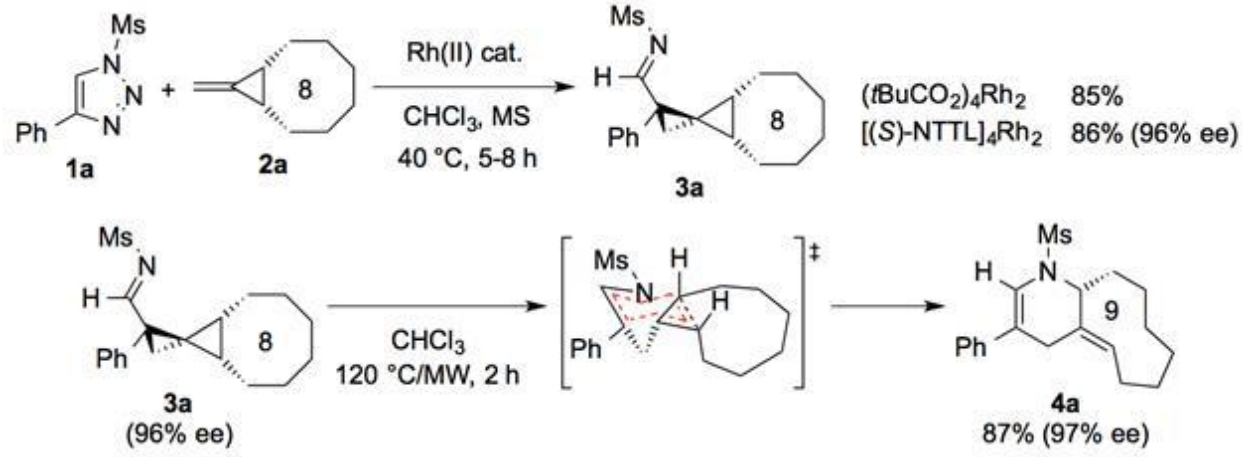
Student Takayuki Nakamuro[1], Associate Prof. Tomoya Miura[1], Prof. Masahiro Murakami[1]
[1]*Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, kyoto/katsura, Japan*

Poster Session 1

Medium-sized cyclic trans-alkenes are significantly less stable than their cis counterparts. They take twisted forms, and are characterized by planar chirality. This poster presents an efficient one-pot two-step procedure for asymmetric synthesis of piperidine-fused trans-cycloalkenes. The method consists of 1) the enantioselective installation of cyclopropane ring onto methylenecyclopropanes (MCPs) and 2) thermal skeletal rearrangement in which the installed as well as inherent cyclopropane rings are both opened. A concerted mechanism is proposed together with a closed transition state model for the latter thermal rearrangement reaction.

1-Mesyl-4-phenyl-1,2,3-triazole (1a) was treated with MCP 2a in the presence of $(tBuCO_2)_4Rh_2$ (1.0 mol %) and 4 Å molecular sieves (MS) in $CHCl_3$ at 40 °C. The cyclopropanation reaction was complete in 5 h, and after chromatographic purification, imino-substitutued spiropentane 3a was obtained as a single diastereomer in 85% yield. The reaction was successfully applied to the asymmetric version by using chiral Rh(II) catalyst, giving 3a with 96% ee.

Next, the thermal reactivities of 3a were investigated, and an unprecedented rearrangement reaction was identified; when 3a in $CHCl_3$ was heated at 120 °C under microwave irradiation (MW) in a sealed vial for 2 h, the piperidine-fused trans-cyclononene 4a was cleanly formed. The enantiopurity observed with 4a ensures the integrity of chirality transfer during the skeletal rearrangement.



P-252

NOVEL CHIRAL BICYCLIC N-HETEROCYCLIC CARBENE (NHC) LIGAND PRECURSORS and THEIR PALLADIUM COMPLEXES

Assoc. Prof. M. Emin Günay[1], Dr. Rukiye Fırıncı[1], Prof. Dr. Bekir Çetinkaya[2]
[1]Adnan Menderes University, Department of Chemistry, 09100, Aydın, TURKEY, Aydin, TURKEY, [2]Ege University, Department of Chemistry, 35100, Izmir, TURKEY, Izmir, TURKEY

Poster Session 1

N-heterocyclic carbenes (NHCs) have become increasingly attractive in coordination chemistry due to their readily tunable steric and electronic parameters, rivalling phosphines as ancillary ligands in transition metal catalysis for a variety of reaction.[1] While the majority of NHCs employed as ligands are based on imidazole core, analogues with ring-expanded NHCs have recently being attracted attention, as it has been established that they posses quite different properties in comparison to the more traditional five-membered derivatives.[2]

In this study, the synthesis and characterization of the new chiral bicyclic (NHC)PdX_2(pyridine) complexes were described. The NHC precursor salts (2), prepared from R,S-tmcp, an initial ring closure and subsequent introduction of the exo N-substituents. All of the precursors (2) were converted to the Pd-NHC complexes (3) by treatment with $PdCl_2$, KBr, K_2CO_3 and pyridine. The salts and complexes were fully characterized by using spectroscopic methods and X-ray crystallography. Besides, the catalytic performance of the Pd-NHC complexes for Suzuki-Miyaura cross-coupling reaction was investigated.

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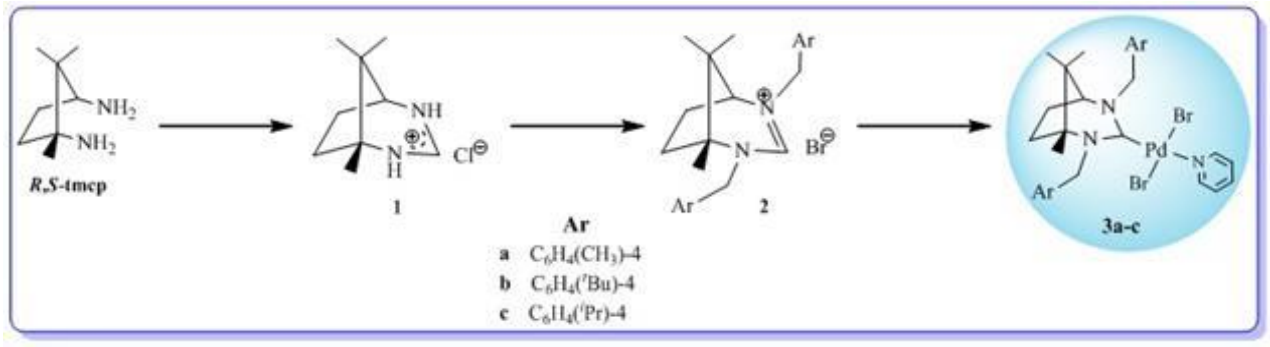
Acknowledgement: This work financially supported by the Technological and Scientific Research Council of Turkey [110T765].



P-253

Cu-Catalyzed Aromatic Fluorination and [[sup]18[/sup]F]Fluorination

Naoko Ichiishi[1], Melanie Sanford[1]
[1]*University of Michigan Ann Arbor, Ann Arbor, USA*

Poster Session 1

Organofluorine compounds are of significant interest in pharmaceuticals, agrochemicals and Positron Emission Tomography (PET) applications. This report describes the mild Cu-catalyzed nucleophilic fluorination of unsymmetrical diaryliodonium salts using potassium fluoride. The substrate scope, selectivity, and mechanism of this method will all be described. This protocol has also been successfully translated to radiofluorination under mild conditions. The radiofluorination of bioactive molecules using this new method will be discussed in detail.

P-254

Development of a method for the synthesis of trisubstituted oxazoles by Suzuki-Miyaura Coupling

Dr Kohei Yamada[1], Naoto Kamimura[1], Hikaru Fujita[1], Dr Munetaka Kunishima[1]
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Poster Session 1

Oxazole scaffolds are often found in natural products and pharmaceuticals. Therefore, it is important to develop an efficient method for the synthesis of oxazoles. Previously, we reported a new method for the one-pot synthesis of 5-(triazinyloxy)oxazole (1) from a carboxylic acid and an amino acid using dehydrocondensing reagent, 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) (Scheme 1).1 Recently, on the other hand, it was reported a Nickel-catalyzed Suzuki-Miyaura Coupling using triazinyloxybenzene as a starting material.2 Thus, we envisioned that combination of these two methods would enable a facile two-step synthesis of oxazoles bearing three different substituents, each of which is derived from a carboxylic acid, an amino acid, and a boronic acid, respectively.

Upon treatment of 1, prepared from benzoic acid and alanine, with phenylboronic acid under modified conditions gave the desired trisubstituted oxazole (2) in 73% yield. It can be considered that this concise method would be suitable for the construction of a trisubstituted oxazole library, because the starting materials for the reaction are readily available from a variety of sources.

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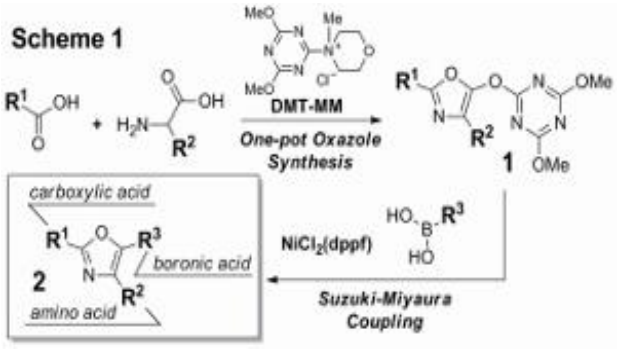

P-256

Facile Access to Functionalized Sultam Motifs from Aryl Sulfonamides and Alkynes Using a Cobalt Catalyzed Directing Group C-H Activation Approach

Oriol Planas[1], Dr Christopher Whiteoak[1], Dr Anna Company[1], Dr Xavi Ribas[1]

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Poster Session 1

Sulfonamide containing compounds have found application in numerous pharmaceutical drugs.[1] In particular, cyclic sulfonamides (sultams) have found use as anti-inflammatory drugs, carbonic anhydrase inhibitors and Calpain I inhibitors. Consequently, there has been increased interest in new catalytic protocols towards sultams through the use of C-H activation approaches, providing facile and sustainable synthetic routes starting from readily available starting materials. To this end, in 2012 Cramer and co-workers reported on a Rh-catalyzed protocol for the synthesis of sultams from aryl sulfonamides containing acyl directing groups with moderate regioselectivities.[2] More recently, Daugulis and co-workers have shown that through Co-catalysis alkynes can be coupled to aryl amides containing an 8-aminoquinoline directing-group with high regioselectivity.[3] With these precedents in mind we decided to investigate the possibility of realizing a Co-catalyzed aryl sulfonamide coupling with alkynes, with the hope of providing improved regioselective control over the previously reported Rh-catalyzed approach. We report the optimization and application of this facile Co-catalyzed route towards sultam motifs starting from easily prepared aryl sulfonamides containing an 8-aminoquinoline directing group. The reaction shows a broad substrate scope with products obtained in good to excellent isolated yields (60-97%) and with higher regioselectivites than previously reported.

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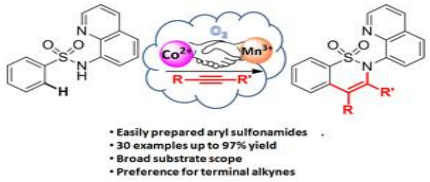

P-257

The Alkylation of C-H Bonds in Aromatic Amides with α,β-Unsaturated Lactones Catalyzed by Rhodium Complex

Mr. Kaname Shibata[1], Prof. Naoto Chatani[1]
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Poster Session 1

The direct utilization of C-H bonds, which are ubiquitous in organic molecules, is a straightforward method in organic synthesis. Transition metal catalyzed C-H bond functionalization reaction has been one of the most efficient methods for construct new C-C bond. In most cases, a monodentate chelation system has been used for the catalytic functionalization of C-H bonds. Recently, we focused our efforts on the catalytic functionalization of C-H bonds utilizing an N,N-bidentate chelation system. Recently, we found a direct alkylation of C-H bonds in aromatic amides with α,β-unsaturated carbonyl compounds. I wish to present here an unprecedented type of C-H bond alkylation reaction of aromatic amides with α,β-unsaturated lactones catalyzed by a rhodium-complex. In this reaction, C-C bond formation was occured between the ortho-position of aromatic amides and γ-position of α,β-unsaturated lactones. The presence of an 8-aminoquinoline moiety as the directing group is essential for the reaction to proceed. A variety of functional groups was tolerated in this reaction.

P-258

Rapid Synthesis of Sialic Acid Derivatives via Ligand-Controlled, Stereodivergent Propargylation of Unprotected Aldoses

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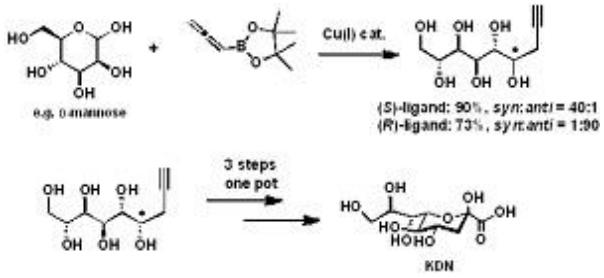
[1]*The University of Tokyo, Tokyo, Japan,* [2]*ERATO, Japan Science and Technology Agency, Tokyo, Japan*

Poster Session 1

Sialic acids represent one of the most important constituents of glycoconjugates in biological system. Thus, rapid and scalable supply and broadening the structural diversity of sialic acids are an urgent demand in the current glycochemistry and glycobiology. Despite significant improvement on synthetic efficiency during past decades, there are still several points to be overcome: limited scope, unsatisfactory yield and scalability. Moreover, the flexibility in structural and stereochemical alternation are limited.
To realize efficient and scalable synthesis of wide variety of natural and unnatural sialic acid derivatives, we developed a copper-catalyzed propargylation of unprotected aldoses. The reaction proceeded in high yield and high diastereoselectivity even in a gram-scale. In addition, the diastereoselectivity of the reaction could be switched by changing the ligand's stereochemistry. Variety of aldoses were applicable (13 examples) including a disaccharide, β-D-lactose. The products could be converted to the corresponding sialic acids through a one-pot reaction.



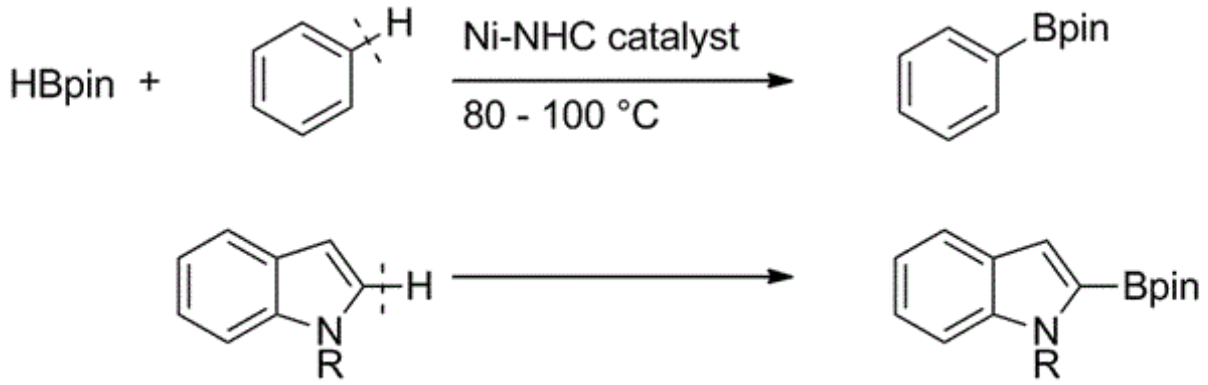
P-259

Nickel-Catalyzed C-H Borylation of Arenes and Indoles

Mr. Takayuki Furukawa[1], Prof. Mamoru Tobisu[1], Prof. Naoto Chatani[1]
[1]*Osaka University, Osaka, Japan*

Poster Session 1

Direct borylation of aromatic C-H bonds with a transition metal catalyst has emerged as a powerful method to introduce synthetically useful boron functionalities. Iridium complexes ligated with a bipyridine-based ligand are the catalyst of choice for the efficient and regioselective borylation of arenes.1 One remaining challenge in this methodology is the development of base metal catalysts. Recently, several groups demonstrated the catalytic activity of base metal complexes such as Fe2 and Co3, but the full potential of base metal catalysts to promote C-H borylation has not been explored especially in the case of metals other than Fe and Co. In this presentation, we wish to present the first example of nickel-catalyzed borylation of C-H bonds in arenes and indoles.
We found that the reaction of benzene with pinacolborane in the presence of a nickel-NHC catalyst gives a borylated product via C-H bond cleavage. This nickel-catalyzed borylation reaction is also applicable to indole to give a C2-borylated product selectively. Practical utility of the nickel-catalyzed system is also demonstrated by its application to the gram-scale synthesis of 2-borylated indole.



P-260

Control of Metal Nitrogen Multiple Bond in Vanadium(V) Hydrazido Complexes toward Reactions

Takashi Sakuramoto[1], Control of Metal Nitrogen Multiple Bond in Vanadium(V) Hydrazido Complexes toward Reactions Toshiyuki Moriuchi[1], Control of Metal Nitrogen Multiple Bond in Vanadium(V) Hydrazido Complexes toward Reactions Toshikazu Hirao[1,2]
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Poster Session 1

Complexes with metal nitrogen multiple bonds are considered to be intermediates of nitrogen fixation. Therefore, imido and hydrazido complexes have attracted much attention. Molybdenum complexes have been studied because molybdenum center is present in an active site of nitrogenases. However, vanadium, which is known to be a constituent of nitrogenases, is less focused on. We embarked upon the design of vanadium(V) complexes possessing vanadium nitrogen multiple bonds[sup]1, 2[/sup] and demonstrated oxidative coupling reaction by using imido vanadium(V) complexes.[3] Also, vanadium(V) hydrazido complexes are expected to show their reactivities as an amine source. However, vanadium(V) hydrazido complexes including aliphatic alkoxide ligands have never been synthesized. We herein report the structural characterization of metal nitrogen multiple bonds in the vanadium(V) hydrazido complexes with aliphatic alkoxide ligands. The effect of the substituents on hydrazido moieties for metal nitrogen multiple bond is also described.
The vanadium(V) hydrazido complexes 1 were obtained by the reaction of vanadium(V) oxytriisoproxide with N,N-dimethylhydrazine or N,N-diphenylhydrazine. Hydrazido complexes 1 with isopropoxide ligands formed dimerized structure in solid state. The vanadium(V) hydrazido complexes 2 was prepared from 1a and triethanolamine. On the contrary to 1, such dimerized structure was not observed in the crystal structure of hydrazido complexe 2. The crystal structure showed that the V-N-N bond angle of 1a (177°) is bigger than that of 2 (173°).

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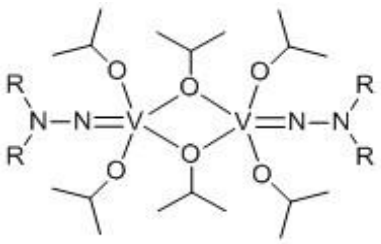
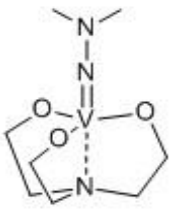


1a : R = Me, **1b** : R = Ph



2

P-261

Cationic Iridium/S-Me-BIPAM-Catalyzed Asymmetric Intermolecular Direct Hydroarylation of bicycloalkenes

Tomohiko Shirai[1], Cationic Ir/S-Me-BIPAM-Catalyzed Asymmetric Intermolecular Direct Hydroarylation of bicycloalkenes Yasunori Yamamoto[2]

[1]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan, [2]Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan

Poster Session 1

Transition-metal-catalyzed C-H bond functionalizations at the ortho position of directing-group have become an efficient C-C bond-forming method. In particular, the asymmetric addition reactions of C(sp2)-H bond to unsaturated bond such as C=C, C=O, C=N are a powerful strategy for the construction of carbon stereocenters. However, there are few examples of enantioselective transformation using this methodology. Recently, we have reported the cationic iridium-catalyzed enantioselective intramolecular direct hydroarylation of α-ketoamides to produce 3-hydroxyoxindoles[1]. In that study, we have already reported that a chiral bidentate phosphoramidite ligand (Me-BIPAM) was efficient. Herein, we report a highly efficient catalytic system for the enantioselective hydroarylation of bicycloalkenes with N,N-dialkylbenzamides. In the cource of our study on bidentate phosphoramidite as chiral ligands for enantioselective bond-forming reactions, a new bidentate phosphoramidite (S-Me-BIPAM) based on S-linked-BINOL was synthesized. This ligand was highly effective for iridium-catalyzed asymmetric intermoledular direct hydroarylation of 2-norbornene.

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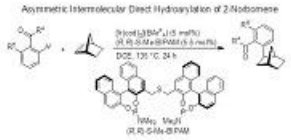

P-262

Salt-free Reduction of Base Transition Metal Compounds to Generate Amorphous Nanoparticles for Catalytic C—C Bond Formation

Dr. Taiga Yurino[1], Yohei Ueda[1], Dr. Yoshiki Shimizu[2], Shinji Tanaka[3], Haruka Nishiyama[1], Dr. Hayato Tsurugi[1], Prof. Dr. Kazuhiko Sato[3], Prof. Dr. Kazushi Mashima[1]

[1]Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Japan, [2]Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan, [3]Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Poster Session 1

Nanoparticles (NPs) of transition metals are unique and versatile catalysts that have attracted special interest of their boundary and bilateral nature between homo- and heterogeneous catalysts. These NPs are applicable as catalyst for organic transformation, such as C—C bond forming reactions. In general, noble metal crystalline NPs (cNPs) exhibited brilliant catalytic activity in these reactions. In contrast, however, cNPs of more abundant base metals are ineffective in the reactions. In this context, we revealed that amorphous Ni NPs (Ni aNPs) exhibited prominent activity as base metal NPs catalyst for C—C bond forming reactions for the first time.[1]

We found that 2,3,5,6,-tetramethyl-1,4-bis(trimethylsilyl)-1,4,dihydropyrazine (1) was able to reduce wide variety of transition metal compounds in a salt-free manner to give the corresponding metal(0) particles.[2] We demonstrated reductive C—C bond forming reactions, such as Ullmann coupling reactions and reductive arylation of aldehyde, catalyzed by these metal(0) particles, and successfully revealed that the combination of Ni NPs generated from $Ni(acac)_2$/1 and excess amount of 1 was specific for these reactions to give the target compounds in high yield (Scheme 1). The transmission electron microscopy (TEM) images and electron diffraction (TED) patterns of these Ni NPs clearly indicated that they were Ni aNPs, and this nature was the important factor to exhibit their catalytic activity in C—C bond forming reaction.

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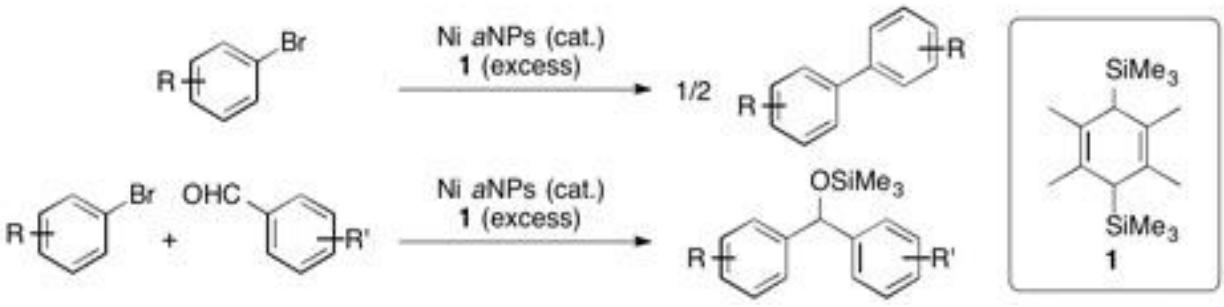
Scheme 1. Ni NPs catalyzed reductive C—C bond forming reaction



P-263

Rhenium-Catalyzed Synthesis of 1,3-Diiminoisoindolines via Insertion of Carbodiimides into a C-H Bond

Dr. Shunsuke Sueki[1,2], Mr. Zijia Wang[1], Prof. Dr. Motomu Kanai[1], Prof. Dr. Yoichiro Kuninobu[1,2]
[1]*The University of Tokyo, Tokyo, Japan,* [2]*CREST-JST, Tokyo, Japan*

Poster Session 1

1,3-Diiminoisoindolines are important compounds as partial structures of phthalocyanines and bioactive compounds. The conventional synthetic methods require strong acidic or basic reaction conditions to produce symmetrical 1,3-diiminoisoindolines. Recently, we developed a rhenium-catalyzed synthesis of 3-iminoisoindolinones from imidates and isocyanates via C-H bond activation.[1] Based on the reaction, we found that a reaction between imidates and carbodiimides proceeded smoothly in the presence of a rhenium catalyst to give 1,3-diiminoisoindolines including an unsymmetrical 1,3-diiminoisoindoline in good to excellent yields.[2]

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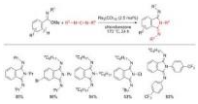

P-264

Nickel/Aluminum-catalyzed para-Selective Alkylation of Benzamides

Mr Shogo Okumura[1], Dr Teruhiko Saito[1], Prof. Kazuhiko Semba[1], Prof. Yoshiaki Nakao[1,2]

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Poster Session 1

Transition metal-catalyzed C–H functionalization reaction is an efficient method for transformation of arenes in terms of step- and atom-economy. Although a large number of ortho-selective C–H functionalization of substituted benzenes has been accomplished with the aid of directing groups,[1] para-selective functionalization is very rare.[2] Here we report para-selective C–H alkylation of benzamides with alkenes by cooperative nickel/aluminum catalysis. para-Selective alkylation of N,N-dialkylbenzamide with terminal alkenes has been achieved in the presence of a bulky N-heterocyclic carbene ligated nickel complex and a bulky aluminum Lewis acid. The reaction scope is compatible with various alkenes, giving p-alkylbenzamides in modest to high yields with high regioselectivities.

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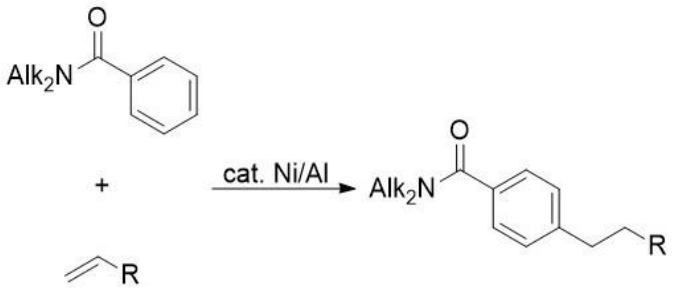


P-265

Palladium Catalyzed Aryl C−H Olefination with Unactivated, Aliphatic Alkenes

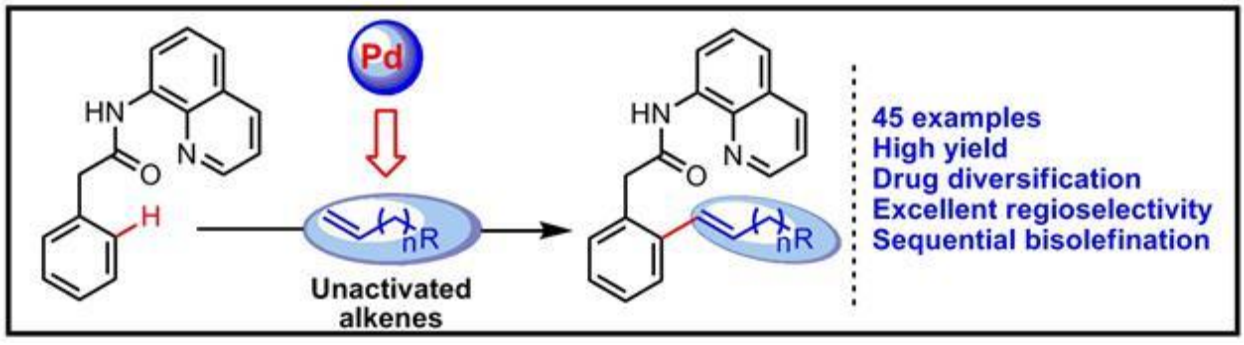
Mr. Arghya Deb[1], Dr. Debabrata Maiti[2]
[1]*Indian Institute of Technology, Bombay, Mumbai, India,* [2]*Indian Institute of Technology, Bombay, Mumbai, India*

Poster Session 1

Synthetic transformation using unactivated C-H bond as a target, is a subject of prime attraction because of its vast availability in all types of organic molecules. Inspite of its low reactivity, the challenge of using C-H bond as a potential synthon has been extensively attributed by transition metal catalysis in the last few decades that leads to making of new carbon-carbon (C-C) and carbon-heteroatom bond for the purpose of synthesizing valuable compounds. Palladium-catalyzed coupling between aryl halides and alkenes (Mizoroki−Heck reaction) is one of the most popular C-C bond forming reactions for synthesizing complex organic molecules. The limited availability, problematic synthesis and higher cost of aryl halide precursors (or their equivalents) have encouraged exploration of direct olefination of aryl carbon−hydrogen (C−H) bonds (Fujiwara−Moritani reaction). Despite significant progress, the restricted substrate scope (activated olefins), has discouraged the use of this greener alternative. To address these issues, directing group assisted C(aryl)–H olefination reactions have been discovered in recent years.

Despite significant efforts with various directing groups and transition metals, previous reports are limited to activated or electronically biased olefins only. In addition, regioselectivity issues due to lack of intrinsic biasness in aliphatic alkene and the migration of C–C double bond along the aliphatic chain was triggered as serious problem. Till date, unbiased alkene remains the most challenging partner for C¬–H olefination reaction.

Overcoming this serious limitation, we report here a palladium-catalyzed chelation-assisted ortho C−H bond olefination of phenylacetic acid derivatives with unactivated, aliphatic alkenes in good to excellent yields with high regio- and stereoselectivities. The versatility of this operationally simple method has been demonstrated through drug diversification and sequential C−H olefination for synthesizing divinylbenzene derivatives.



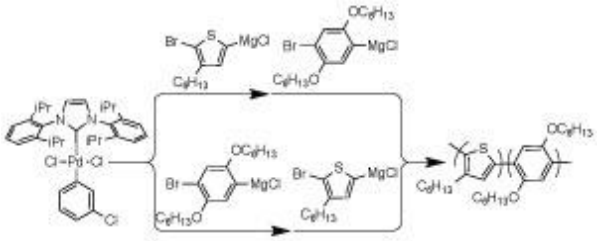
P-266

A new class of catalyst for catalyst-transfer polycondensation: polymerization performance and mechanistic studies of PEPPSI-IPr

Mitchell Smith[1], Prof. Anne McNeil[1]
[1]*University of Michigan Department of Chemistry, Ann Arbor, USA*

Poster Session 1

In the last decade, catalyst transfer polycondensation (CTP) has been developed as a method for the controlled synthesis of a variety of conjugated polymers. These polymers have diverse applications in organic electronics, including light-emitting diodes, photovoltaic solar cells, and field-effect transistors. For high performance in these devices, finely tuned HOMO and LUMO energy levels are required. A common strategy is the copolymerization of electronically diverse monomers. However, the nickel biphosphine catalysts that were first reported to undergo CTP are unsuitable for preparing these copolymers, as it has been demonstrated that they are unable to cross-propagate between even slightly electronically differentiated monomers. In 2012, we demonstrated that PEPPSI-IPr, a commercially available, air-stable palladium N-heterocyclic carbene catalyst, is competent in synthesizing phenylene and thiophene homopolymers and their blocklike copolymers with both orders of addition. In this work, we will discuss the mechanistic origins of this improved reactivity using rate and spectroscopic studies.



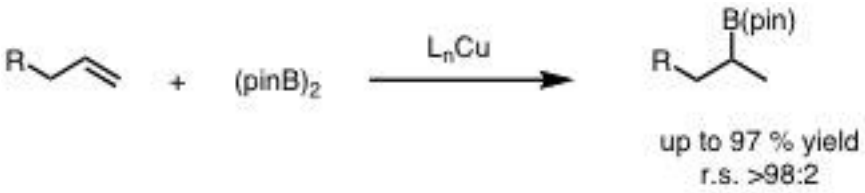
P-267

Conversion of Terminal Olefins to Secondary Alkyl Boranes

Ms. Hilary Kerchner[1], Prof. John Montgomery[1]
[1]*University of Michigan, Ann Arbor, USA*

Poster Session 1

Regioselective hydroboration of terminal alkenes has been developed to synthesize secondary branched alkyl boranes. The use of a bulky copper-N-heterocyclic carbene (NHC) in the presence of a diboron reagent and methanol affords the branched alkyl borane in high regiocontrol. The methodology shows a wide variety of chemoselectivity, tolerating protected alcohols, aryl bromides, and allyl heterocycles. Furthermore, the secondary alkyl borane products can be converted to potassium trifluoroborane salts for use in cross-coupling reactions.



P-268

Tuning the Reactivity of Mononuclear Nonheme Iron(IV)-Oxo Complexes Toward Oxidation Reactions

PhD Ilaria Gamba[1], MSc Joan Serrano[2], PhD Miguel Costas[3]

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Poster Session 1

Iron-containing metalloenzymes can efficiently and selectively perform oxidative processes under mild and environmentally benign conditions.[1] In particular, high-valent iron(IV)-oxo intermediates are involved in a large number of naturally occurring reactions (e.g. C-H bond activations and oxygen or halide transfers reactions). Nowadays, the development of synthetic model catalysts to mimic enzymes activities is a great challenge.[2]

In this context, mononuclear nonheme iron(IV)-oxo species were extensively studied and showed high ability to perform oxidative trasformations.[3] Therefore, the aim of the present study is to analyze and correlate structural, spectroscopic and reactivity properties of Fe(IV)=O species.

With this end, iron(IV)-oxo intermediates were afforded, with the aid of sacrificial oxidizing agents, starting from a novel family of Fe(II) complexes, carrying tetradentate ligands and equipped with two available cis-labile coordination positions.

[1] Chem. Rev. 2000, 100, 235−349
[2] Chem. Rev. 2005, 105, 2227−2252
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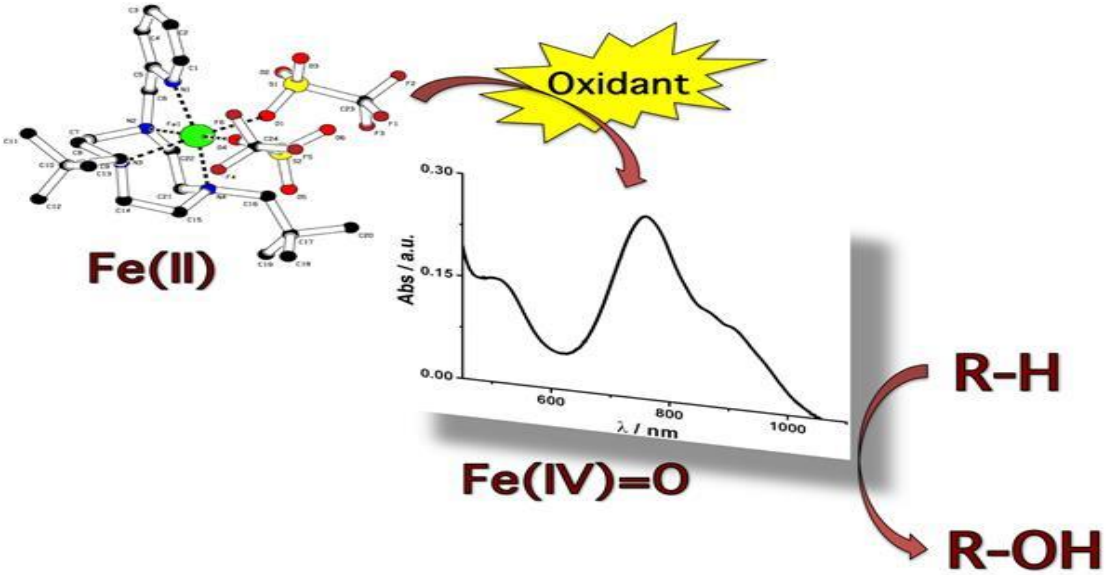

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Vanadium Complex Catalyzed Enantioselective Synthesis of Oxa[9]helicene

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Poster Session 1

Optically active helicenes and other related helical molecules have received considerable attention due to their high potential as catalysts, liquid crystals and molecular devices. However, efficient enantioselective synthetic method of helicenes, in particular, oxahelicenes, is rather limited. Herein, we report a vanadium catalyzed enantioselective domino oxidative coupling/intramolecular cyclization of polycyclic phenol 1. The vanadium complex (R_a,S)-3 works as a redox[1] and Lewis acid catalyst[2] to promote this sequential reaction to give oxa[9]helicenes 2 in up to 86% yield and 94% ee. The enantiopure 2a (R = H) was readily obtained by a single recrystallization of the product and the absolute configuration of resulting 2a was determined to be (M)-form by X-ray crystallographic analysis.

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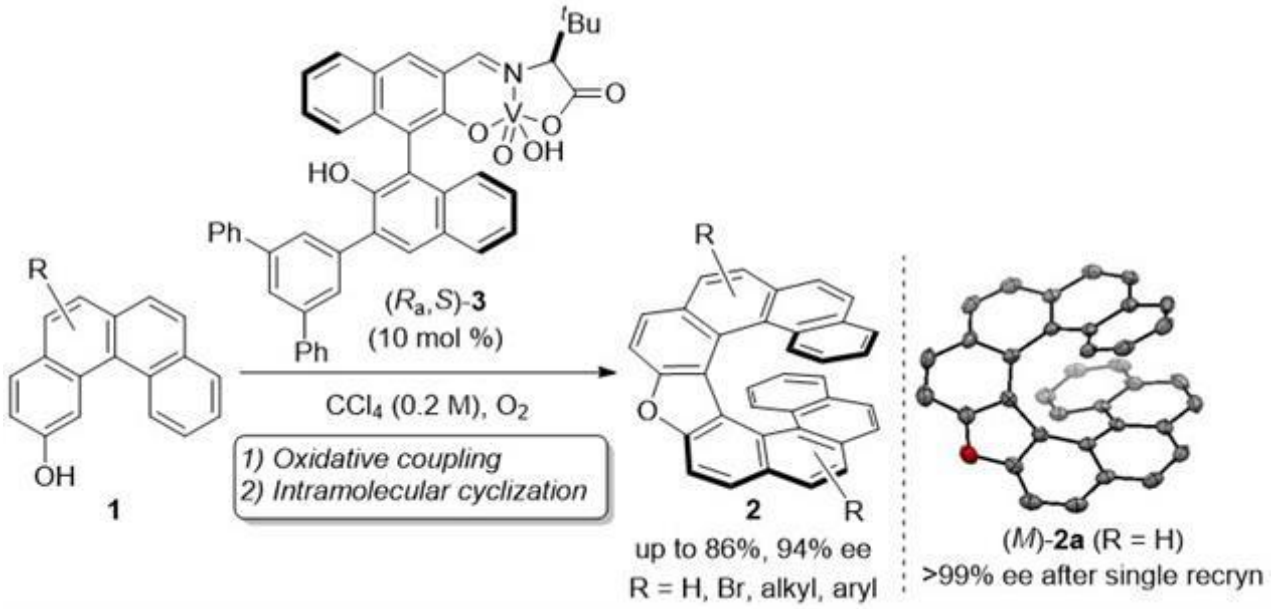

P-270

4,4'-Bipyridine-Catalyzed Diboration through "Reductive Addition" of Boron–Boron σ-Bond

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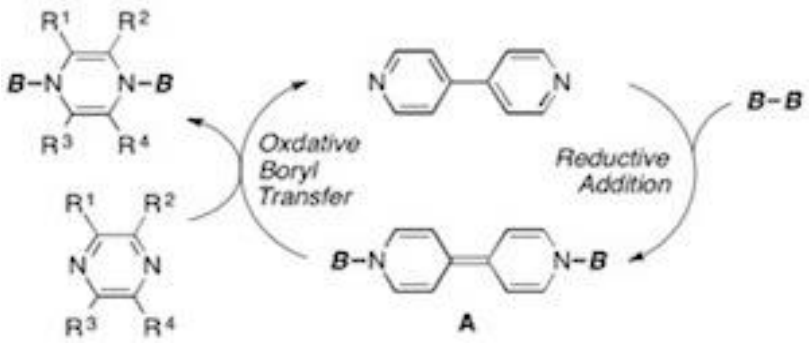
Poster Session 1

Transition metal catalysts have played privileged roles in the development of catalytic additions of nonpolar σ-bond across carbon–carbon and carbon–heteroatom multiple bonds. A key feature of transition metal catalysts is their high ability to activate nonpolar σ-bonds, mainly through oxidative addition. On the other hand, rapid progress in organocatalysis has also enabled activation of nonpolar σ-bonds, as exemplified by frustrated Lewis pair-catalyzed hydrogenation of imines and Lewis base-catalyzed diboration of alkenes. These new reactions clearly suggest further development of useful transformations through organocatalytic activation of nonpolar σ-bonds.
Herein, we describe a 4,4'-bipyridine-based catalyst system for diboration of sterically hindered pyrazines. The catalyst cycle consists of the following two steps: (1) reductive addition of the boron–boron bond of bis(pinacolato)diboron to 4,4'-bipyridine to form N,N'-diboryl-4,4'-bipyridinylidene (A), and (2) oxidative boryl transfer from the intermediate A to pyrazine to give N,N'-diboryl-1,4-dihydropyrazine with regeneration of bipyridine.



P-271

NHCs bearing a chelating scaffold as supporting ligands for iron complexes

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Poster Session 1

The use of N-Heterocyclic Carbenes (NHCs) as supporting ligands for transition metal complexes is a topic that has become important in the recent years. Their advantage relies on their strong σ-donation property, which can give rise to strong M-C bonds, what generates catalysts resistant towards decomposition and that can stabilize high-valent intermediates. Moreover, their electronic and steric properties can be easily tuned, what is highly desirable in coordination chemistry. Furthermore, among to their inherent advantages, the complex stability and reactivity can be modulated by adding in the NHC structure a chelating scaffold[1].

NHC complexes have been extensively studied using different metal centers, such as Pd and Rh. Nevertheless, Fe-NHC complexes have remained unexplored for a long period of time due to the difficulty of its synthesis. However, the desirable use of these iron complexes as catalyst arises from the combination of the previously described advantages of NHCs as ligands and the use of iron as an environmentally benign metal center. For this reason, some applications of these iron catalysts have been already described[2].

Herein, we present the synthesis of new carbene ligands incorporating a chelating scaffold of a 1,4-dimethyl-1,4,7-triazacyclononane moiety, which has affinity to coordinate to iron as it has been studied previously[3]. As well as, the generation of the corresponding Fe-NHC complexes is also studied.

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2 Riener, K.; Haslinger, S.; Raba, A.; Högerl, M. P.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. Chem. Rev. 2014, 114, 5215.
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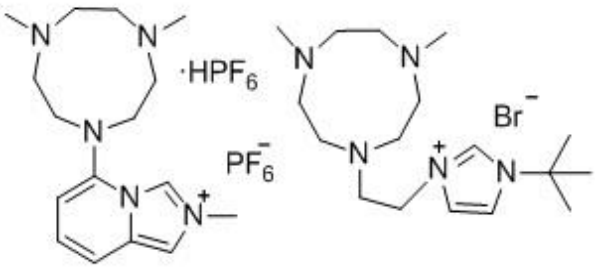

P-272

Synergistic Interplay of a Non-Heme Iron Catalyst and Amino Acid Coligands in H2O2 Activation for Asymmetric Epoxidation of a-Alkyl-Substituted Styrenes

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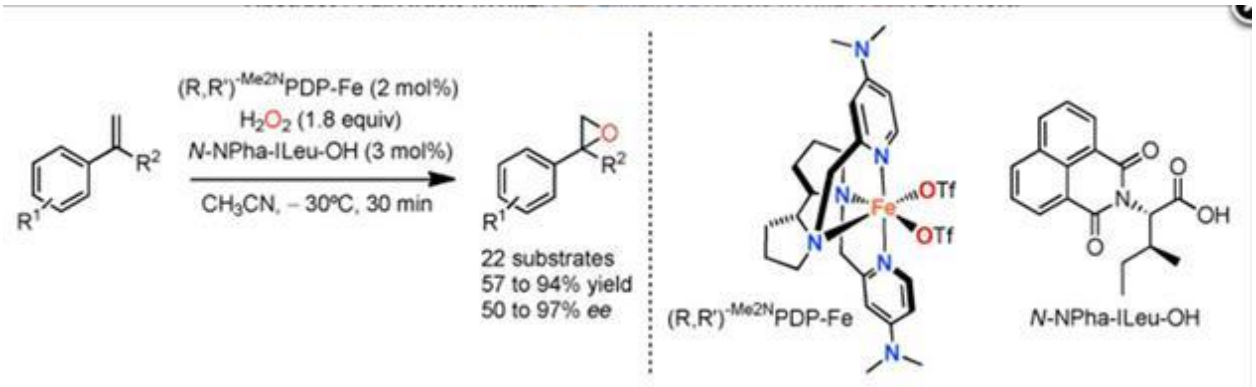
Poster Session 1

Inspired by oxidations taking place at oxygenases, the combination of iron-based catalysts and hydrogen peroxide is an attractive approach for developing oxidation methods because of availability, low cost and low toxicity considerations.[1] Cytochromes P450 (Cyt-P450) constitute a paradigmatic example where the powerful electron-donating properties of the apical thiolate and the H-accepting character of a nearby threonine residue assist the O−O cleavage step of ferric hydroperoxide species via the so-called "push−pull" effect.[2] On 2013, our group reported the electron-rich groups on the pyridine of PdP-Fe-$(OTf)_2$ facilitates the heterolityc O-O cleavage and stabilizes the high valent iron-oxo, leading to stereoselective oxygen atom transfer. The present work shows the use of amino acids as suitable coligands in epoxidation reactions with aqueous H_2O_2 using electron-rich bioinspired non-heme iron catalysts, extending the substrate scope of these systems to the challenging terminal olefins. The present approach is appealing as it provides proof of concept that the versatility of these systems can be extended straightforwardly towards novel classes of substrates without requiring an elaborate development of novel chiral catalysts.



P-273

LIC-KOR Promoted Nitrone Reactivity with Metalated Alcoxydienes

Dr Annamaria Deagostino[1], Stefano Parisotto[1], prof Cristina Prandi[1], prof Paolo Venturello[1]
[1]*Dipartimento di Chimica - Università di Torino, Torino, Italy*

Poster Session 1

Our research group has been studying for several years the reactivity of α,β-unsaturated acetals, as masked acyl anions, in the presence of Li-K mixed bases also called Schlosser-Lochmann mixed bases, easily prepared by mixing 1 or 2 eq. of Na or K alkoxyde with a solution of RLi.[1] α,β-Unsaturated acetals afford in a regio- and stereoselective manner functionalised alcoxy-1,3-dienes. The reaction has been extended to cyclic α,β-unsaturated acetals, and several electrophiles have been used.[2]
In this communication we wish to present our preliminary results on the reactivity of N,α-diarylnitrones with alcoxydienes in the presence of Schlosser-Lochmann superbases. Nitrones, are very interesting substrates, not only known in organic chemistry, but also in medicinal chemistry and polymer science. They show electrophilic character and give nucleophilic addition with several nucleophiles and organometallic reagents.[3]
Preliminary results obtained using α,N-diarylnitrones as electrophilic partners of metalated alcoxydienes in superbasic medium, seems to indicate the formation of a highly conjugate imine (3) by a domino process. As evidenced in Scheme 1, the addition of the nitrone 2 to the intermediate vinylic carbanion would be followed by the elimination of a hydroxyl species with the formation of an imine by a E1cb. At our knowledge this type of reactivity of α,N-diarylnitrones, partially due to the presence of the LICKOR base, has never been reported. (Scheme 1)
The obtained imines were hydrolysed in acidic conditions affording cyclopentenones in good yields. We hypothesised a process where a proton attacks the imine double bond followed by an intramolecular electrophilic addition to the terminal double bond of the dienic portion, finally the elimination of ethanol leads to the corresponding 2-phenylamino-α,β-cyclopentenone (Scheme 2).

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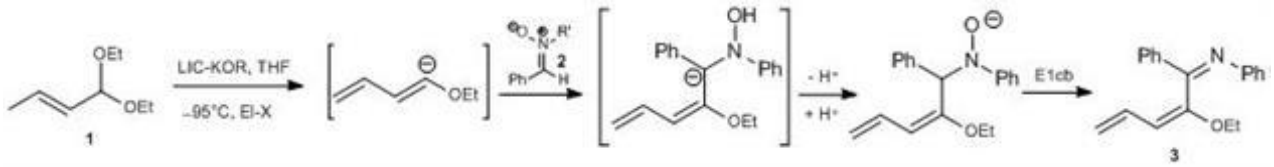


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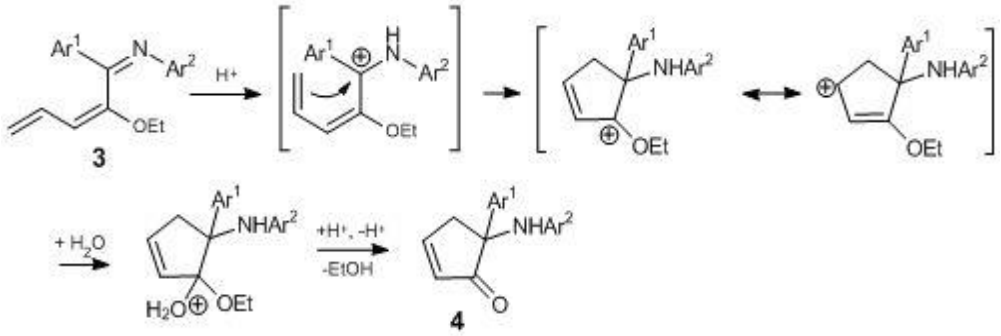
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+H+, -H+
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P-274

C-H bond oxidations reactions catalyzed by bioinspired non-heme iron complexes

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Poster Session 1

The selective functionalization of aliphatic C-H bonds represents one of the main challenges of modern synthetic organic chemistry and accordingly increasing efforts have being devoted towards this research goal. Oxidation of C-H bonds mediated by transition metal complexes are fundamental steps in fine and industrial chemistry, and in many biochemical transformations. The factors that govern regioselectivity in these reactions have been actively pursued and identified(1). In most cases C-H site selectivity is dictated by the innate properties of C-H bonds, irrespective of the nature of the oxidant. Inspired by oxidations taking place at oxygenases, the combination of iron-based catalysts and hydrogen peroxide is an attractive approach for developing oxidation methods because of availability, low cost and low toxicity considerations(2). On 2013, our group reported the electron-rich groups on the pyridine of PdP-Fe-(OTf)2 facilitates the heterolityc O-O cleavage and stabilizes the high valent iron-oxo, leading to stereoselective oxygen atom transfer(3). The present work shows the use of secondary amides as directing groups in C-H bond oxidation reactions with aqueous H2O2 using electron-rich bioinspired non-heme iron catalysts.

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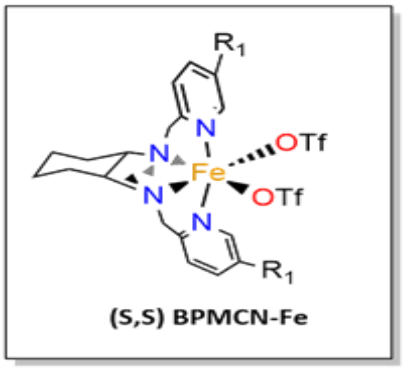
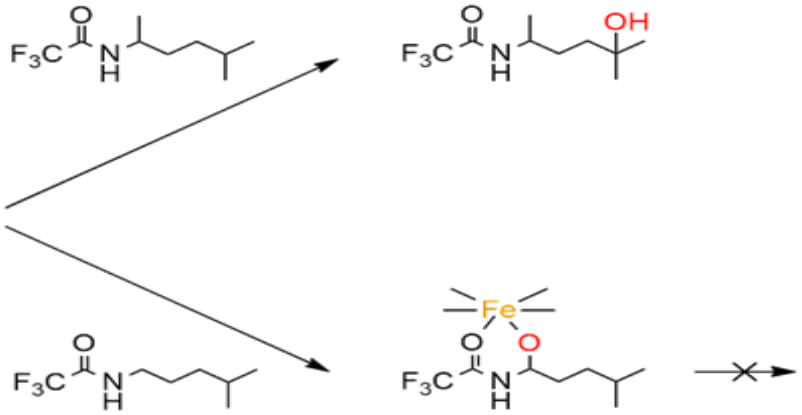
(S,S) BPMCN-Fe (3 mol%)
H_2O_2 (2.5 eq)
AcOH (1.5 eq)
CH_3CN, 0°C, 30 min



(S,S) BPMCN-Fe



P-275

Development and Application of Rhodium-Catalyzed Hydroacylation-Suzuki Coupling Cascades for the Preparation of Functionalized Heterocycles

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Poster Session 1

The hydroacylation of alkenes and alkynes is a highly atom economic C-H activation reaction which allows the formation of ketones or enones. [sup]1-2[/sup] The Willis group has previously reported a Suzuki-type coupling of simple aryl methyl sulfides with boronic acids, in which the directing group for the hydroacylation can act as a leaving group in a cross-coupling reaction.[3] A three-component hydroacylation/Suzuki (H-S) cascade process was developed using a preformed Rh(I) precatalyst featuring a small-bite-angle bis-phosphine ligand R2PCH2PR2 (R = i-Pr). In this poster, we have changed the catalyst used in this H-S cascade process to the commercially available Rh(nbd)2BF4 alongside a bis-phosphine ligand, that allows the formation of the catalyst in situ, instead of being preformed. This avoids the use of the expensive [BArF4][sup]-[/sup]counterion and the use of Schlenk techniques. Highly reactive heterocyclic alkenyl-sulfide aldehydes are employed as substrates and react efficiently with alkynes or alkenes and subsequently boronic acids, delivering in high yields a wide range of heterocyclic enone derivatives. Application of these products to biologically interesting molecules, such as piperidine derivatives used in applications towards Parkinson's disease, Alzheimer's disease, and diabetes,[sup]4-5[/sup] are underway.

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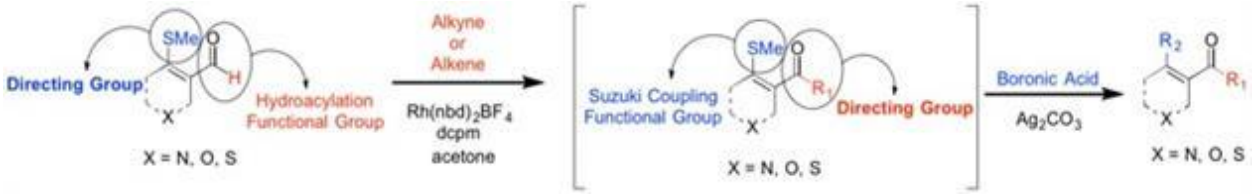

P-276

Development of a Rhodium-Catalysed Tishchenko Dimerisation of Aldehydes: Applications to Polymerisation

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Poster Session 1

Polyesters are truly versatile materials, with applications ranging from biomedical devices to sustainable petrochemical alternatives.[1] The presence of additional functionalities, such as free hydroxyl groups, confer highly attractive properties to these materials.[2] However, current syntheses are limited to using elaborate protecting group strategies or highly substrate specific enzymes.[3] We report the development of a novel and efficient synthetic route to functionalised polyesters, using rhodium catalysis to polymerise dialdehydes.

The work initially focused on finding suitable reaction conditions to dimerise aldehydes containing β-sulfur atoms, to give the corresponding Tishchenko-type ester product (Scheme A). The reaction also appeared to be tolerant towards functional groups such as hydroxyl groups and amides.

These reaction conditions were successfully applied to the polymerisation of dialdehydes. To optimise the molecular weights of the resulting polymeric materials, a range of concentrations, catalyst loadings and solvents were evaluated for the polymerisation of dialdehyde I (Scheme B).

Work was then undertaken to synthesise a range of functionalised dialdehydes which could be evaluated in the polymerisation reaction. Substrates containing hydroxyl groups were a primary focus due to their potential biomedical applications. After investigating several synthetic strategies, the hydroxyl-containing dialdehyde II was generated and successfully polymerised, delivering polymeric material of Mw ~ 5000 (Scheme C). To our knowledge, this represents the first example of a hydroxyl-containing polyester synthesis without the need for protecting groups or a substrate selective enzyme catalyst.

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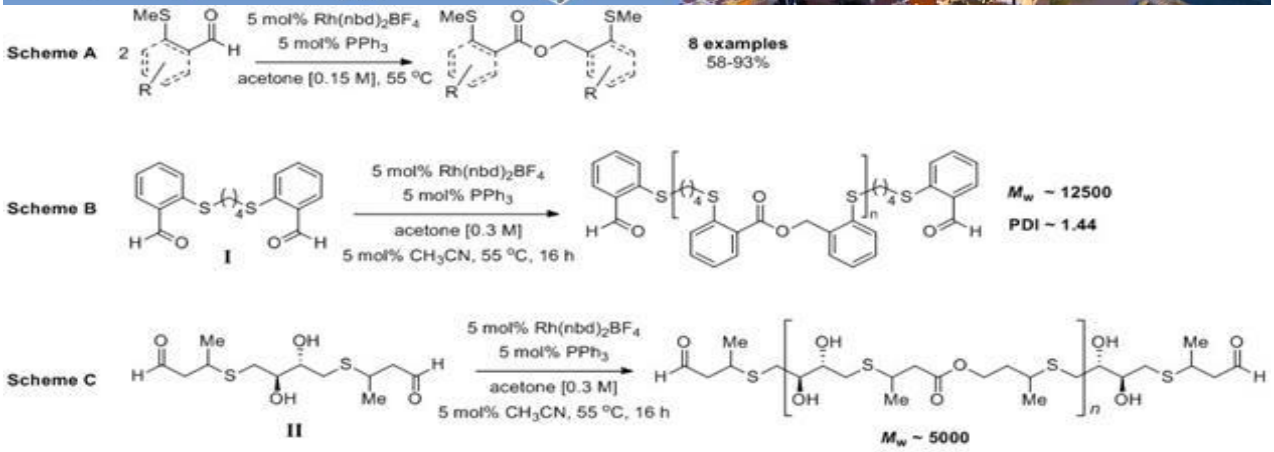

Figure 1: **Scheme A**: The dimerisation of aldehydes containing sulfur atoms to give Tishchenko-type ester products; **Scheme B**: Optimised polymerisation conditions for dialdehyde **I**, determined from screening studies; **Scheme C**: Successful polymerisation of hydroxyl group-containing dialdehyde **II**.

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Versatile Ruthenium(II)-Catalyzed C–H Cyanations of Benzamides

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Poster Session 1

Aromatic nitriles constitute key structural motifs of important pharmaceuticals, dyes, agrochemicals and natural products.[1] The cyano group serves as a versatile functional group that can easily be transformed into amines, ketones or aldehydes, among others.[2] The syntheses of aryl nitriles continue to rely on classical approaches, such as the Sandmeyer[3a] or the Rosenmund–von Braun reaction,[3b] which have severe limitations, including the use of stoichiometric or even super-stoichiometric amounts of metal cyanides as well as harsh reaction conditions. Within our program on sustainable C–H functionalization,[4] we herein report a robust ruthenium(II)-catalyzed direct cyanation of arenes and heteroarenes bearing only weakly coordinating amides.[5] The user-friendly C(sp2)–H functionalization occurred with the assistance of carboxylate with high site-selectivity, excellent functional group tolerance and ample substrate scope.[6]

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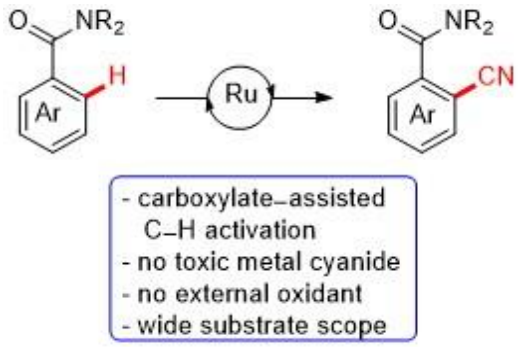

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Oxygen activation process through the controlled cleavage and formation of the O-O bond and the potential reversibility of the process by iron dimeric complexes

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Poster Session 1

Nature can reversibly bind and activate O2, which are key reactions in O2-transport and oxygenation of various substrates, in a lot of cases performed by non-heme metalloproteins with bimetallic iron centers (ref. 1) . Through O2-activation, these metallic centers are able to form active highly oxidizing species such as oxodiiron(IV) (ref. 2), which are responsible of the oxidation of challenging substrates in soft conditions. So mimicking the enzymes with model diiron complexes is of significant importance to understand these mechanisms.

In this context, we target the development of diiron systems with polydentate N-donor ligands (figure 1) with the aim to promote the cleavage of the O-O bond, and to explore the reversibility of the process favored by proximity of the two metallic centers.

The reactivity of the complexes against different oxidants are studied, and high-valent iron species resulting from these reactions are characterized by spectroscopic techniques. The oxidation ability of these species are studied as well as their ability to reverse O-O bond cleavage.

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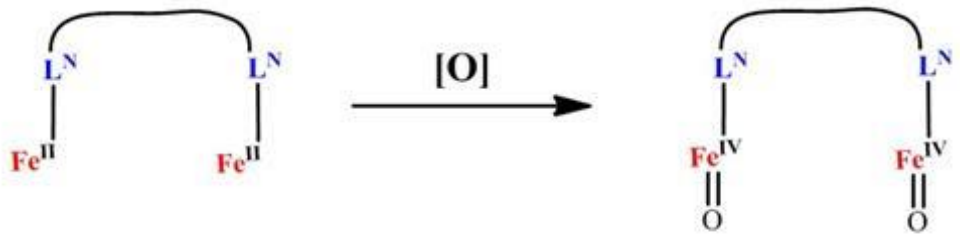

Figure 1. schematic dioxoiron(IV) formation from diiron (II) complex

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HIGH-VALENT NON-HEME TOSYLIMIDO-IRON (IV) SPECIES IN TACN-BASED N5-PENTADENTATE LIGANDS

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[1]Grup de Química Bioinorgànica i Supramolecular (QBIS). Institut de Química Computacional i Catàlisi (IQCC). Departament de Química. Universitat de Girona. , Girona, Spain, [2]DSV/iRTSV/CBM, UMR 5249 CEA-Université Grenoble I-CNRS/Equipe de Physicochimie des Métaux en Biologie, Grenoble, France

Poster Session 1

High valent iron complexes have been postulated as reaction intermediates in challenging oxidation reactions performed by bioinspired oxidation catalysts.[1]

The capacity of non-heme oxo – iron (IV) complexes to transfer the oxo moiety to different substrates has been widely studied[2] and it is well known that they are capable of performing such an interesting and challenging chemistry as the abstraction and hydroxylation of C-H bonds, even those as strong as in cyclohexane.[3]

Related interesting compounds are tosylimido – iron (IV) species, which are analogue to oxo – iron (IV) complexes, thus should be capable of isolobal amination reactivity. Recent studies reported its potential showing the ability of heme and non - heme tosylimido – iron (IV) compounds to transfer the tosylimido moiety to nucleophilic substrates, such as sulphides.[4]

In this work we have prepared and completely characterized two novel non – heme tosylimido-iron (IV) compounds and we have investigated its reactivity towards thioanisole substrates to understand the transfer of the tosylimido moiety to the sulphur atom. A comparative analysis of kinetic parameters has been performed, as well as characterization studies of the reaction products by ^{1}H - NMR.

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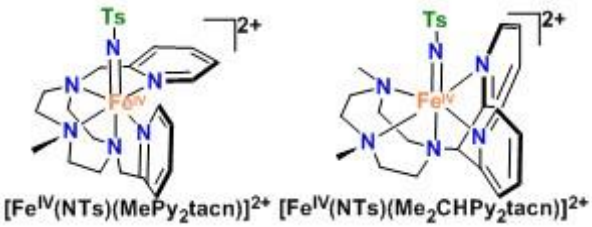

$[Fe^{IV}(NTs)(MePy_2tacn)]^{2+}$ $[Fe^{IV}(NTs)(Me_2CHPy_2tacn)]^{2+}$

P-280

Iridium-Catalyzed Regiodivergent C–H Borylation of Multifunctionalized Heteroarenes

Jumpei Taguchi[1], Dr. Ikuo Sasaki[1], Shotaro Hiraki[1], Prof. Dr. Hajime Ito[1], Dr. Tatsuo Ishiyama[1]
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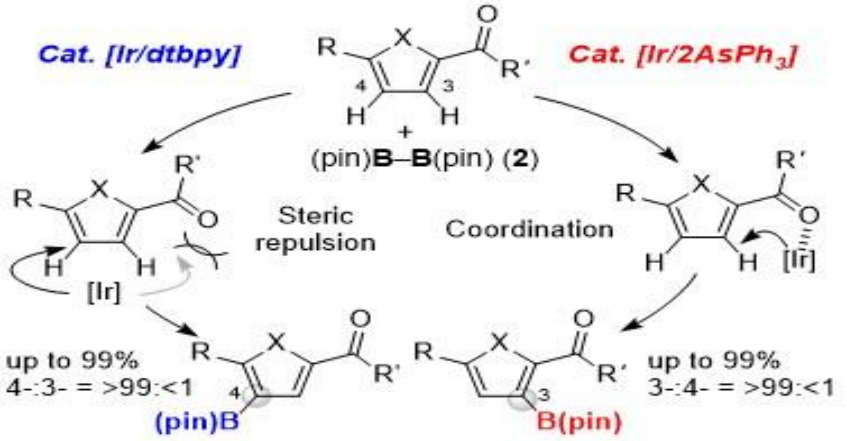
Poster Session 1

Multifunctionalized heteroarenes are important structure motifs which are often found in many natural products, biologically active compounds and functional organic materials. Regioselective C–H borylation of mono- or bis-substituted heteroarenes in combination with further derivatization of the resultant heteroaryl boronic acid esters offer the convenient and reliable synthetic methods to access the multi-substituted heteroarenes. The most important requirement for C–H borylation is the site selectivity controlling, because C–H bonds are ubiquitous in organic compounds. Herein we report a catalyst-controlled regiodivergent C–H borylation of multi-functionalized heteroarenes using iridium complex. (Sasaki, I.; Taguchi, J.; Hiraki, S.; Ito, H.; Ishiyama, T. Chem. Eur. J., 2015, accepted.)

To achieve the regiodivergent borylation of heteroarenes, we first examined the borylation of furan derivative 1, which is substituted by propionyl and methyl groups at the 2- and 5-position respectively. The reaction of 1 with bis(pinacolato)diboron (2) (1.1 equiv) in the presence of [Ir(OMe)(cod)]2 (1.5 mol%) and dtbpy (3.0 mol%) ligand afforded the 4-borylated product in 74% yield with high regioselectivity. In contrast, the borylation of 1 proceeded regioselectively in the presence of [Ir(OMe)(cod)]2 (1.5 mol%) and AsPh3 (6.0 mol%) ligand at 120 °C to give the 3-borylated product in 99% yield with high regioselectivity. Furthermore, we investigated the reactivity and regioselectivity of the borylation reactions of heteroarenes having various functional groups, such as sterically hindered alkyl, methoxy or halogeno group at the 5-position. The desired 4- and 3-bolylated products were obtained in moderate to high yields with high regioselectivities.

To demonstrate the synthetic utility of this regiodivergent borylation, we synthesized two different analogue molecules for biologically active compounds from the common furan derivative bearing carbamoyl group at the 2-position and bromo group at the 5-position. The one-pot, three-step procedure involving regiodivergent C–H borylation and stepwise Suzuki-Miyaura cross-coupling reaction produce the desired compounds.



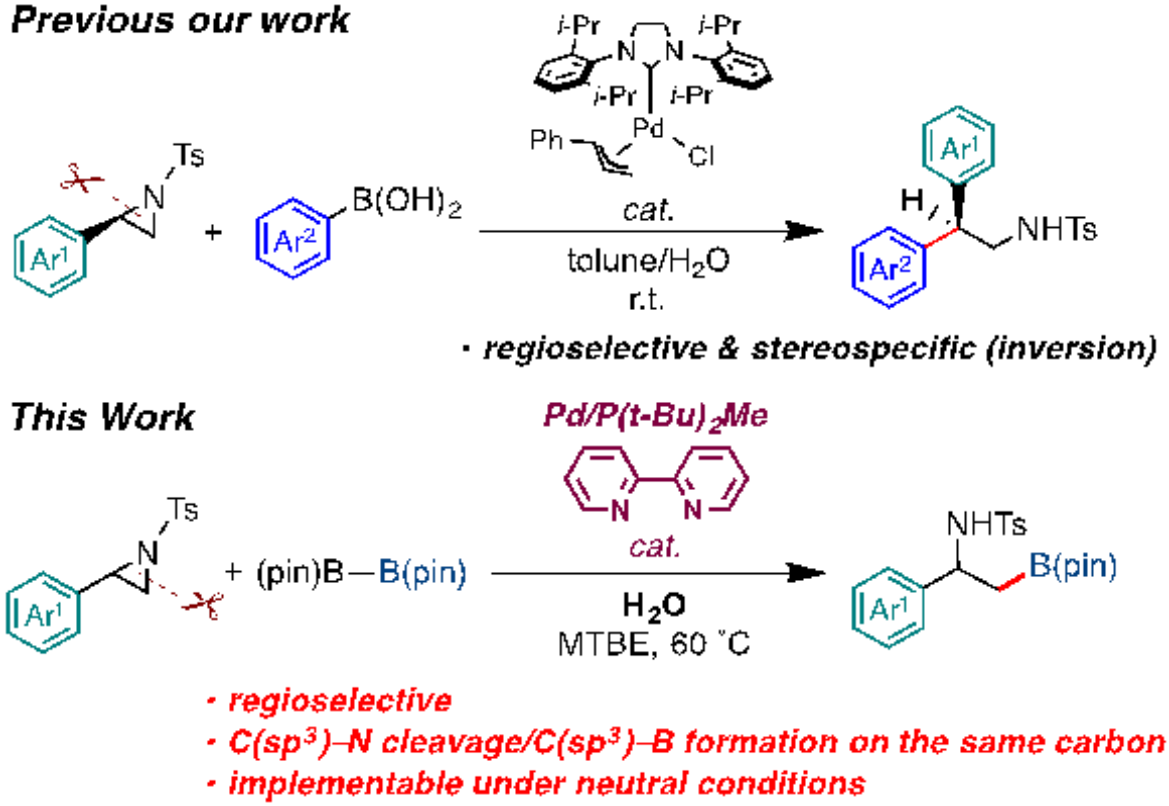
P-281

Pd/phosphine-catalyzed Regioselective Ring-opening Borylation of 2-Arylaziridines with Bis(pinacolato)diboron

Prof. Satoshi Minakata[1], Mr. Akinobu Kuroda[1], Dr. Youhei Takeda[1]
[1]*Department of applied Chemistry, Graduate School of Engineering, Osaka University, Osaka, Japan*

Poster Session 1

The last couple of years have seen a significant progress in the transition-metal-catalyzed cross-coupling reactions that utilize aziridines as a nonclassical electrophile, making the use of unique reactivities of the three-membered strained heterocycles to oxidatively add to low-valent late transition metal complexes at a C–N bond in a regioselective and stereospecific manner. In this regards, we recently have reported a Pd/NHC-catalyzed enantiospecific and regioselective ring-opening cross-coupling of 2-arylaziridines to give 2-aryl-2-phenethylamine derivatives in a completely stereo-controlled manner (JACS, 2014, 136, 8544). Herein we will showcase a Pd/phosphine-catalyzed regioselective ring-opening borylation of 2-arylaziridines with bis(pinacolato)diboron to produce 3-borylated 1-phenethylamine derivatives in good to high yields. It should be noted that this reaction represents the first example of direct substitution of a C(sp^3)–N bond with a boryl group on the same carbon (i.e., formal S_n2 reaction).



P-282

Ortho-C–H Benzylation of Aryl Imines with Benzyl Phosphates under Cobalt–Pyphos Catalysis

Mr. Wengang Xu[1], Dr. Paira Rupankar[1], Prof. Yoshikai Naohiko[1]
[1]*School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore, Singapore*

Poster Session 1

Diarylmethane moieties are present in many pharmacologically active compounds as well as in several approved drugs and agrochemicals. Established synthetic approaches to the diarylmethane moiety include Friedel–Crafts-type benzylation of electron-rich arenes with benzylic electrophiles and transition metal-catalyzed cross-coupling between arylmetal reagents and benzyl electrophiles or between benzylmetal reagents and aryl electrophiles. These approaches, however, have their own drawbacks. The Friedel–Crafts reaction often affords a mixture of regioisomeric products, while the cross-coupling reaction requires two prefunctionalized starting materials. Hence, the development of alternative aryl-benzyl bond forming methods, such as those based on heteroatom-directed C–H bond activation, is desirable. However, directed aromatic C–H benzylation reactions reported thus far often require non-transformable or expensive directing groups and high reaction temperatures. Herein, we report on a directed C–H benzylation reaction of aryl imines with benzyl phosphates promoted efficiently by a cobalt catalyst complexed with 2-(2-(diphenylphosphino)ethyl)pyridine (pyphos). The diarylmethane product serves as a versatile starting material for the synthesis of anthracene, anthrone, and antraquinone derivatives.

P-283

Cobalt-Catalyzed Direct Alkenylations with Alkenyl Esters by C–H/C–O Cleavages

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Poster Session 1

Cobalt-catalyzed C–H activation represents a powerful tool for the sustainable synthesis of biologically active compounds and functional materials,[1] which were as of yet mostly achieved by the use of more expensive second row transition metal-complexes. In recent years, considerable success has been accomplished with the development of cobalt-catalyzed C–H arylations and alkylations with organic electrophiles.[2] As of yet, cobalt-catalyzed olefinations were solely accomplished by hydroarylations of alkynes.[3] Despite significant advances, this method faces considerable limitations, including the restriction to the synthesis of acyclic alkenes.
Herein, we present a cobalt-catalyzed C–H olefination with easily accessible enol derivatives.[4] Notable features of our isohypsic strategy are nor limitied to a predictable regio-control, challenging C–H/C–O functionalizations with unactivated alkenyl acetates, phosphates, carbonates, and carbamates in a stereo-convergent fashion, as well as oxidant-free olefinations under remarkably mild conditions at 23 °C.

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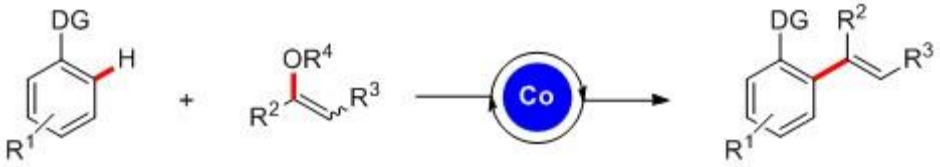

P-284

GOLD-CATALYZED SYNTHESIS OF EXOCYCLIC VINYLOGOUS AMIDES AND beta-AMINO KETONES

Dr Dina Scarpi[1], Prof. Ernesto G. Occhiato[1], Prof. Enrique Gómez-Bengoa[2], Mr Béla Fiser[2], Prof. Cristina Prandi[3]

[1]University of Florence, Dept Chemistry, Sesto Fiorentino, Italy, [2]Universidad del País Vasco / UPV-EHU, Departamento de Química Orgánica, Donostia-San Sebastián, Spain, [3]University of Torino, Dept Chemistry, Torino, Italy

Poster Session 1

The gold(I)-catalyzed reaction of N-Boc-protected 6-alkynyl-3,4-dihydro-2H-pyridines, which affords synthetically useful vinylogous amides (β-enaminones), has been studied in detail in order to optimize the reaction conditions and have insights into the mechanism and the structural features that selectively favour the 6-endo dig oxyauration of the triple bond. Experimental studies and DFT calculations demonstrate that the 6-endo dig approach is exclusive with substituted alkynes, whereas with terminal alkynes the 5-exo dig cyclization prevails. The same selectivity is observed with N-Cbz-protected 2-alkynyl piperidines that afford β-amino ketones as a consequence of the 6-endo dig attack to a substituted triple bond. Sedamine alkaloids are easily obtained by this approach and the first synthesis of a natural compound from Sonneratia hainanensis has been realized.

P-285

Palladium-Catalyzed Direct C–H Arylation of Isoxazoles at The 5-Position

Masashi Shigenobu[1], Palladium-Catalyzed Direct C–H Arylation of Isoxazoles at Their 5-Position Kazuhiro Takenaka[1], Palladium-Catalyzed Direct C–H Arylation of Isoxazoles at Their 5-Position Hiroaki Sasai[1]
[1]*ISIR, Osaka University, Ibaraki-shi, Japan*

Poster Session 1

Isoxazoles, a major class of five-membered heterocycles, are embedded in a variety of pharmaceutically important compounds. In contrast to many successful examples of the direct C–H arylation for other heterocyclic compounds, such reactions of isoxazoles are scarce and limited to their C4 position. Since, unique spiro-type chiral ligands possessing an isoxazole coordination site were developed in our laboratory, the direct C5 arylation of isoxazoles has the potential to be utilized for modification of the ligands. Herein we report a Pd-catalyzed direct C5 arylation of the isoxazole ring.

After extensive optimization of reaction conditions, we found a smooth formation of desired coupling products. Thus, the reaction of isoxazole substrates with 2 equiv of aryl iodides in the presence of 5 mol % of $PdCl_2(MeCN)_2$, 10 mol % of 1,2-bis(diphenylphosphino)benzene (DPPBz), and 2 equiv of AgF in DMA at 100 °C proceeded to give arylated products up to 86% yield after 24 h (Scheme 1). We further explored the application of this coupling reaction. When spiro-type chiral ligand 11 bearing an isoxazole coordination unit was subjected to the direct arylation as a substrate, an aromatic ring was installed selectively at the desired position (Scheme 2). We next examined the enantioinduction ability of 2 in the Pd-catalyzed asymmetric tandem cyclization of dialkenyl alcohol 3.2 The optical purity of target product 4 was found to be improved from 97% ee with ligand 1 to 99% ee with 2a under otherwise identical conditions (Scheme 3). In the presentation, the plausible mechanism will also be discussed.

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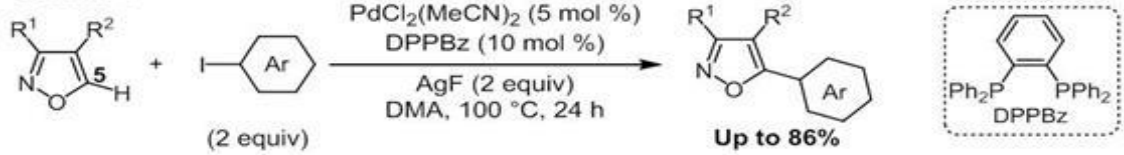
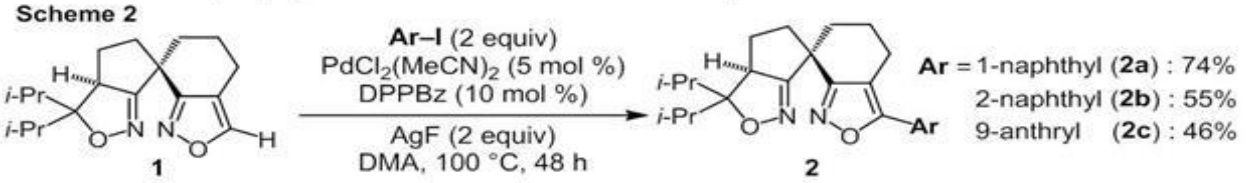
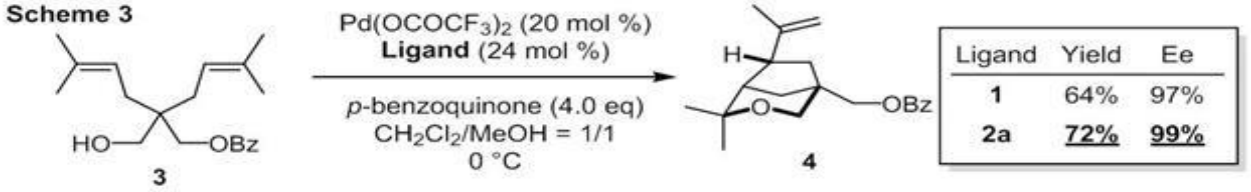
Scheme 1



Scheme 2



Scheme 3



Ligand	Yield	Ee
1	64%	97%
2a	**72%**	**99%**

P-286

Ruthenium-Catalyzed Tandem-Isomerization/Asymmetric Transfer Hydrogenation of Allylic Alcohols

PhD Student Tove Slagbrand[1], Mrs Helena Lundberg[1], Dr Hans Adolfsson[1]
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Poster Session 1

Catalysis is the best alternative for formation of many chemical compounds since it is possible to obtain both mild reaction conditions and high selectivity. Furthermore, it is possible to avoid large amounts of waste and by-products, which makes the transformations environmentally benign. Catalytic protocols are therefore a very good target for research, especially if many reaction steps can occur subsequently, e.g. in tandem reactions. These transformations are challenging and the benefits are formation of complex products that usually require many separate steps via formation and use of unstable intermediates that normally cannot be isolated and also, lower amounts of waste are formed.

We have recently developed an efficient protocol for the subsequent isomerization and asymmetric reduction of allylic alcohols into saturated and asymmetric alcohols in one step catalyzed by ruthenium. Both transformation steps, isomerization and transfer hydrogenation, are well studied but very little is reported on the combination of these two steps in a tandem reaction. Previously published protocols required high temperatures and long reaction times with little or no enantioselectivity.

In this work, the same transformation was investigated, however, with the use of a more active catalyst that allowed milder reaction conditions and yielded much higher enantioselectivity than previously reported. A substrate scope was evaluated and the result was published last year. This year, the group of Sowa reported similar result using Noyori´s catalyst.

P-287

Well-Defined and Robust Rhodium Catalysts for the Hydroacylation of Terminal and Internal Alkenes

Dr Maitane Fernandez[1], Dr Amparo Prades[1], Dr Sebastian D Pike[1], Prof Michael C Willis[1], Prof Andrew S Weller[1]

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Poster Session 1

The catalytic hydroacylation reaction between an aldehyde and alkynes or alkenes is an attractive, atom-efficient, route to ketones.[1] We have recently reported that small bite-angle rhodium phosphine complexes are efficient and selective catalysts for this type of reaction, allowing the coupling of terminal and activated–internal alkenes with β–substituted aldehydes.[2] However, challenging internal alkenes are still out of reach with this system. Thus, the objective of the work presented here is the development of new Rh-complexes that allow hydroacylation reaction with 1,1- and 1,2-disubstituted alkenes.

In this context, we have developed a new family of rhodium bis-phosphine complexes based upon asymmetric ligands $R_2PCH_2PR'_2$. These new complexes have shown high robustness for hydroacylation, allowing detailed mechanistic studies (rate, order and labelling studies) to further understand the reaction mechanism and the reasons behind the high activity and selectivity of these catalysts. Most importantly, the exceptional reactivity and consequent utility of these catalysts has also been demonstrated, by coupling β-substituted aldehydes to a wide scope of challenging internal, previously unusable, functionalized alkenes.

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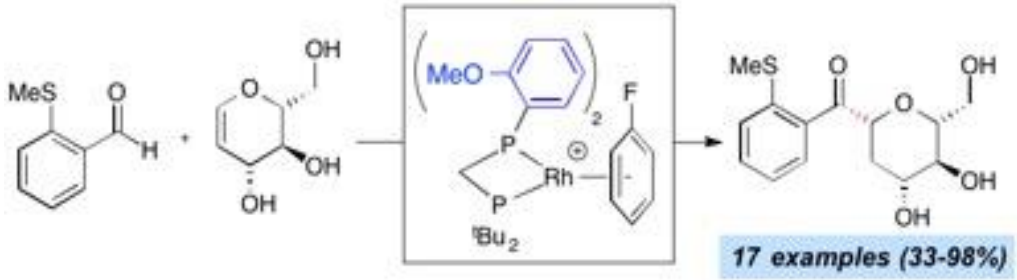

P-288

Synthesis of gamma-Lactams by Palladium(0)-Catalyzed C(sp3)–H Alkenylation

Mr. David Dailler[1], Dr. Phillip Holstein[1], Mr. Julien Vantourout[1], Mr. Janah Shaya[1], Pr. Olivier Baudoin[1]
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Poster Session 1

In the last decade, the transition metal-catalyzed intramolecular activation of unactivated C-H bonds has emerged as powerful method to transform otherwise inert entities[1]. Within this field, we developed a straightforward access to hexahydroindoles by intramolecular C(sp^3)-H alkenylation[2] and applied it to the total synthesis of marine natural products[3]. Recently, Cramer and co-workers described an enantioselective intramolecular C(sp^3)-H alkylation, allowing the synthesis of chiral γ-lactams[4].

In this communication, we will report the synthesis of γ-lactams which are prevalent scaffolds found in numerous bioactive natural molecules, by intramolecular C(sp^3)-H alkenylation from acyclic bromoalkenes. Starting from easily available C-H activation precursors, this new methodology allows to obtain a broad range of γ-lactams by modifications of groups R^1-R^4.[5]

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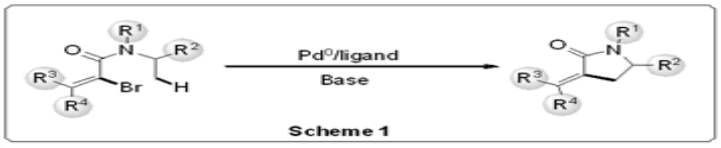

Scheme 1

P-289

Palladium Catalyzed Domino C - H Functionalization: Using all the Oxidation States

Mr Zafar Qureshi[1]
[1]*University of Toronto, Toronto, Canada*

Poster Session 1

The direct functionalization of C – H bonds has given chemists the ability to access to complex molecular scaffolds in a direct manner from simple building blocks. In the early 1990's Catellani reported the use of palladium and norborene in a multi-component domino process which selectively functionalizes the ortho C – H bond of an aryl iodide. This reaction is a rare example in which the transition metal cycles through 3 different oxidation states. Doubly functionalized aromatic compounds can also be accessed with a relatively simple palladium/triarylphosphine catalyst system. In the present work, combining an aryl iodide, an alkyl iodide and an olefin the core of the natural product (+)-linoxepin was synthesized. Following sequential cyclization reactions, the natural product was synthesized in 8 steps with an overall 30% yield. Varying the conditions for the final Heck reaction also led to a structural isomer of the natural product, iso-linoxepin. The expansion of this domino C – H functionalization methodology to include the use of more complex substrates will be also be presented. Using secondary alkyl iodides, the scope of this reaction was increased, allowing for a potentially expedient route to the ergot alkaloids.

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P-291

Facile Synthesis of o-Diborylarenes via C–H Borylation with a Removable Directing Group Attached on a Boron Atom

Ms Aoi Ishibashi[1], Dr. Takeshi Yamamoto[1], Prof. Michinori Suginome[1]
[1]*Kyoto Univ., Kyoto, Japan*

Poster Session 1

C–H borylation is one of the most efficient methods for the synthesis of arylboronic acid derivatives. In addition to the non-directed C–H borylation, increading attention has been focused on the directed C–H borylation, by which high site selectivity can be attained. From the viewpoint of application to organic synthesis, development of traceless and convertible directing groups for C–H borylation is highly desirable.

We have developed convertible directing groups B(pza) and B(aam), which are readily formed from a boronyl group ($B(OH)_2$) with 2-pyrazolylaniline ($pzaH_2$) and anthranilamide ($aamH_2$), respectively, for Ru-catalyzed directed C–H silylation. After directed o-C–H silylation, the PZA and AAM groups are easily removed to liberate reactive $B(OH)_2$ group for further functionalization. We herein report on the use of the B(pza) group as convertible directing group in iridium-catalyzed aromatic C–H borylation of organoboronic acid derivatives for the synthesis of o-diborylarenes. In the presence of $[Ir(OMe)(cod)]_2$, ortho-C–H boryaltion of PZA-masked arylboronic acids proceeded in high yields, giving various substituted 1,2-diborylarenes with high site selectivities.

Scheme 1. Directed C–H Borylation of PZA-Masked Arylbonic Acids

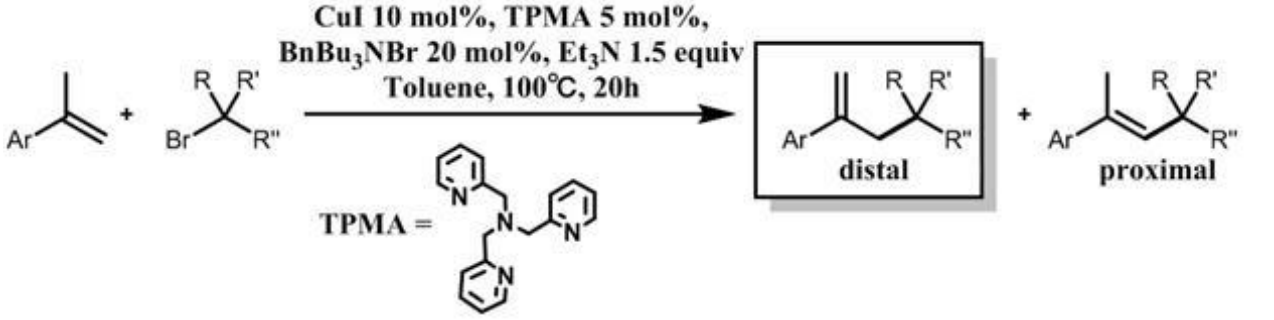
P-292

REGIOSELECTIVE DOUBLE BOND FORMATION IN COPPER - CATALYZED TERTIARY - ALKYLATIVE OLEFINATIONS

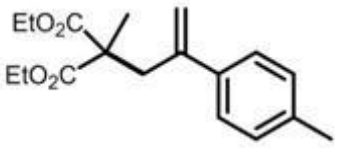
Mr Kimiaki Nakamura[1], Mr Kohei Itonaga[1], Dr. Shingo Ishikawa[1], Dr. Takashi Nishikata[1]
[1]*Yamaguchi University, Ube, Japan*

Poster Session 1

Mizoroki-Heck (M-H) reaction is one of the most useful reactions of all metal catalyzed organic reactions. In the M-H reaction with alpha-alkylated olefins, there are two possible pathways for beta-hydride elimination, i.e., those in which the proximal hydrogen atom or the distal hydrogen atom with respect to the newly formed C–C bond. The M-H reaction generally tends to give olefin possessing an internal double bond (proximal selectivity). To obtain distal selectivity in the reaction of organic halides and olefins, a radical reaction is one of the most promising reactions. During the course of our continuous radical study, we found that the reaction of alpha-bromocarbonyl compounds and alpha-alkyl styrenes in the presence of Cu(I)-TPMA catalyst undergoes distal-selective oelfinations.1 In this presentation, we will discuss on details of this reaction.



Products / Yields (proximal : distal)



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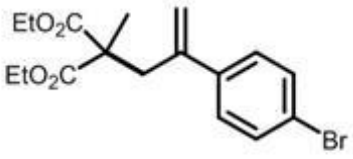

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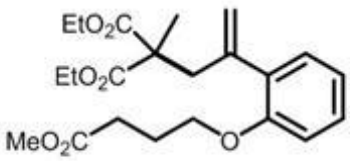

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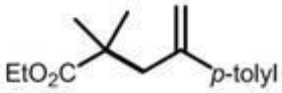

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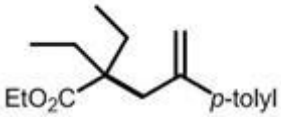

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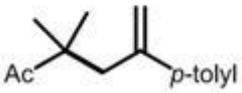

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Scheme 1. Distal-selective olefinations.

P-293

COPPER-CATALYZED TERTIARY-ALKYLATION OF STYRENES

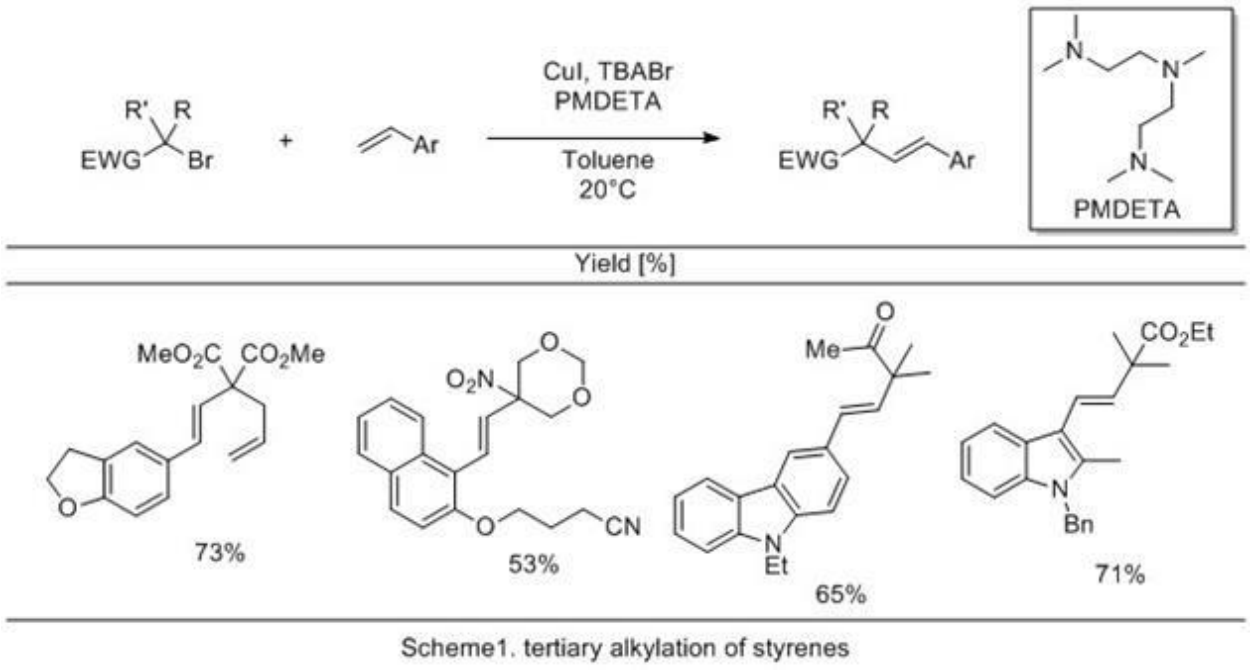
Mr Yushi Noda[1], Mr Ryo Fujimoto[1], Dr Takashi Nishikata[1]
[1]*Graduate School of Science and Engineering, Yamaguchi University, ube, Japan*

Poster Session 1

The substitution of terminal carbon–carbon double bond with tertiary-alkyl group is one of the most difficult reactions in synthetic organic chemistry due to the bulkiness of tertiary-alkyl group. Although significant new reactions have been developed, tertiary alkylation chemistry in the presence of a transition-metal catalyst has not been well developed.

Recently we found that a copper-triamine complex is an excellent catalyst for the tertiary alkylation of styrenes under mild conditions with an α-bromocarbonyl compunds possessing a ketone, ester, or nitro group (Scheme 1).

In this presentation, we will discuss on details of our reaction.



Scheme1. tertiary alkylation of styrenes

P-294

Approaches for Developing Ligand Scaffolds of Non-Heme Fe and Mn Catalysts

Carlota Clarasó[1], Dr. Miquel Costas[1], Dr. Alfons Polo[1]
[1]*Departament de Química, Facultat de Ciències, Universitat De Girona, Girona, Spain*

Poster Session 1

The selective oxofunctionalization of hydrocarbons is an important goal in synthetic organic chemistry, because of their inert nature.[1] Selective oxidation of C-H and C=C moieties with excellent levels of region and stereocontrol is accomplished in Nature through oxygenase enzymes. Mimicry of structural aspects of enzyme active sites by synthetic transition metal complexes is regarded as a promising strategy to develop C-H and C=C oxidation catalysts.[2]

Non-heme iron and manganese based catalysts have been developed as promising systems for enzymatic oxidation processes; some of them can catalyze oxidative reactions by metal centered mechanisms, avoiding radical pathways. [3] The complexes that use N4-donor aminopyridine ligands are shown as one of the most successful catalysts for chemo-, regio- and enantioselective transformations of organic substrates with peroxide type of oxidants.

With this knowledge in mind, we aim at widening the structural versatility of those ligands. So, in this work, we focus on the elaboration of various diamines employed as backbones for these N4-donor ligands, being different from the usual used ones (Figure 1).

To understand their reactivity there were tested in some basic C-H and C=C oxidative catalysis. We hope that this structural versatility will allow us to extend the reactivity and to modify the selectivity of these catalysts.

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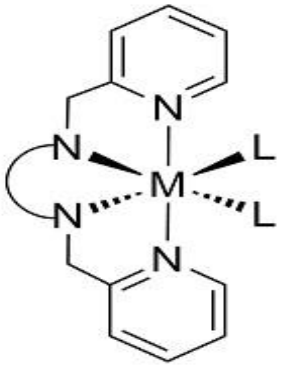


P-296

OXYGEN ACTIVATION OF pinB-SePh AND pinB-SPh ON EPOXIDES AND BICYCLIC COMPOUNDS

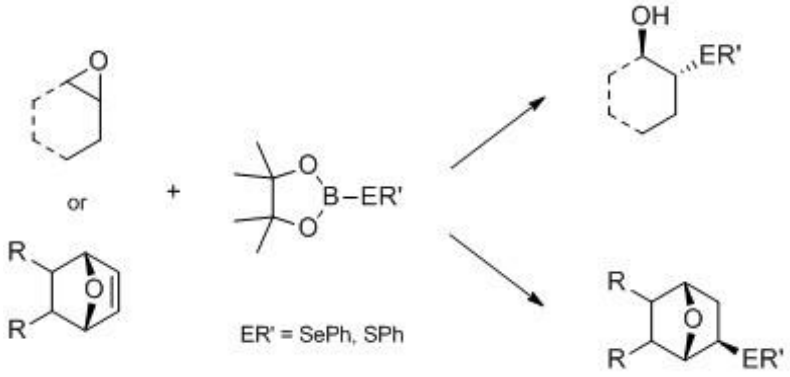
Xavier Sanz[1,2], Mr. Christopher M. Vogels[3], Prof. Carles Bo[2], Prof. Stephen A. Westcott[3], Dr. Elena Fernández[1]

[1]Universitat Rovira i Virgili, Tarragona, Spain, [2]Institute of Chemical Research of Catalonia, Tarragona, Spain, [3]Mount Allison University, Sackville, NB, Canada

Poster Session 1

The activation of pinB-SePh and pinB-SPh by α,β-unsaturated carbonyl compounds has made possible the synthesis of β-seleno[1] and β-sulfido[2] carbonyl compounds in a metal-free context at room temperature.

Now, we describe the first attempt to activate pinB-SePh and pinB-SPh by oxygen in epoxides and bicyclic substrates (Scheme 1). DFT-based mechanistic proposals unveiled that the B-O interaction plays a key role in the activation of the reagent and enhances the nucleophilic character of the SePh and SPh moieties.



Scheme 1

[1] X. Sanz, C. M. Vogels, A. Decken, C. Bo, S. A. Westcott, E. Fernández, Chem. Commun., 2014, 50, 8420.
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P-297

Expanding the substrate scope for the β-borylation reaction: homoallylic boronate ester derivatives.

Alba Pujol Santiago[1], Andy Whiting[1], Elena Fernández[2]
[1]*Durham University, Durham, UK* , [2]*Universitat Rovira i Virgili, Tarragona, Spain*

Poster Session 1

Establishing new catalytic enantioselective approaches to chiral molecules is an important goal for organic chemists. Our group has been developing methodologies for the conjugate addition of boryl nucleophiles into α,β-unsaturated aldehydes 1 via imines 2 (Scheme 1).

Scheme 1 General overview of the conjugated addition of boron into α,β-unsaturated aldehydes via amine-derived imines.

Herein an enantioselective one-pot methodology leading to homoallylic boronate 5 was established. In this report, we evaluate compound 5 as a platform for the synthesis of multifunctional chiral compounds by the introduction of a second boryl unit (Scheme 2).

Scheme 2 Synthesis of homoallylic boronate 5 and subsequent β-borylation.

P-298

DIASTEREOSELECTIVE CARBENOID INSERTION INTO UNSYMMETRICAL DIBORON SPECIES

Dra. Ana Belén Cuenca González[1], Dra. Jessica Cid[1], Mr. Diego García[1], Dr. Jorge J. Carbó[1], Dra. Elena Fernández[1]

[1]*Universitat Rovira I Virgili, Tarragona, Spain*

Poster Session 1

1,1-Diborylalkanes are attracting the attention of synthetic researchers since Shibata and co-workers demonstrated in 2010 that two consecutive Suzuki-Miyaura cross-coupling (SMC) reactions can be performed in a chemo and regiospecific manner, even at room temperature.[1] The unsymmetrical formation of 1,1-diborylalkane compounds has elegantly been performed by the groups of Hall[2] and Yun[3] through copper mediated asymmetric borylation of β-boronylacrylates and copper mediated asymmetric hydroboration of borylalkenes, respectively. Here we describe a new access to multisubstituted sp3-carbon through 1,1-diboration of ketones and aldehydes by means of mixed diboron reagents. We could locate a transition state for the formation of the two carbon-boron bonds that indicates the occurrence of a concerted, yet asynchronous, mechanism.

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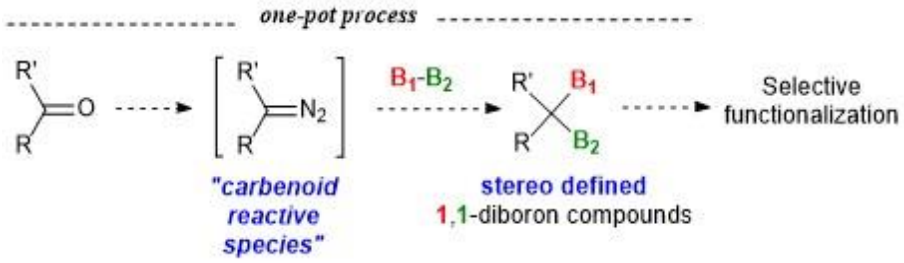

P-299

Studies Towards the Total Synthesis of Microsclerodermin B: Application of Organometallic Chemistry in the Synthesis of Unusual Amino Acids.

Miss Ekaterina Melikhova[1], Mr Robert Pullin, Prof Timothy Donohoe
[1]*University of Oxford, Oxford, UK*

Poster Session 1

The microsclerodermins are a family of macrocyclic hexapeptides isolated from lithistid marine sponges Microscleroderma and Theonella. Microsclerodermin B has a complex molecular structure featuring four unusual amino acid residues: a tryptophan derivative (Trp-2-CO2H), a γ hydroxy γ lactam core (Pyrrolidinone), the γ amino α hydroxybutanoic acid unit (GABOB) and a chiral polyhydroxylated β amino acid (AMMTD).

The most complex of these is the AMMTD fragment 5, which possesses five contiguous stereocentres and an aliphatic side-chain. The key step in construction of AMMTD – introduction of the aminohydroxyl moiety at C2 and C3 –could be achieved via a diastereoselective osmium catalysed tethered aminohydroxylation reaction (TA), which was previously developed in the Donohoe group. The other two hydroxyl groups in the amino acid were introduced by a Sharpless asymmetric dihydroxylation reaction. The side chain was installed using a cuprate displacement reaction with subsequent cross metathesis to introduce the styrene moiety.

In order to assemble the northern hemisphere of microsclerodermin new efficient strategies to prepare 2 tryptophan carboxylate 8 and the pyrrolidinone core 11 were developed. The tryptophan derivative 8 was synthesised using the Negishi coupling of iodoalanine with the corresponding indole bromide 7, whilst the pyrrolidinone amino acid 11 was synthesized using the Blaise reaction as a key step. This latter step involved formation of an organozinc compound from tert-butyl bromoacetate, followed by addition to the nitrile 10.

All six amino acids were coupled using various peptide coupling procedures, delivering the linear hexapeptide 12, which was subsequently converted into the fully protected cyclic peptide 13.

Thus far protecting group cleavage has proved to be challenging. After extensive investigations the protecting group strategy has been carefully designed and research towards global deprotection is currently ongoing. Following this, introduction of the hydroxyl group at the C44 position will complete microsclerodermin B.

P-300

Synthesis of Ethene-bridged Terthiophenes via Double Sonogashira Cross-Coupling and Sequential Cyclization

Dr. Koichi Mitsudo[1], Hidehiko Sato[1], Jun Goto[1], Arata Yamasaki[1], Prof. Seiji Suga[1]
[1]*Okayama University, Okayama, Japan*

Poster Session 1

Thienoacenes, which are acene derivatives that contain sulfur atoms, have received considerable attention as potent components for use in organic materials such as organic field effect transistors, and the syntheses and properties of numerous thieno-acenes have been reported. One of the key skeletons of these thienoacenes is benzodithiophene (BDT). Several kinds of thienoacenes containing BDT skeletons have been reported.

We recently reported the first synthesis of tetrabromoterthiophene and its conversion to nitrogen-bridged terthiophenes by tandem Buchwald–Hartwig coupling reactions.[1] During the course of this study, we also developed an efficient synthetic method for preparing multi-brominated terthiophenes by regioselective Negishi coupling. We next turned our attention to the use of these brominated terthiophenes for the synthesis of other fused terthiophenes, and especially focused on ethene-bridged terthiophene (EBTT). To the best of our knowledge, there has been only one previous report on the synthesis of EBTT by flash vacuum pyrolysis[2] and there is no convenient approach to EBTT skeletons under mild conditions. Moreover, their electrochemical and optical properties have not been characterized.

This prompted us to develop a method for the facile synthesis of EBTTs. We report here a novel and facile method for synthesizing EBTT and its derivatives.

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(2) Imamura, K.; Hirayama, D.; Yoshimura, H.; Takimiya, K.; Aso, Y.; Otsubo, T. Tetrahedron Lett. 1999, 40, 2789–2792.

P-301

Turn-‘ON’ Fluorescent Chemosensor for Al3+ Ion in Aqueous alcoholic Medium: Reversible Breaking and Formation of Spirolactum Bond

Turn-‘on’ Fluorescent Chemosensor for Al3+ Ion in Aqueous Alcoholic Medium: Reversible Breaking and Formation of Spirolactum Bond Nabanita Chatterjee[1], Turn-‘on’ Fluorescent Chemosensor for Al3+ Ion in Aqueous Alcoholic Medium: Reversible Breaking and Formation of Spirolactum Bond Parimal K. Bharadwaj[1]
[1]*Indian Institute of Technology Kanpur, Kanpur, India*

Poster Session 1

Design and synthesis of molecular probe that can recognize biologically important and environmentally relevant metal ions have been attributed significant interest during last few decades due to its wide-ranging applications in chemosensing and bio-imaging.[sup]i The increasing concentration of free Al3+ in the environment and surface water via acid rain not only hamper the growth of plants but also can perturb many biological functions.[sup]ii Unconscionable accumulation of Al3+ can cause potential toxicity leading to neurological disorders such as Parkinson’s disease, Alzheimer’s disease etc.[sup]iii Therefore, detection of Al3+ ion is essential due to its potential impact on environment and human health. Towards this goal, we have synthesized few rhodamine based fluorescent probes those can provide selective recognition of Al3+ ion in aqueous alcoholic medium even at very low concentration.[sup]iv Our design criteria based on a rhodamine dye for its excellent photophysical properties of large molar extinction co-efficient, high emission quantum yield value with visible excitation and emission profiles.[sup]v Rhodamine derivatives are colourless and non-fluorescent in the acyclic xanthene form, whereas spirolactum ring opening induced by the Al3+ ion causes significant enhancement in fluorescence response along with visual change from colorless to pink that allows its detection through chromogenic pathway as well.

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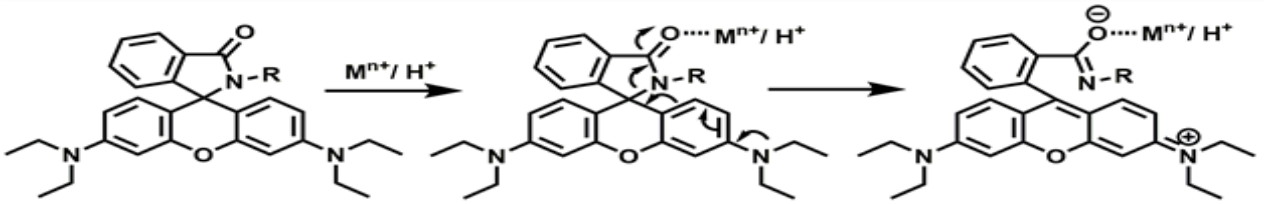

Colourless

Fluorescent Pink red colour

R = Receptor molecule

M^{n+}= Metal ion (Al^{3+})

P-302

One-Pot Synthesis of Highly Substituted Pyrroles via Linear-Selective Rhodium-Catalysed Hydroacylation

Miss Manjeet Majhail[1], Prof. Michael Willis[1]
[1]*University of Oxford, Oxford, UK*

Poster Session 1

Due to the importance of pyrroles we have chosen to investigate the synthesis of these ring systems in an experimentally straightforward fashion, which enables the direct installation of useful functionality. Rhodium-catalysed hydroacylation has proven itself to be a valuable synthetic tool, especially when preparing intermediates for heterocycle synthesis.[1] It employs simple substrates in a wholly atom-economical manner to catalytically construct enones or ketones.[2] This work looks at expanding the substrate compatibility of intermolecular hydroacylation to couple functionalised propargylic amines with β-sulfur tethered aldehydes in a novel pyrrole synthesis. Initial reactions showed that this coupling lacked regiocontrol (typically 2:1 linear: branched). Consequently, with the use of small-bite-angle, electron-rich ligands, we have achieved dramatically enhanced regioselectivity and efficiency. The resultant linear γ-amino enones can undergo a quantitative dehydrative acid-catalysed cyclisation in the same pot to afford functionalised pyrroles. Pleasingly, this hydroacylation-cyclisation cascade achieves excellent yields with low catalyst loadings (e.g. 1 mol%) under ambient conditions. Once this method was established, we expanded the methodology to the synthesis of 2,3-dihydropyrroles using allyl amines as the coupling partner. Further diasteroselective reductions of these products can form useful pyrrolodines in good yields. In conclusion, we have demonstrated that functionalised propargylic/ allylic amines can undergo regioselective Rh-catalysed hydroacylation in the one-pot synthesis of tri- or tetra-substituted pyrroles/dihydropyrroles.

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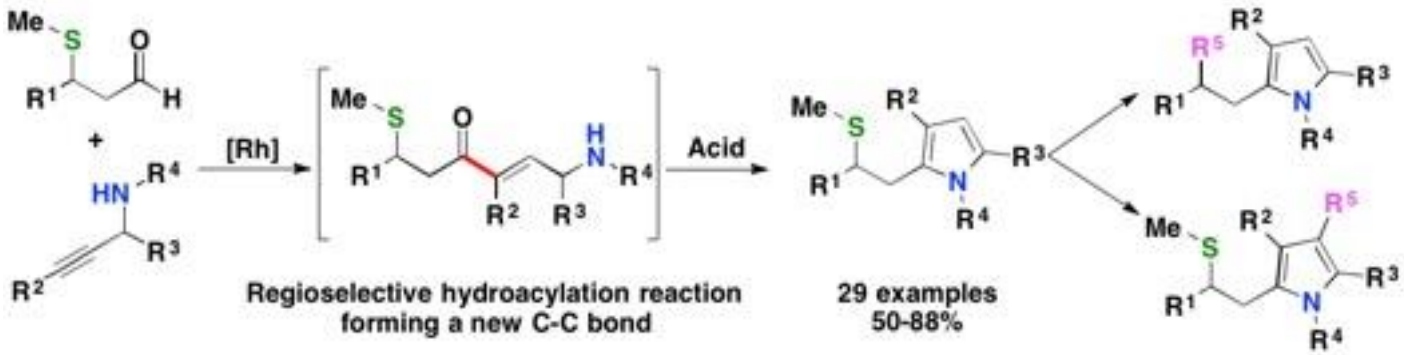

P-304

YNONES ACTIVATE ArS-Bpin AND PhSe-Bpin TO SYNTHESIZE α-KETO VINYL SELENIDES AND SULFIDES

Mr Marc G. Civit[1], Mr Xavier Sanz[1,2], Mr Christopher M. Vogels[3], Prof. Carles Bo[2], Prof. Stephen A. Westcott[3], Prof. Elena Fernández[1]

[1]*Universitat Rovira I Virgili, Tarragona, Spain,* [2]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*
[3]*Mount Allison University, Sackville, Canada*

Poster Session 1

We have previously reported the addition of selenodioxaborolanes(1) and thiodioxaborolanes(2) to α,β-unsaturated carbonyl compounds. Due to the synthetic importance of vinyl selenides(3) and vinyl sulfides(4) in organic chemistry, we became interested to explore the face to face activation of PhSe-Bpin and ArS-Bpin by α,β-acetylenic ketones. The Lewis acid-base interaction between the carbonyl and the Bpin moiety favours the stereoselective formation of the Z-isomer at 50ºC without any additives. This mechanism is supported by DFT calculations.

References:
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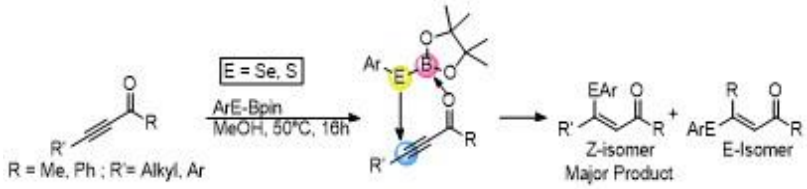

P-305

Silicon-Tethered Strategy for Regio- and Stereoselective Alkylboration of Unsymmetrical Alkynes with Copper(I) Catalyst

Silicon-Tethered Strategy for Regio- and Stereoselective Alkylboration of Unsymmetrical Alkynes with Copper(I) Catalyst Hiroaki Iwamoto[1], Koji Kubota[1], Eiji Yamamoto[1], Hajime Ito[1]

[1]*Faculty of Engineering, Frontier Chemistry Center, Hokkaido University, Sapporo, Japan*

Poster Session 1

Copper(I)-catalyzed carboboration of alkyne with carbon electrophile is an efficient synthetic method for construction of multisubstituted alkenes. Recently, the copper(I)-catalyzed carboboration with various carbon electrophiles such as allyl and benzyl halides as well as carbon dioxide have been reported. However, the reactions with unactivated alkyl halides required long reaction times due to the low reactivity. Furthermore, the low regioselectivity was observed for the carboboration of unsymmetrical alkynes.

In this study, we employed the silicon-tethering strategy to achieve high reactivity and regioselectivity. This strategy has two advantages. Intramolecular reaction mode can improve the reactivity, and the electronic effect of silyl group can control the regioselectivity. The product in this strategy can be considered as a formal intermolecular alkylboration of product because the silicon-tethering group can be readily removed through derivatization reactions. Therefore, we designed and synthesized the alkyne substrates connecting with an unactivated alkyl halide through a silicon-tether moiety (Kubota, K.; Iwamoto, H.; Yamamoto, Y.; Ito, H. Org. Lett. 2015, 17, 620.).

We performed a copper(I)-catalyzed intramolecular alkylboration of the silicon-tethered alkynes in the presence of copper chloride(I)/ligand (5 mol %) as the catalyst with stoichiometric amounts of bis(pinacolato)diboron and K(O-t-Bu) (1.2 equiv) in THF at 50 ºC. Ligand screening experiments showed that the reaction using IMes•HCl gave the corresponding cyclization product containing 1,2-silylboryl alkene moiety in a quantitative yield with excellent regio- and stereoselectivity (99%, Z/E = >99:1). Next, we subjected various silicon-tethered alkyne substrates to the intramolecular alkylboration. The reaction showed high functional group tolerance and afforded the corresponding products containing silyl ether, alkyl chloride, acetal, and ether group in good yields with perfect regio- and stereoselectivity (42–98%, Z/E = >99:1). Moreover, we successfully transformed the cyclization product to the tetrasubstituted trans-stylbene derivatives through cross-coupling sequence and ring opening functionalization using silyl and boryl groups.


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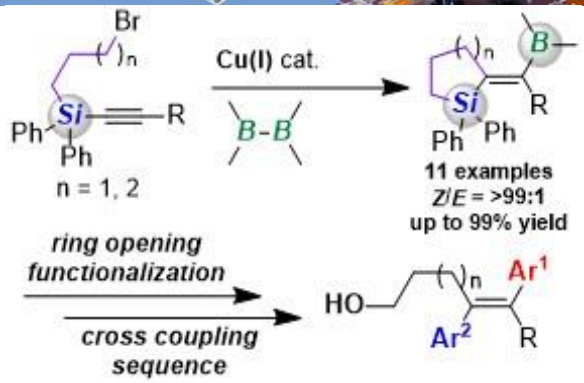
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11 examples
Z/E = >99:1
up to 99% yield
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functionalization
cross coupling
sequence
HO
Ar1
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P-306

Nickel-Catalyzed Carboxylation of Alkynes Using Sulfur-Modified Au-Supported Nickel Nanoparticles Catalyst (SANi)

Mr. Takahisa Taniguchi[1], Dr. Nozomi Saito[1], Dr. Naoyuki Hoshiya[1], Dr. Katsumasa Fujiki[2], Dr. Satoshi Shuto[1], Dr. Tetsuo Honma[3], Dr. Hiromichi Fujioka[2], Dr. Mitsuhiro Arisawa[2,4], Dr. Yoshihiro Sato[1,4]

[1]Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, Japan, [2]Graduate School of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Japan, [3]Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Japan, [4]ACT-C, Japan Science and Technology Agency (JST), Sapporo, Japan

Poster Session 1

Supported transition metal nanoparticle catalysts have received much attention as low-leaching, recyclable metal sources, the nature of which is useful for the synthesis of various pharmaceuticals and fine chemicals. Although the utilization of Pd nanoparticles (NPs) catalysts for C-C bond forming reactions has been widely investigated, the example of other NPs of earth-abundant metals such as Ni are still limited. Recently, we have succeeded in developing a sulfur-modified Au-supported Pd material (SAPd) and applied to various cross-coupling reactions.[sup]1,2[/sup] SAPd is very practical as an immobilized Pd NPs catalyst with respect to both remarkably low leaching level and highly recyclable character.

Herein, we report a novel sulfur-modified Au-supported Ni material (SANi). According to the similar method for preparation of SAPd, SANi was prepared by treatment of a sulfur-modified Au mesh and $Ni(acac)_2$ as a Ni source in the presence of 4-$MeOC_6H_4CH_2$

sub]OH (15 equiv. to Ni) as a reductant in Me_4-benzene at 200 °C. The Ni-K edge X-ray absorption fine structure (XAFS) of the SANi suggested that the zero-valent Ni NPs was immobilized on the surface of Au.

Next, we investigated the reactivity of SANi in carboxylation of alkyne with CO_2.[3] When diphenylacetylene (1) was treated with $ZnEt_2$ in the presence of SANi in [sup]n[/sup]PrCN at 100 °C for 24 hours under closed CO_2 atmosphere, the corresponding acrylic acid ester 2 was obtained in 88% yield after the acidic workup followed by methylation.

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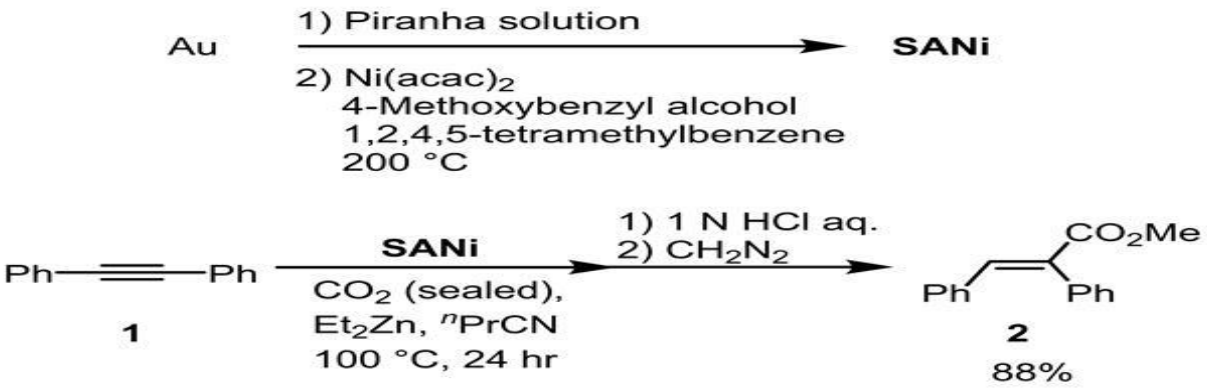
Au
1) Piranha solution
2) Ni(acac)2
4-Methoxybenzyl alcohol
1,2,4,5-tetramethylbenzene
200 °C
SANi
Ph
Ph
1
SANi
CO2 (sealed),
Et2Zn, nPrCN
100 °C, 24 hr
1) 1 N HCl aq.
2) CH2N2
CO2Me
Ph
Ph
2
88%

P-307

Hydrogenation of Carbon Dioxide to Formate Catalyzed by Copper Complexes

Master Ryo Watari[1], Dr. Yoshihito Kayaki[2], Dr. Shin-ichi Hirano[1], Dr. Norio Matsumoto[1], Dr. Takao Ikariya[2]
[1]Central Research Institute of Electric Power Industry, Abiko-shi, Japan, [2]Tokyo Institute of Technology, Meguro-ku, Japan

Poster Session 1

The catalytic hydrogenation of CO_2 to formate has attracted attention as a potential method for synthesizing a hydrogen energy carrier. Although homogeneous catalysts, such as Ir complexes, have taken a significant role in the hydrogenation,[1] earth-abundant metal catalysts have recently emerged. In this context, Cu complexes have not been thoroughly investigated in the formate synthesis, whereas several Cu–phosphine complexes have been applied to catalytic hydrogenation of ketones. In this presentation, we evaluate the utility of Cu complexes for the hydrogenation of CO_2 to formate salts.[2]
As shown in Scheme 1, we have found the catalytic hydrogenation of CO_2 was promoted by using Cu salts such as CuOAc and $Cu(OAc)_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. Among a range of guanidine and amidine bases, DBU was most effective for the formate formation, and extra ligands are not required for the Cu/DBU system. Notably, treatment of CuI with DBU (3 equiv) in CH_3CN provided a mononuclear Cu–DBU complex which also served as the hydrogenation catalyst with a turnover number comparable to those of the Cu salt system, indicating that DBU acts as a ligand as well as a base in the Cu/DBU system. The mechanistic aspects of the Cu/DBU system will also be discussed.

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P-308

Palladium(II)-Catalyzed Selective 1, 4-Addition of Arylboronic Acids to Linear α, β, γ, δ-Unsaturated Ketones

Mr Kennard Gan[1]
[1]*Nanyang Technnological University, Singapore, Singapore*

Poster Session 1

We describe the regio-specific, asymmetric 1, 4-addition of arylboronic acids onto linear α, β, γ, δ-unsaturated ketones catalyzed by a phosphapalladacycle catalyst. This methodology proved to be robust toward a variety of diversified polyconjugated ketones and arylboronic acids, with yields of up to 94 % and ee of up to 99 % obtained.

P-309

Nickel-Promoted Carboxylation of Alkenes: Synthesis of Acrylic Acid Derivatives

Mr. Naoya Awaji[1], Mr. Naoto Taguchi[1], Dr. Nozomi Saito[1], Mr. Takahisa Taniguchi[1], Dr. Yoshihiro Sato[1,2]
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Poster Session 1

Carbon dioxide (CO_2) is an abundant, cheap and relatively non-toxic C1 unit in synthetic organic chemistry. Recently, transition metal-promoted carboxylation of various organic compounds has attracted much attention, and various types of reaction have been reported. In particular, nickel(0) complexes have been widely employed for the synthesis of carboxylic acid from carbon-carbon unsaturated compounds and CO_2.[sup]1)[/sup] We herein report nickel-promoted carboxylation of alkenes for the synthesis of acrylic acid derivatives.[sup]2)[/sup] First, the reaction of 4-methoxystyrene (1) as a substrate and CO_2 (10 atm) was carried out in the presence of $Ni(cod)_2$ (1 equiv) and ligand 2 (1 equiv) in $C_6H_5CF_3$ (Scheme 1, eq 1). After acidic work-up with HCl/Et_2O followed by methylation, saturated ester 4 and α,β-unsaturated ester 5 were obtained in 48% yield and in 31% yield, respectively. This result indicated that nickelalactone 3 was formed in a regioselective manner via oxidative cycloaddition of 1 and CO_2 to nickel(0) complex. On the other hand, when the reaction of 1 and CO_2 with nickel(0) complex in the presence of $MgBr_2$ was carried out, transmetallation between 3 and $MgBr_2$ followed by β-elimination from the resultant 6 occurred to give 5 in 72% yield as a sole product (eq 2). Further studies to establish a catalytic cycle as well as to expand the scope of alkene substrates are in progress.

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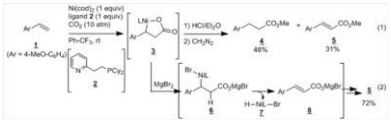
2) For very recent examples, see: a) Vogt, D. et al. Chem. Eur. J. 2014, 20, 12037. b) Limbach, M. et al. Chem. Eur. J. 2014, 51, 16858.



P-310

Room-temperature Oxidative Trifluoromethylation of Copper Acetylides : Practical Synthesis of Trifluoromethylated Alkynes

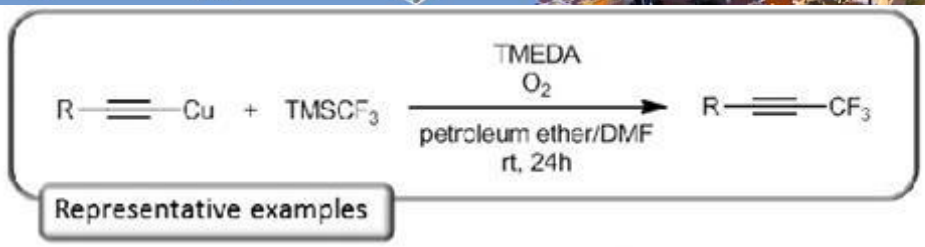
Céline Guissart[1], Prof. Gwilherm Evano[1]
[1]*Université Libre De Bruxelles, Bruxelles, Belgium*

Poster Session 1

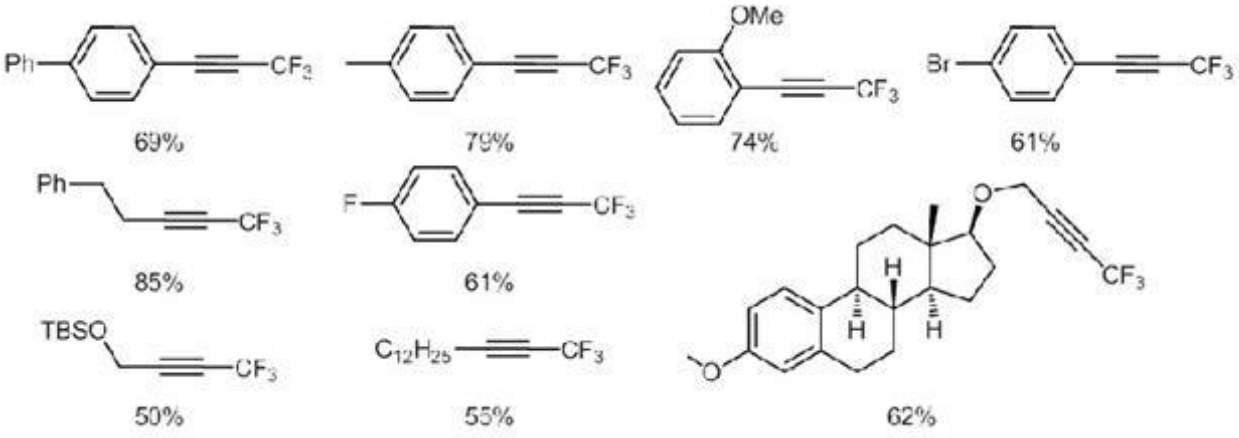
The introduction of fluorine atoms within organic molecules allows to deeply modify their properties, including lipophilicity, bioavailability, metabolic stability or even their recognition towards receptors. For this reason, numerous compounds from the pharmaceutical and agrochemical industries possess at least one fluorine atom. Among emerging fluorinated groups in organic chemistry, trifluoromethylated alkynes are especially interesting and have been underestimated so far, despite their huge potential. This organofluorinated group can also be found in various bioactive compounds displaying for example anticancer or fungicide properties.

Despite their apparent simplicity, trifluoromethylated alkynes are quite difficult to prepare and the development of new methods allowing an easy access to these building blocks is therefore an important topic in organic chemistry. Based on our experience with unreactive, bench stable and readily available copper acetylides that can be activated under mild oxidizing conditions and act as especially reactive electrophilic alkyne transfer agents, we envisioned that they could be especially suitable reagents for the development of a general and user-friendly entry to trifluoromethylated alkynes.

In the presence of TMEDA and molecular oxygen, we have demonstrated that copper acetylides indeed readily react with the Ruppert-Prakash reagent $TMSCF_3$ at room temperature, yielding the corresponding trifluoromethylated alkynes in good yields without the need for other additives (fluoride, base) typically required in related reactions. The development of this process, its scope and limitations will be discussed.



Representative examples



P-311

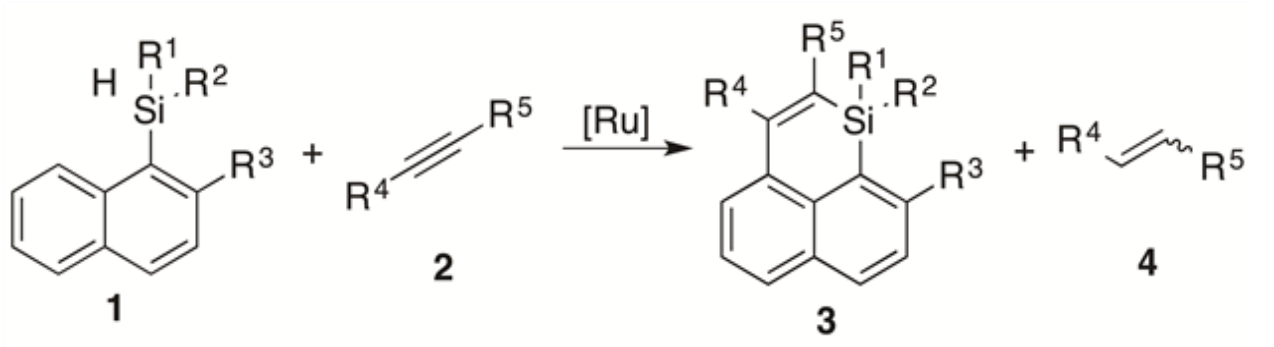
Synthesis of Silaphenalenes via Ruthenium-catalyzed C–H Cleavage of 1-Naphthylsilanes

Dr. Yuichiro Tokoro[1], Mr. Kengo Sugita[1], Dr. Shin-ichi Fukuzawa[1]
[1]*Chuo University, Kasuga, Bunkyo-Ku Tokyo, Japan*

Poster Session 1

Silicon-containing π-conjugated molecules are useful for electron accepting materials and for precursors to more complicated π-conjugated systems. The π-conjugated organosilicons were usually prepared by lithium reagents or transition metal-catalyzed cyclization. Recently, cyclization reactions through C–H activation have been developed, and hydrosilyl groups sometimes worked as directing groups.

This presentation will report ruthenium-catalyzed annulation between 1-naphthylsilanes and alkynes through silyl-directed C–H activation to afford silaphenalenes. Scope of substituents on the silicon revealed that the phenyl group increased the yield of the silaphenalene as compared with alkyl groups. The methyl group on 2-position of the naphthalene ring was also improved the yield without activation of sp^3 C–H bonds. Various diphenylacetylenes with electron-donating or -withdrawing group were tolerated in this reaction.



P-312

Aromatic C-H activation in the excited state of cyclometalated platinum(II) complexes using visible light

MSc Fabio Juliá[1], Dr Pablo González-Herrero[1]

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Poster Session 1

The photochemically initiated activation of C-H bonds by transition metal complexes usually requires irradiation with UV light, which causes the dissociation of a neutral ligand and generates a vacant coordination site. This facilitates the coordination and subsequent cleavage of the C-H bond,[1] but the process takes place in the electronic ground state.

Pt(II) complexes with heteroaromatic ligands have been extensively studied because of the wide technological applicability of their luminescence, which usually arises from a triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state.[2] However, there are only a few studies on their photochemistry, which have shown that the 3MLCT state can initiate the oxidative cleavage of the C-X bond in alkyl halides.[3]

In this communication, we present the synthesis of bis-cyclometalated Pt(II) complexes, [Pt(C^N)$_2$], by irradiating precursors of the type [PtMe(C^N)(HC^N)] (HC^N = 2-(2-phenyl)pyridine and related ligands) with visible light at room temperature. These reactions cannot be accomplished thermally. Experimental data and computational calculations indicate that the C-H activation proceeds through a stepwise oxidative addition in the excited state initiated by ^{3}MLCT population of the Pt(II) precursors to give a platinum(IV) hydride intermediate. This mechanism has no precedent in metal-mediated C-H activations.

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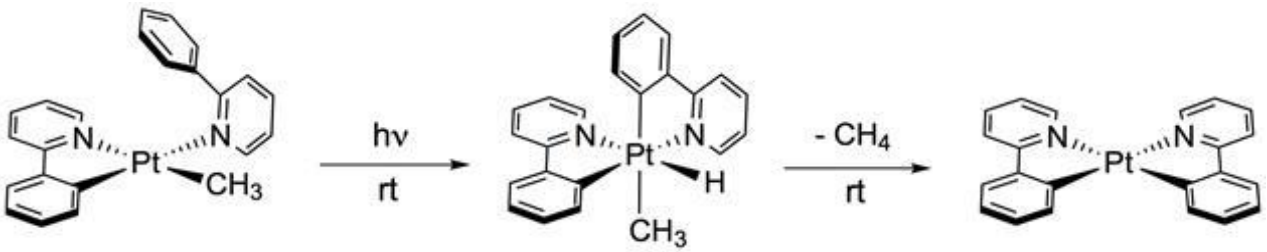

P-313

Asymmetric hydroboration of 1,1-disubstituted alkenes with simple phosphite-based PHOX iridium catalysts

Mr Marc Magre[1], Ms Maria Biosca[1], Mr Oscar Pàmies[1], Ms Montserrat Diéguez[1]
[1]*Universitat Rovira i Virgili, Tarragona, Spain*

Poster Session 1

Chiral organoboron compounds have received a great deal of attention lately.[1] They are valuable organic intermediates because the C-B bond can be readily transformed to chiral C-N, C-O and C-C bonds.[2] The synthesis of these compounds by transition-metal catalyzed asymmetric hydroboration is attracting considerable interest. However, whereas the asymmetric hydroboration of monosubstituted olefins (i.e., styrenes) and internal 1,2-disubstituted olefins (i.e., norbornadiene) has been well studied, the hydroboration of 1,1-disubstituted olefins remains a challenge (Scheme 1). [3]

We have identified [4] a readily simple phosphinooxazoline-based phosphite-oxazoline catalytic system that can hydroborate 1,1-disubstituted aryl olefins with high enantioselectivity (up to 94%), excellent yields and perfect regioselectivity. A broader range of olefins, containing α-tert-butylstyrenes with aryl substitutents with different electronic and steric properties, have been effectively hydroborated, compared to previous phosphinooxazoline ligands.[3a] This work complements previous results with N-heterocyclic copper catalysts [3b], the only other system reported to date that has achieved these reactions.

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Figure 1. Iridium-catalyzed asymmetric hydroboration of 1,1-disubstituted alkenes

P-314

SYNTHESIS AND ACTIVITY OF RUTHENIUM COMPLEXES CONTAINING QUINONE MOIETY

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Poster Session 1

Olefin metathesis is a commonly utilized technique of C-C double bond formation which enables the synthesis of numerous molecules under mild conditions. This methodology is very useful, however it still finds limited applications in organic synthesis because of some significant drawbacks.[1] One of them is isomerization of olefins which can drastically decrease the yield of the desired product by formation of mixtures of isomers. Over the past years, researchers developed some new methods that prevent this undesired side-process. One of the most commonly used method is addition of quinones to the reaction mixture.[2]
In our work we have developed new olefin metathesis complexes which contain quinone moiety as well as investigating their activity and influence on isomerization process.

Figure 1. Possible reactions of linear alkenes in the presence of a metathesis catalyst.

Acknowledgement:
This work has been supported by NCN, 2011/03/D/ST5/06079

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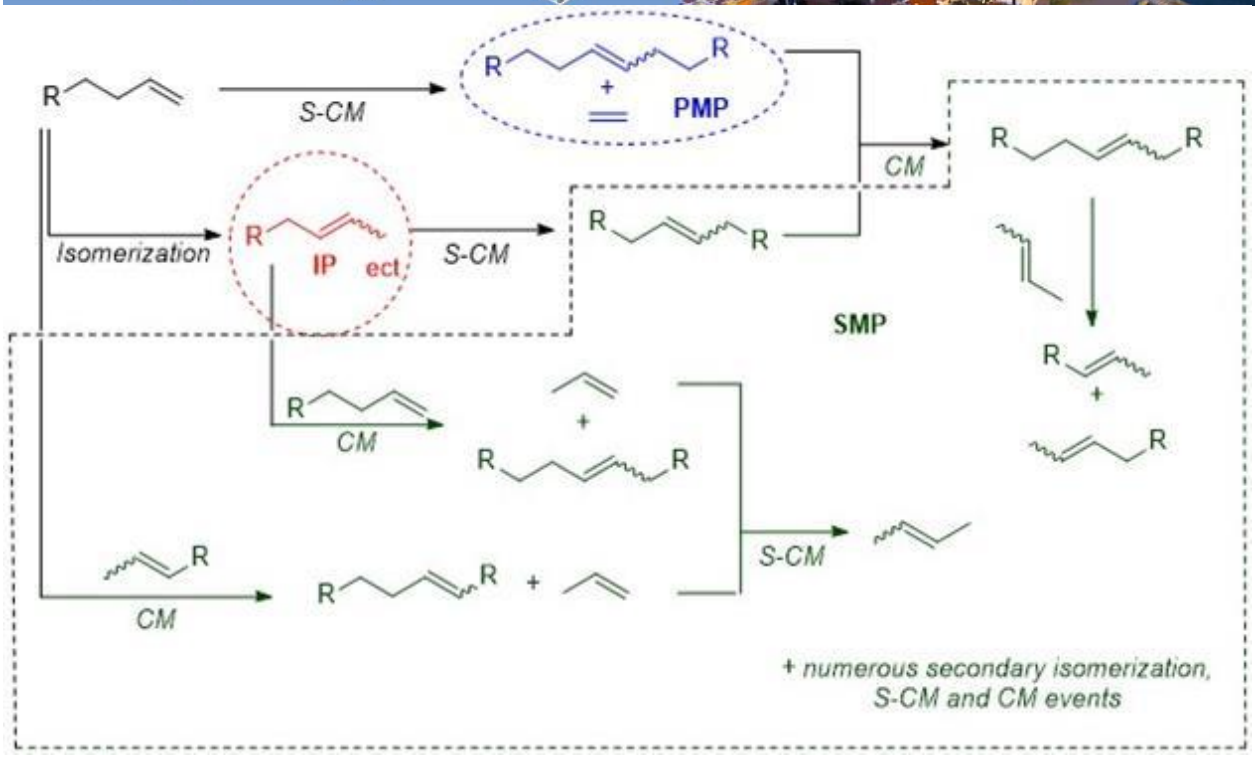
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P-315

(NHC) Cu(I) Complexes bearing Dipyridylamine ligands : Synthesis, Structural, Photoluminescent Studies and Applications in Luminescent Materials.

Margaux ELIE[1], Dr Fabien SGUERRA[2], Dr Florent DI MEO[3], Michael D. WEBER[4], Dr Ronan MARION[1], Dr Matthieu HAMEL[2], Dr Mathieu LINARES[3], Dr Rubèn COSTA[4], Pr Jean-Luc RENAUD[1], Dr Sylvain GAILLARD[1]

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Poster Session 1

We present in this communication the synthesis of new cationic tricoordinated copper complexes bearing bidentate dipyridylamine (dpa) ligands and NHC as ancillary ligands [Cu(NHC)(HDPA)][X]. These copper complexes have been fully characterized by NMR, X-ray analysis, electrochemistry, and photophysics. TD-DFT calculations were also undergone to rationalize the assignment of the photophysical properties.
Some of these copper complexes exhibit very bright blue emission with high quantum yield at solid state. A variation of the electronic properties on both NHC and dipyridylamine ligands, has been carried out and permitted to establish a structure – properties relationship, also supported by TD-DFT calculations.
Since emissive cationic organometallic complexes can be good candidates for LEC (Light emitting Electrochemical Cells) applications, a selection of copper complexes was achieved for the preparation of those lighting devices. Here is presented the proof of concept that our copper complexes, of general formula [Cu(NHC)(dpa)][X], can be applied for LEC devices. To the best of our knowledge, we are presenting here the first blue emitting LEC device incorporating cationic copper complexes.

P-316

Borylation of Diaryliodonium Salts

Mrs Núria Miralles[1], Mr Martín Romero[2], Prof. Elena Fernández[1], Prof. Kilian Muñiz[2]
[1]*Universitat Rovira i Virgili, Tarragona, Spain,* [2]*Institute of Chemical Research of Catalonia, Tarragona, Spain*

Poster Session 1

Arylboronic esters are frequently used as key intermediates in organic synthesis due to their high versatility. In particular, they participate in a variety of cross-coupling processes, such as the Suzuki-Miyaura reaction.

Although transition-metal catalysts exhibit high efficiency and selectivity in direct C-H bond borylation of arenes (1,2), we were intrigued to broaden the synthetic spectrum. To this end, we here report that diaryliodonium salts (3) can react with the Lewis acid-base adduct [RO-BpinBpin]- to generate a series of Ar-Bpin compounds (Scheme 1). Worthy to note, the aryl iodide by-product generated alongside the C-B bond formation, can itself be efficiently coupled to the obtained boronic ester within a subsequent palladium catalyzed reaction. The overall process provides a suitable example of an atom economic C-C bond formation within a one pot reaction (4).

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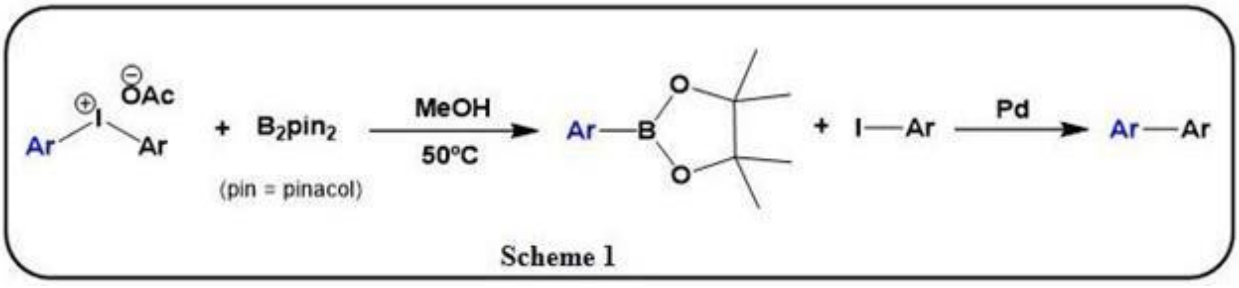

Scheme 1

P-317

Copper-Catalyzed N-Aryl-β-Enaminonitrile Synthesis Utilizing Isocyanides as the Nitrogen Source

Mr. Seoksun Kim[1], Prof. Soon Hyeok Hong[1]
[1]*Departmentof Chemistry, College of Natural Science, Seoul National University, Gwanak-gu, South Korea*

Poster Session 1

For several decades, enaminonitrile has been highlighted as a useful building block in heterocycle synthesis.[1] This building block could be applied to polymers[2] and pharmaceutical chemistry.[3] Because of its importance, several aspects of β-enaminonitrile have been studied, such as tautomerization, isomerization, and photochemical reaction.
Despite the importance of β-enaminonitrile, substrate scope of traditional methods was limited to only N-unsubstituted- or N-alkyl-β-enaminonitrile. Recently, we found that copper-catalyzed one-step reactions between isocyanides and benzylcyanides could afford diverse N-aryl-β-enaminonitriles in excellent yields and with high atom-efficiency under mild conditions (Scheme 1).[4] This method could also be applied to the synthesis of N-alkyl-β-enaminonitriles. A mechanism involving an imidoyl-copper intermediate was proposed based on mechanistic studies and previous reports.[5] In addition, we demonstrated that synthesized N-aryl-β-enaminonitriles could be utilized for the synthesis of a β-keto nitrile compound and 3-aminopyrazole.

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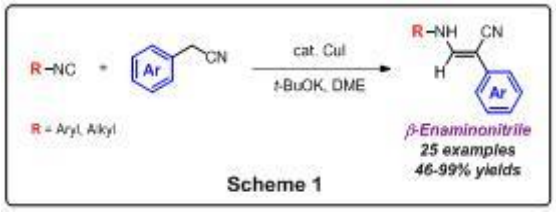

Scheme 1

P-319

Enantio- and Diastereoselective Conjugate addition of 1-Pyrroline 5-Carboxylate Esters to Nitroalkenes Catalyzed by Chiral Silver and Copper Complexes

Mr. Akihiro Koizumi[1], Ms. Midori Kimura[1], Dr. Yuichiro Tokoro[1], Dr. Shin-ichi Fukuzawa[1]
[1]*Chuo University, Kasuga, Bunkyo-Ku, Tokyo, Japan*

Poster Session 1

Waldmann and co-workers have reported the copper-catalyzed enantioselective 1,3-dipolar cycloaddition of a dihydropyridine ester with a nitroalkene where an optically active *N*-bridged amine was obtained in a high yield. Whereas, Wang's research group and we independently reported the enantioselective synthesis of chiral 7-azanorbornane esters by 1,3-dipolar cycloaddition of 1-pyrroline 5-carboxylate ester with *N*-substituted maleimide by using chiral silver complexes. A cyclic azomethine ylide is an active intermediate in either reaction. When we applied the silver-catalyzed reaction of 1-pyrroline 5-carboxylate ester to with nitroalkene instead of *N*-substituted maleimide, the corresponding cycloadduct was hardly obtained and the conjugate adduct was obtained instead. Chiral 1-pyrroline 5-carboxylate esters are key intermediates of proline derivatives, which are important class of biologically active compounds and natural products and also themselves have been employed as organocatalyst: 1-Pyrroline 5-carboxylate can be readily converted into proline esters upon hydrogenation of the imine group.
In the present study, we have examined silver- and copper-catalyzed reaction of 2-substituted 1-pyrroline 5-carboxylate esters with nitroalkenes by using chiral phosphine ligands. The reaction proceeded at room temperature smoothly to give the corresponding *syn* or *anti* conjugate adduct in good yields with high diastereo and enantioselection. The diastereoselectivity of the reaction was predominantly controlled by silver and copper complexes, giving the *syn* and *anti* isomer, respectively.

P-321

Pd/C-catalyzed Umpolung Aminocarbonylation of Organoboronic Acids with in situ Formed N-Cl Bonds

Dr Wanfang Li[1], Dr. Habill. Xiao-feng Wu[1]
[1]*Leibniz-Institut für Katalyse e. v. an der Universität Rostock , Rostock, Germany*

Poster Session 1

Aryl(pseudo)halides (C-X bonds) based carbonylation reactions have been extensively studied during the past decades. From both academic and synthetic point of view, the exploring of carbonylative transformation N-X bonds will be interesting and attractive. On this background, we realized the first carbonylative cross-coupling between N-chloroamines and organo boronic acids. This new type of aminocarbonylation proceeded at mild temperatures (45 to 55 °C) with 2 mol% Pd/C (10 wt.%) as the ligand-free catalyst. Not only arylboronic acids, but also alkenyl- and alkylboronic acids can be applied as the substrates and bromides and iodides can be tolerated in the substrates. Initial mechanistic investigations were performed as well.

P-322

Allylic Arylation Reaction with a ppb to ppm Loading Amount of a Palladium NNC-Pincer Complex Catalyst

Assitant Prof. Go Hamasaka[1,2], Ph.D. Student Fumie Sakurai[1,2], Prof. Yasuhiro Uozumi[1,2,3,4]

[1]Institute for Molecular Science, Okazaki, Japan, [2]SOKENDAI, Okazaki, Japan, [3]RIKEN Center for Sustainamble Resouce Science, Wako, Japan, [4]JST-CREST and JST-ACCEL, Okazaki, Japan

Poster Session 1

We have developed the efficient allylic arylation reaction using a palladium NNC-pincer complex.[1] The allylic arylation of various allyl acetates with sodium tetraarylborates proceeded in the presence of a ppb to ppm loading amount of the palladium NNC-pincer complex to give the corresponding arylated products in excellent yield (Scheme 1). Total turnover number reached up to 500,000,000.

Reference

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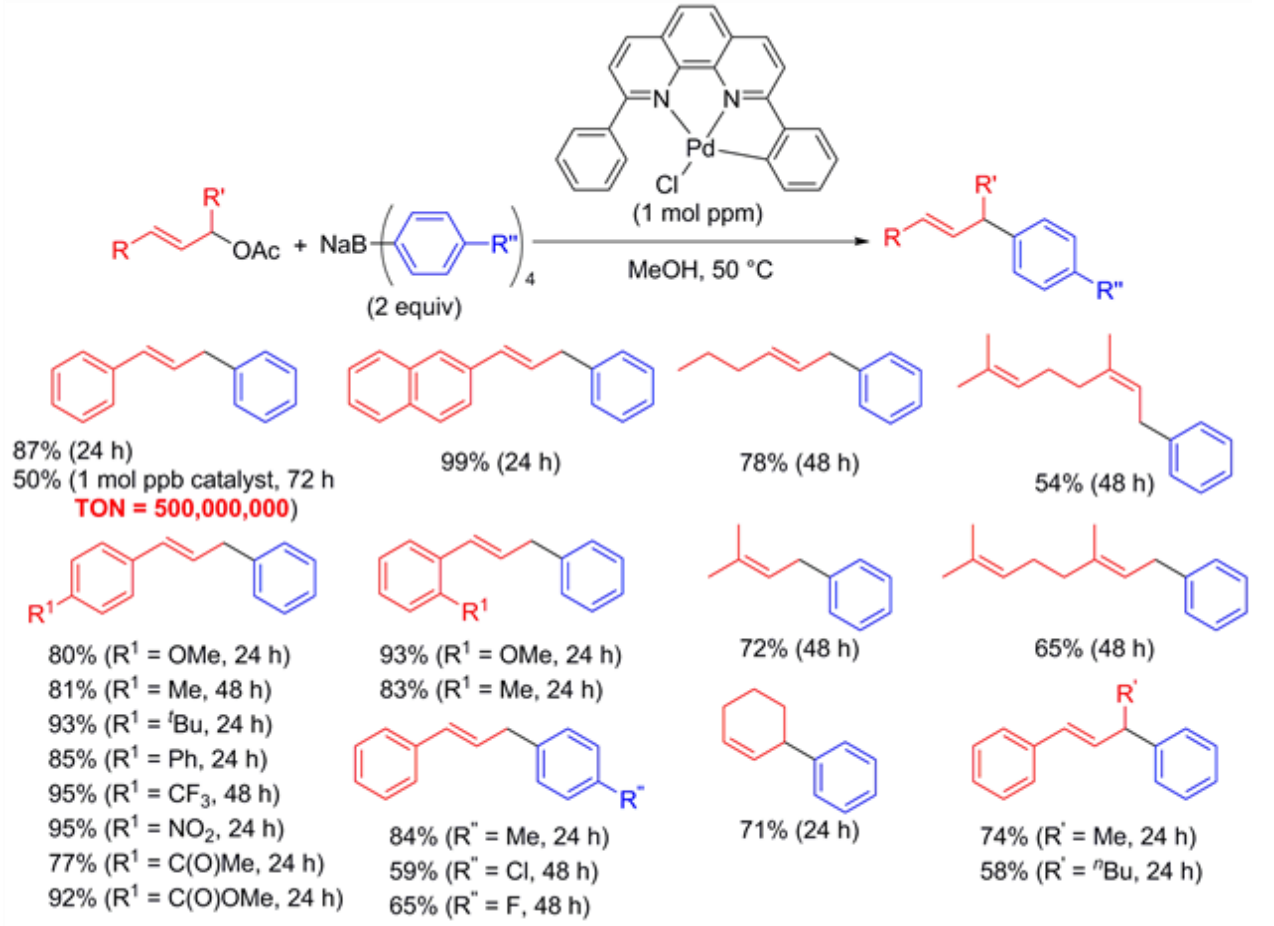

Scheme 1. Allylic arylation of allyl acetates with sodium tetraarylborates.

P-323

A general and scalable synthesis of aeruginosin marine natural products based on two strategic C(sp3)–H activation reactions

Dr Grégory Danoun[1], Mr David Dailler[1], Prof. Olivier Baudoin[1]
[1]*ICBMS, Grenoble, France*

Poster Session 1

In 1994, Murakami et al. reported the isolation of aeruginosin 298A from a toxic blue algae Microcystis aeruginosa, the first compound of new family of linear peptides.[1] This new family contains currently more than twenty different compounds, which all present biological activities as serine protease inhibitors.[2]
We decided to synthesize this class of compounds using new methodologies based on metal catalysis. Our retrosynthetic analysis envisaged classical peptidic coupling reaction (blue) to form this class of compounds starting from four molecules: two basic building blocks (1 and 3) and two more complex building blocks (2 and 4). These latter might be synthesized using recent C(sp^3)–H activation reactions.[3] Indeed, with regard to 2, the application of our recent C–H functionnalization method (red) was envisaged to lead quickly to 2 in a diastereoselective manner.[4] The synthesis of fragment 4 would be synthesized by a directed C–H functionnalization (green) allowing the synthesis of a large class of analogs of this fragment (Scheme1).[5]
In addition to the challenge of synthesizing these compounds using C–H activation, our retrosynthesis provides a straightforward access to a large library of analogous.[6]

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P-324

Copper-Mediated Vinylic Finkelstein Reaction: an Efficient and General Synthesis of Vinyl Chlorides and Bromides

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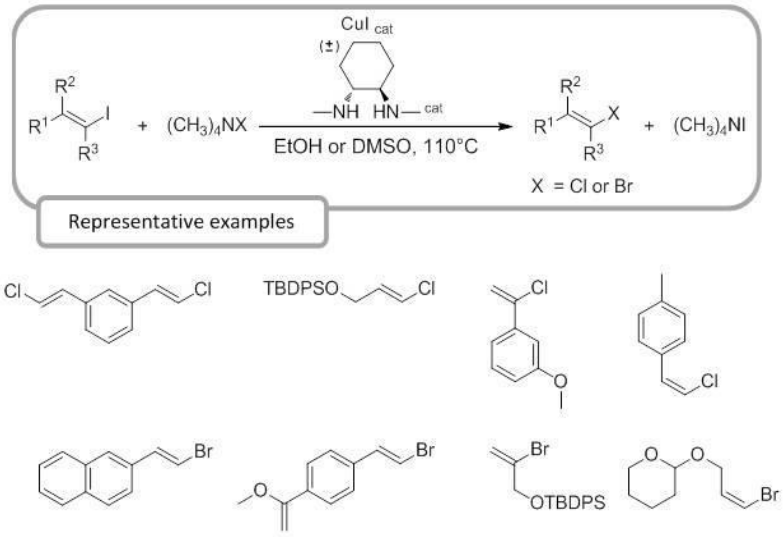
Poster Session 1

Vinyl halides are especially useful building blocks commonly used in chemical synthesis, notably in metal-catalyzed cross-coupling reactions. They have in addition implications in many others sectors of sciences including polymers, natural product synthesis, material, pharmaceutical and agrochemical sciences, just to cite a few.

Despite their apparent simplicity, classical methods for their preparation, which mostly rely on the trapping of vinyl metal species with electrophilic halogen source or on the Stork-Zhao and Takai olefinations, still suffer from major limitations such as a poor substrate scope, moderate levels of stereoselectivity, the use of toxic reagents or solvents and, more importantly, the poor efficiency of these reactions for the synthesis of vinyl chlorides and fluorides.

In an attempt to tackle this challenge, which has important implications in organic synthesis, and capitalizing on the greater availability of vinyl iodides compared to their homologues possessing lighter halogen atoms, we have developed an efficient system enabling the direct preparation of the latter from the former. Indeed, if the halogen/halogen exchange reaction, known for more than a century in the aliphatic series as the Finkelstein reaction, has been extensively studied recently with aryl halides, its use with halogenated alkenes has been only scarcely studied, despite its huge potential. By using catalytic amounts of copper(I) iodide and a simple diamine ligand, we have shown that alkenyl iodides could be smoothly converted to their chlorinated and brominated derivatives in good yields and with full retention of the double bond geometry. The development of this reaction, its scope and limitation and its use in natural product synthesis will be discussed.



P-325

Highly Selective Coupling Reactions between Oxetanes and Carbon Dioxide

Jeroen Rintjema[1], Wusheng Guo[1], Eddy Martin[1], Eduardo, C. Escudero-Adán,[1], Arjan, W. Kleij[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

The use of carbon dioxide (CO_2) as a renewable carbon feed stock for the preparation of value added organic structures and polymers has grown tremendously over the years.[1] Therefore it remains important to develop new and efficient catalytic strategies that help to widen the scope of products that incorporate CO_2 as a molecular synthon.[2] The field of cyclic carbonates has been dominated by the formation of five-membered structures through the coupling of oxiranes (epoxides) and CO_2. The coupling reaction between oxetanes and CO_2 to give six-membered carbonates has been largely neglected; activation of oxetanes and their coupling reaction with CO_2 is generally considered a huge challenge with only a few effective catalytic systems reported to date.[3] Here we describe a highly efficient method for their synthesis relying on the use of Al-catalysis. Apart from a series of substituted six-membered cyclic carbonates, also the unprecedented room temperature coupling of oxetanes and CO_2 is disclosed giving, depending on the structural features of the substrate, a wide variety of five- and six-membered heterocyclic products. The presented functional carbonates and carbamates may hold great promise as building blocks in organic synthesis and development of new biodegradable polymers.

P-326

Palladium-Catalyzed Oxirane-Opening Reaction with Arenes via C-H Bond Activation

Zhen Wang[1]
[1]*The University Of Tokyo, Tokyo, Japan*

Poster Session 2

We achieved a palladium-catalyzed C-H activation/C-C coupling reaction between arenes with a pyridyl, aminoquinolinyl, imino, or amide directing group and oxiranes. The reaction proceeded at room temperature without any additives and tolerated a wide variety of functional groups, and the products were obtained in good to excellent yields even in gram scale. When N-methoxybenzamide and oxiranes were used as substrates, coupling reaction and successive cyclization proceeded and 3-substituted isochroman-1-ones were obtained. The coupling reaction proceeded with stereoretention. Kinetic isotope effect experiments suggested that C-H bond activation is the rate-determining step.

Reference

1. Z. Wang, Y. Kuninobu, M. Kanai, submitted for publication.

P-327

Unique Reaction Behaviors about the Novel Radical Polymerization Initiated with Some Kind of Ionic Liquid

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[1]*Tohoku Seikatsu Bunka University, Sendai-Shi, Japan*

Poster Session 2

TIonic liquids are compounds composed entirely of ions and are liquid at relatively low temperatures (< 100 ℃). Many kinds of ionic liquids containing a variety of cations and anions of different sizes have been synthesized to provide specific characteristics. Meanwhile, the author has shown for the first time that some kinds of ionic liquids can be used to an initiator of radical polymerization.1-6 In this investigation, the author would like to present some of the author's latest research results about the radical initiating ability of ionic liquids. For instance, the author has used the imidazolium ionic liquid such as 1-ethyl-2,3-dimethylimidazolium bromide ([edmim]Br, see Scheme 1) as an initiator of methyl methacrylate (MMA)-polymerization. The effect of solvents on the polymerization of MMA initiated with [edmim]Br under air at 60 ℃ were examined and shown in Figure 1. As shown in this figure, the polymerizations in dimethyl sulfoxide (DMSO), carbon tetrachloride (CCl4), and toluene were perfectly inhibited. In contrast to the fact, the polymerization in N,N-dimethylformamide (DMF) proceeded smoothly. The polymerization behavior as described above was completely different from that of conventional radical polymerization. For this reason, the polymerization initiated with ionic liquid was investigated in detail.

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2 Kanno, S., Japanese Patent, Patent Number 4719080.
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5 Kanno, S., BOOK OF ABSTRACTS 2nd International Conference on Ionic Liquids in Separation and Purification Technology, (2014) O14.2. / (The Westin Harbour Castle/ Toronto, Canada)
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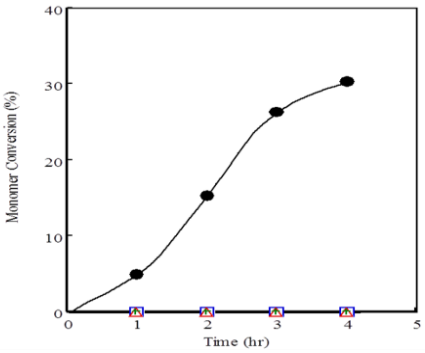

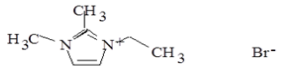

Schme 1. 1-Ethyl-2, 3-dimethylimidazolium bromide ([edmim]Br).

P-328

HYDROGENATION OF AMIDES CATALYZED BY RUTHENIUM COMPLEX WITH Zn(OCOCF3)2

Mr. Takafumi Higuchi[1], Dr. Yusuke Kita[2], Dr. Kazushi Mashima[3]
[1]*Osaka University, Toyonaka, Japan,* [2]*Osaka University, Toyonaka, Japan,* [3]*Osaka University, Toyonaka, Japan*

Poster Session 2

Reduction of amides is one of the most versatile synthetic methodologies for producing the corresponding alcohols or amines. It is well-known that stoichiometric amounts of hydride reagents efficiently reduced amides; however, stoichiometric amounts of salt waste were formed. Hydrogenation of amides using heterogeneous catalysts has been applied to give the corresponding amines in a more clean and atom-economical way.[1] Recently, some ruthenium complexes were reported to work as catalysts for hydrogenation of amides to corresponding alcohols,[2] though these homogeneous ruthenium catalyst systems have some drawbacks; (1) severe reaction conditions were required, (2) special ligand system derived by rather long synthetic routes were required. To compensate them, we found a simple catalytic system based on ruthenium complex combined with zinc salts such as $Zn(OCOCF_3)_2$. To gain insights into the additive effects of $Zn(OCOCF_3)_2$, we performed NMR experiments, revealing that $Zn(OCOCF_3)_2$ acted as a source of a trifluoroacetate ligand as well as a Lewis-acid to activate the amide bonds.[3]

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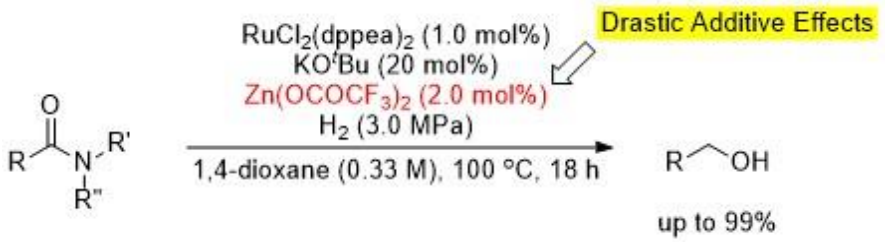

P-329

Rh(I)-Catalyzed Cyclization of Enynes with Tethered Imines via Insertion of a C=N Bond into a Rhodacycle Intermediate

Yoshio Hato[1], Dr. Yoshihiro Oonishi[1], Prof. Dr. Yoshihiro Sato[1,2]
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Poster Session 2

Recently, we have found a Rh(I)-catalyzed cyclization of allenynes with tethered imines, which affords bicyclo[5.3.0]decane or 8-azabicyclo[3.2.1]octane derivatives.[1] This cyclization proceeds through aza-rhodacycle intermediate, which is formed by insertion of a C=N double bond into rhodacycle intermediate. The rarity of the process prompted us to investigate a C=N double bond insertion into other types of rhodacycles. Here, we disclose a cyclization of enynes with tethered imines.

First, the effect of phosphine ligands was examined using 1,6-enyne (S)-1 as a model substrate. When a cationic Rh(I)/(S)-H_8-BINAP catalyst was used, cyclized compound 2 was obtained in 88% yield. A plausible reaction mechanism is as follows. Oxidative cycloaddition of enyne to Rh(I) complex gives five-membered rhodacycle intermediate I. Subsequent insertion of a C=N double bond into Rh-C(sp^2) bond affords aza-rhodacycle intermediate II. Finally, β-Hydride elimination from II followed by reductive elimination gives the product 2. Further studies to determine the substrate scope as well as to clarify the reaction mechanism are in progress.

Reference

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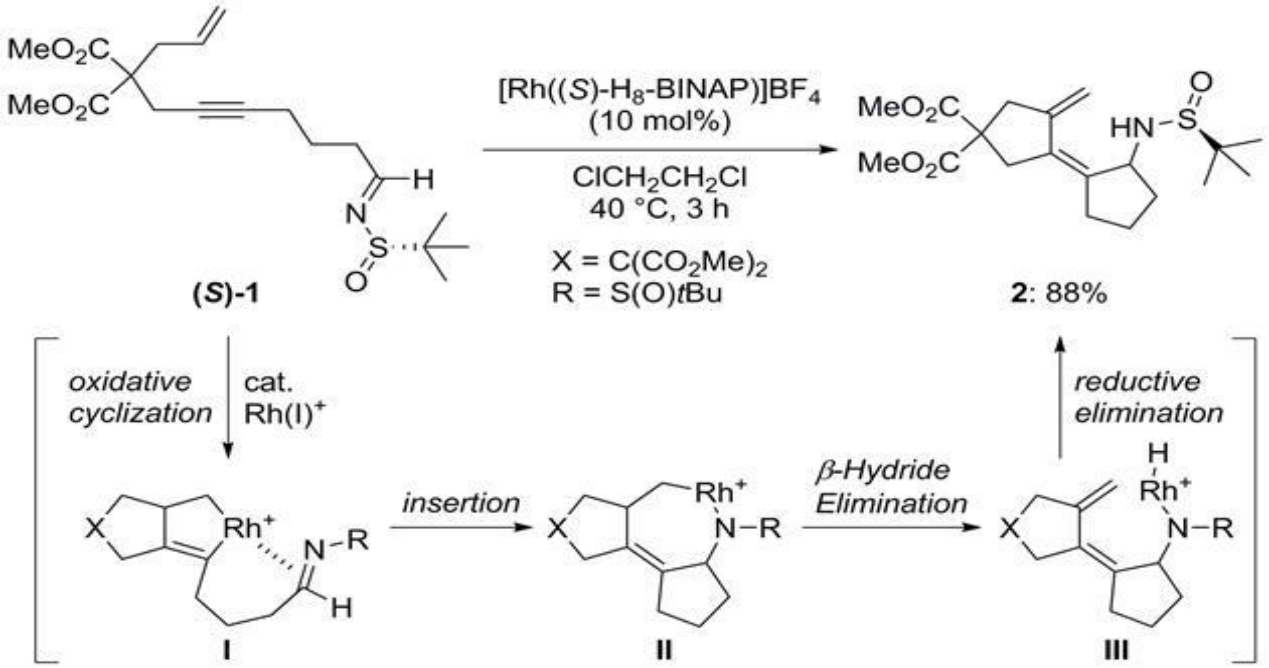

MeO2C
MeO2C
H
N
S
O
(S)-1
[Rh((S)-H8-BINAP)]BF4
(10 mol%)
ClCH2CH2Cl
40 °C, 3 h
X = C(CO2Me)2
R = S(O)tBu
HN
2: 88%
oxidative
cyclization
cat.
Rh(I)+
insertion
β-Hydride
Elimination
reductive
elimination
Rh+
N–R
X
I
II
III

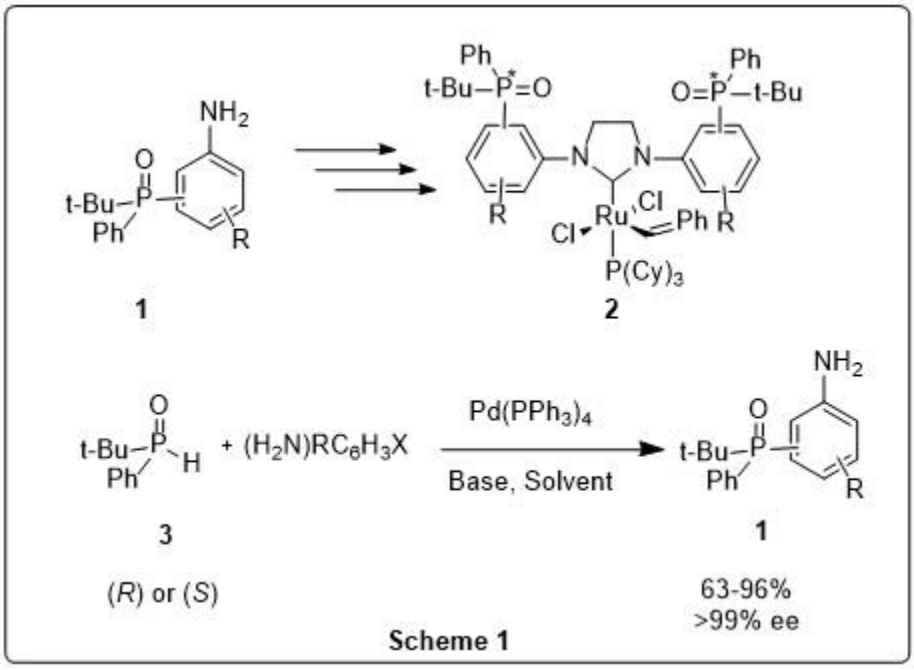
P-330

Palladium(0) catalyzed C-P cross-coupling reaction of optically pure secondary phosphine oxides with haloanilines as a route to key substrates in the synthesis of the chiral, second-generation Grubbs catalysts

Jacek Chrzanowski[1], DSc Dorota Krasowska[1], Małgorzata Urbaniak[1], Prof. Józef Drabowicz[1]
[1]*Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland*

Poster Session 2

In our studies aimed at the synthesis of chiral analogues of the second generation Grubbs catalysts 2 bearing ligands containing a stereogenic phosphorus atom, optically active (aminophenyl)(tert-butyl)phenylphosphine oxides 1 constitute key substrates (Scheme 1). The most convenient way to obtain them seems to be a transition-metal-catalysed cross-coupling reaction [1] of (R or S) tert-butyl(phenyl)phosphine oxide 3 [2] and a haloaniline. In this communication we are going to present the result of our experiments which allowed isolation of optically active (o–aminophenyl)(tert-butyl)phenylphosphine oxide 1a and (p–aminophenyl)(tert-butyl)phenylphosphine oxide 1b as enantiomerically pure samples using palladium-based catalysts. The preparation of other enantiomerically pure tertiary phosphine oxides 1 (analogues of 1a and 1b) in high yields by this approach will also be presented (Scheme 1).



Scheme 1

P-331

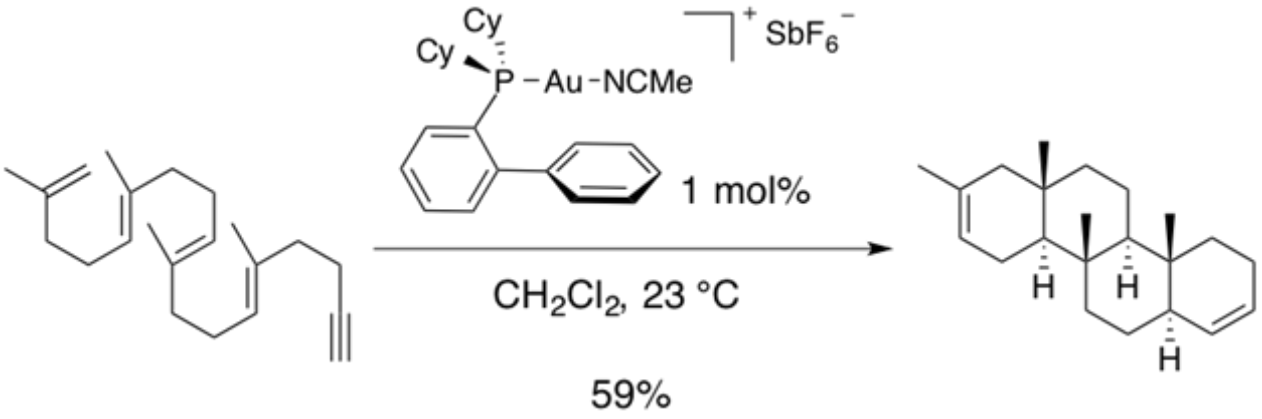
Gold(I)-Catalyzed Squalene Type Cyclizations

Zhouting Rong[1], Antonio Echavarren[1]

[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Tarragona, Spain*

Poster Session 2

A squalene type cyclization initiated by the activation of alkynes has been accomplished with gold(I) complexes as catalysts. This method features excellent stereoselectivity and furnishes a variety of fused- and spiropolycycles.



P-332

Highly Efficient Chiral Amplification Systems Based on Majority-Rule-Type Helical Poly(quinoxaline-2,3-diyl)s for Asymmetric Catalysis

Dr Yuanzhen Ke[1], Dr Yuuya Nagata[1], Prof. Michinori Suginome[1]
[1]*Kyoto University, Kyoto, Japan*

Poster Session 2

The synthesis of optically active molecules via chiral amplification has attracted much attention.[1] Majority-rule-type helical polymers,[2] which adopt non-linearly enhanced single-handed helical conformations, represent one of the most promising platforms for the development of new chiral amplification systems. However, reports on the highly enantioselective production of chiral compounds based on majority-rule-type helical polymers remain unprecedented. Recently, we reported that a single-handed helically chiral poly(quinoxaline-2,3-diyl)s (PQXs) with diarylphosphino pendants serve as an effective chiral ligand for various asymmetric reactions.[3] We also reported solvent-dependent helix inversion of PQXs with chiral side chains between $CHCl_3$ and 1,1,2-trichloroethane,[4] enabling highly enantioselective productions of both enantiomers from a single chiral catalyst.[5] We herein demonstrate a highly efficient chiral amplification in the screw sense of a majority-rule-type PQX. The phosphorous-containing PQX 1 derived from (R)-2-octanol with 23% ee, which is easily accessible by an amino acid-derived catalyst,[6] enabled the highly enantioselective production of both enantiomers in the palladium-catalyzed asymmetric hydrosilylation reaction (94% ee (S) and 95% ee (R)) and Suzuki-Miyaura coupling reaction (93% ee (S) and 92% ee (R)) using the solvent-dependent chirality switch of the helical backbone.

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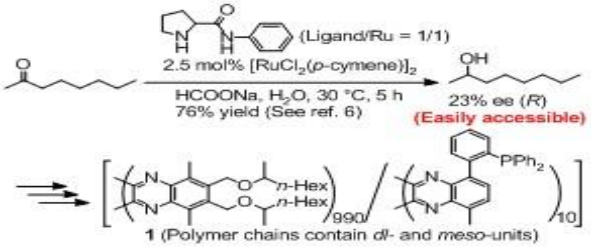

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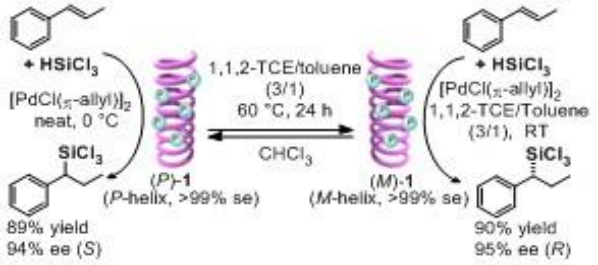


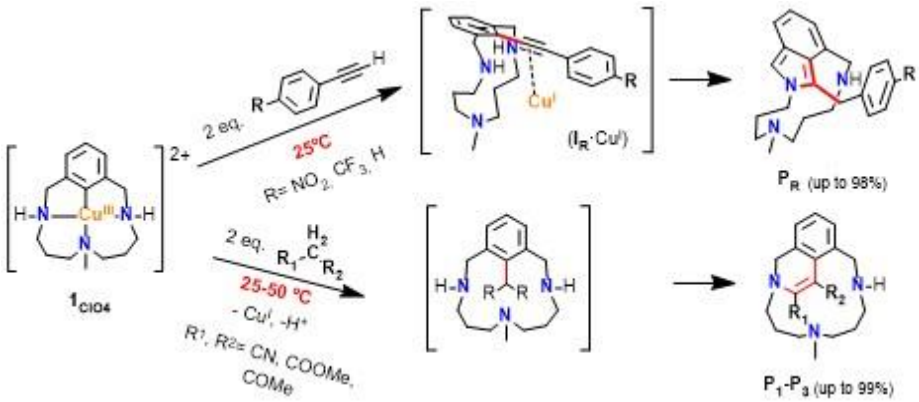
P-333

Copper(III)-mediated Csp^2-Csp and Csp^2-Csp^3 bond formation under milder conditions

Mireia Rovira[1], Marc Font[1], Ferran Acuña[1], Teodor Parella[2], Josep M Luis[1], Julio Lloret-Fillol[1], Xavi Ribas[1]
[1]*IQCC- Universitat De Girona, Girona, Spain,* [2]*Servei de RMN, Universitat Autònoma de Barcelona (UAB), Barcelona, Spain*

Poster Session 2

Modern copper-catalysed cross-coupling reactions have recently evolved as reliable and efficient method for the construction of C-C and C-heteroatom bonds, present in a large number of natural products, and they also find wide pharmaceutical application. Cross-coupling reaction between aryl or alkenyl halides with terminal acetylenes (the Sonogashira-Hagihara reaction) is among the fundamental methods for the Pd-Cu-cocatalyzed C-C bond forming reactions. The role of Cu(I) is proposed to be as transmetallating agent. We have special interest in the palladium-free Sonogashira, called Stephens-Castro reaction (stoichiometric) or Miura's reaction (catalytic). On the other hand, Hurtley reaction is a well-established method for the Cu(I)-catalyzed arylation of acidic Csp^3-H substrates under milder conditions. Despite the long history of copper-mediated Sonogashira coupling and Hurtley coupling reaction, their detailed mechanism is far from being well-understood.
Herein, we report the reactivity of a well-defined aryl-Cu[sup]III[/sup] species with p-R-pheylacetylenes and activated methylenes at room temperature to afford the Csp^2-Csp and Csp^2-Csp^3 coupling products, respectively. Interestingly, these coupling species undergo an intramolecular reorganization to afford final heterocyclic products 2H-isoindole, 1,2-dihydroisoquinoline and 1,2-dihydroisoquinolin-3(4H)-one. In situ spectroscopic studies of the catalytic version of this Csp^2-Csp^3 coupling reaction provide definitive evidence for the involvement of an aryl-copper(III)-halide intermediate as the resting state of the reaction. Our results in model aryl halide substrates provide evidences for the direct engagement of a redox Cu[sup]I[/sup]/Cu[sup]III[/sup] catalytic cycle involving oxidative addition and reductive elimination steps in copper-mediated Sonogashira and Hurtley-type coupling reactions.



P-334

Human Neutrophil Elastase inhibitors: Design, Synthesis and Biological Evaluations.

Antonios Nikitidis[1], Peter Hansen[1], Dave Chapman[1], Hans Lönn[2], Dr. Nafizal Hossain

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Poster Session 2

Human neutrophil elastase (hNE) is a 29-kDa serine protease stored in the azurophilic granules of the neutrophils and is released in response to inflammatory challenges. The uncontrolled and excessive proteolytic activity of hNE has been postulated to the etiology of a number of diseases such as chronic obstructive pulmonary disease (COPD), adult respiratory distress syndrome (ARDS), bronchiectasis and development of emphysema.1, To date one compound from AstraZeneca, AZD9668 (1) 2, has entered into clinical trials for the potential treatment of COPD.

This poster will describe our effort made to identify back up candidate to AZD9668. A series of compounds were designed and synthesised to expand the structure activity relationships (SAR) according to Figure1.

The key intermediates 2 and 3 were derived from a multistep synthetic reaction sequences. The introduction of cyclopropyl group as in 3 was achieved by Palladium/Indium mediated reaction. These intermediates were used to the synthesis of a series of biologically active compounds (4 and 5, Fig. 1). The biological evaluations revealed a series of very potent hNE inhibitors and examplified by (5). The most potent compound was found to have an IC50 value of 500 pM.

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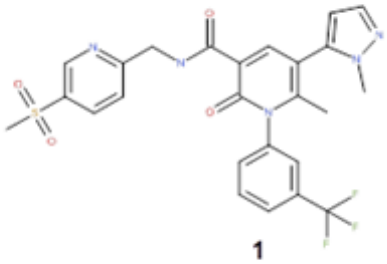
OMCOS18
Organometallic Chemistry
Directed Towards Organic Synthesis
IUPAC International Symposium
Sitges - Barcelona
From June 28th to July 2nd 2015



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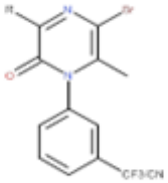
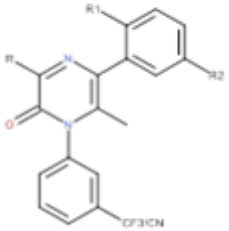


2: R = H, **3**: R = cyclopropyl



4: R = H, **5**: R = cyclopropyl

Figure 1

P-335

Unexpected biradical character of titanium enolates: an opportunity for new radical-type reactions

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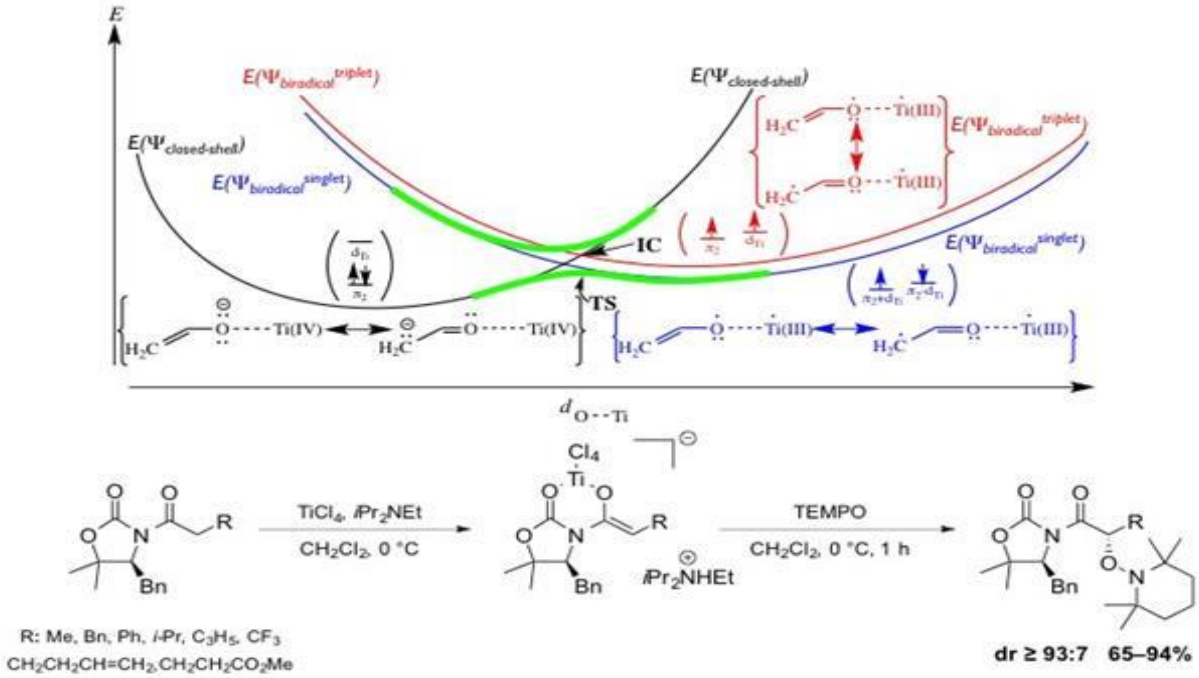
Poster Session 2

Metal enolates have been a classical source for nucleophiles in carbon-carbon and carbon-heteroatom bond forming reactions in which the metal atom possessing a well defined oxidation state acts as the electrophilic center of the reacting species. Titanium(IV) enolates are outstanding examples of such a model.

More recently, high level theoretical calculations and comprehensive spectroscopic analyses uncovered the unexpected biradical character of certain titanium enolates. Indeed, little changes on the titanium-oxygen distance may produce a dramatic modification of the electronic configuration of the whole species to the extent that an open shell configuration becomes the most stable one. This confers to titanium enolates a completely new reacting profile associated with the classical radical reactivity.

The clean and highly stereoselective addition of $TiCl_4$-mediated enolates from chiral N-acyl oxazolidinones to TEMPO proves the feasibility of such a reactivity and enables them to participate in a wide range of radical-like processes. Interestingly, the N-acyl chain can contain a wide range of sensitive functions as cyclopropyl, alkenes, or ester groups, although the reacting center in α,β-unsaturated systems is shifted towards the γ-position.

Eventually, easy removal of the chiral auxiliary affords enantiomerically pure alcohol and methyl ester derivatives, whereas the smooth reduction of the nitrogen-oxygen bond yield the corresponding α-hydroxy adducts in pure form.



R: Me, Bn, Ph, *i*-Pr, C_3H_5, CF_3
$CH_2CH_2CH{=}CH_2$, $CH_2CH_2CO_2Me$

dr ≥ 93:7 65–94%

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Enantioselective Synthesis of Fully Functionalized Chiral Hemiaminals

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Poster Session 2

A novel asymmetric synthesis of fully functionalized chiral N,O- and N,N-acetals has been developed. The reaction tolerates a wide range of aromatic and aliphatic substituents at the stereochemically labile aminal position. Starting from racemic starting materials, the desired products are obtained in high yield and enatiomeric excess. Additionally, we will discuss our investigations towards understanding the mechanistic aspects of this reaction. With the implementation of high-throughput experimentation, the current method was quickly developed and implemented to provide a highly efficient synthesis of a late stage drug candidate.

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Unravelling the mechanism of water oxidation catalysed by novel tacn-based ruthenium complexes

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Poster Session 2

Mechanistic understanding of the metal-catalysed water-oxidation (WO) on a molecular scale is essential for its development. Since water is abundant and its oxidation produces O_2 as by-product, light-driven WO is the most attractive source of electrons to be used in a multi-ton scale. However, WO has been identified as the bottleneck, because it requires a rapid stepwise building up of very high redox potentials only bearable by few chemical species and, thus, difficult to control against side oxidative damage. Despite of all these chemical challenges, WO is absolutely required because it is a fundamental transformation for the development of artificial photosynthetic systems.

Furthermore, ligands based on 1,4,7-tryazacyclononane (tacn) are very robust and they have been proved to stabilise metals in high oxidation states. Therefore, such ligands constitute an excellent platform for the development and study of oxidation catalysts based on either first or second row transition metals.
Herein, a novel family of RuII complexes based on the triazacyclononane moiety has been synthesised and fully characterized. More concretely, the catalytic activity of novel tetradentate [RuIICl(dmso)(Py^{Me2}tacn)]Cl and pentadentate [RuIICl(Py_2^{Me}tacn)]Cl complexes has been studied as water oxidation catalysts. In addition, the WO mechanism has been elucidated in the basis of different studies such as kinetics, isotopic labelling, trapping of the intermediates and computational studies.

P-339

C-N Coupling of Indoles and Carbazoles with Aromatic Chlorides Catalyzed by a Single-Component NHC-Ni(0) Precursor

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Poster Session 2

N-arylindoles are pharmaceutically valuable compounds due to their interesting biological activities, including antifungal, antiviral, and antipsychotic, among others.[1] Metal catalyzed N-arylation of the indole core is the most straightforward route to synthesize these compounds.[2] Copper and to a lesser extent, palladium, have been the metal of choice to accomplish N-arylation of indoles. However, copper cross-coupling methods are limited almost exclusively to the use of aryl iodides and bromides as coupling partners. On the other hand, the scarce palladium based C-N coupling processes rely on the use of excess of phosphine ligands to prevent both deactivation of the catalyst due to strong coordination to NH group of indole and selectivity problems associated with competing N- and C-arylation.

Here, we disclose an unprecedented highly effective method for the C-N couplings of indoles and carbazoles with hetero(aryl) chlorides based on the use of the nickel(0) complex [(IPr)Ni(styrene)$_2$]. Reactions are accomplished in very short reaction times in the presence of 5-10 mol% of the IPr-Ni(0) complex, and without using an excess of the ligand. Competing C-arylation processes were not observed and the C-N coupling products were obtained in good to excellent yields using the least expensive and reactive of aryl halides (Scheme 1).[3]

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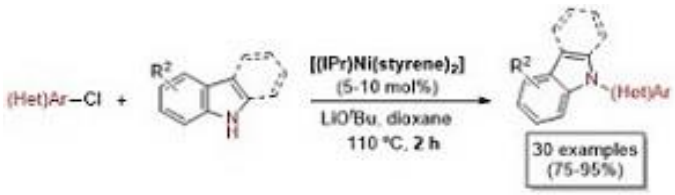

P-340

TADDOL based 1,2-P-OP Ligands for Asymmetric Hydrogenations of Functionalized Alkenes

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Poster Session 2

The substantial progress made in transition metal-mediated asymmetric catalysis has been accelerated by development of new, structurally diverse chiral ligands, which enable high selectivities in myriad transformations. [1] Among them, metal complexes derived from P-OP ligands have proven to be powerful enantioselective catalysts.[2] We herein reported a new series of structurally diverse TADDOL-derived P-OP ligands (1-5) as well as their performance in Rh-mediated enantioselective hydrogenation of various prochiral functionalized olefins: itaconic acid derivatives, a-(acylamino)acrylates, a-arylenol esters, a-arylenamides and b-aryl-a-(acylamino)acrylates. High activities and moderate to excellent enantioselectivities (up to 99 % ee) were obtained for the range of aforementioned substrates.

P-341

Ionic liquid crystals based on pyrazolium salts

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Poster Session 2

Ionic liquid crystals based on organic cations and inorganic anions have generated a great interest because of the possibility of combining the ordering of the liquid-crystalline mesophases and the properties of the ionic liquids within a single material.[1] Several examples of ionic liquid crystal materials have been described, being those based on imidazolium cations widely studied.[2] Related with the azol derivatives as cations we have developed new ionic liquid crystals based on 3-alkyloxyphenyl substituted pyrazolium cations and different inorganic anions.[3]

As an extension, in this work we present the synthesis and study of ionic derivatives containing 3,5-alkyloxyphenyl disubstituted pyrazolium cations with identical or different alkyl chain length (Fig. 1a). The evaluation of the use of symmetrical or unsymmetrical cations towards spherical (Cl[sup]-[/sup]), tetrahedral (BF_4[sup]-[/sup] and ReO_4[sup]-[/sup]) or more planar (CH_3-p-$C_6H_4SO_3$[sup]-[/sup]) anions allows modulating the liquid crystal properties of the new ionic salts as well as selecting those having the best results. Polarised optical microscopy and differential scanning calorimetry studies reveal the mesomorphic nature of the new derivatives. All of them exhibit SmA mesophases (Fig. 1b) in a temperature range which seems to be dependent on the counter anion choice and the molecular asymmetry of the cation. So, those containing the fluorinated anion BF_4[sup]-[/sup] and unsymmetrically substituted cations as well as those with symmetrical substituted pyrazolium cations and the more planar CH_3-p-$C_6H_4SO_3$[sup]-[/sup] anion presented lower transition temperatures. Relationship between the layer-like crystalline and the lamellar mesophase structures can be suggested (Fig. 1c).

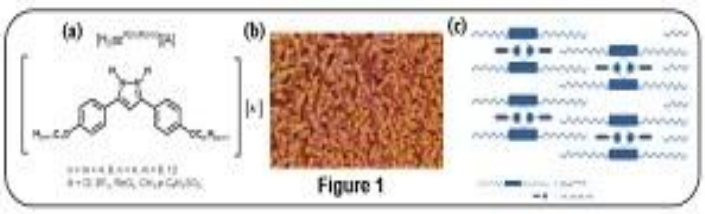

Figure 1

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Microwave-assisted palladium-catalyzed arylation of isoquinoline and quinoxaline

MsC Evelyn M. L. Pina Diniz[1], Natalia A. Pereira[1], MsC Samuel R. A. Ferreira[1], MsC Simone C. Silva[1], Ph.D. Shirley M. M. Rodrigues[1], Ph.D. Giuliano C. Clososki[1]
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Poster Session 2

Nitrogen-containing heterocycles are important compounds in organic chemistry such as isoquinoline and quinoxaline rings. They can be highlighted due to its great pharmaceutical importance. In this work, the arylation of isoquinoline (1) and quinoxaline (5) has been investigated using the Negishi reaction. Aiming to prepare the desired organozinc reagents from the isoquinolines, we began our study by investigating the best conditions for the metalation of 1 and 5 employing different organometallic bases such as LDA, LiTMP, TMPMgCl.LiCl, TMPZnCl.LiCl and $TMP_2Zn.2LiCl$. As expected, the lithiation of both compounds gave the corresponding dimers as major products due to the low stability of the organolithium intermediates. Thus, metalation of 1 was better be performed using 2 equiv of TMPMgCl.LiCl.[1] In the case of quinoxaline, the addition of $ZnCl_2$ prior to the addition of the base was necessary to avoid dimerization. Aiming to find the best conditions for the Negishi reaction, some parameters were investigated such as reaction temperature, different type and amount of Pd-catalysts [$Pd_2(dba)_3$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $PdCl_2$ and $Pd(OAc)_2$] and amount of ligant tri(o-furyl)phosphine. After finding the best reaction condition, a number of 1-aryl-isoquinolines and 2-aryl-quinoxalines were synthesized in good yields (63%-94%) through the microwave-assisted cross-coupling reaction of organozinc reagents of type 2 and 6 with different halides (3) catalyzed by $Pd(PPh_3)_4$. The scope of this methodology and its applicability toward the synthesis of bioactive compounds are currently being investigated in our laboratories.

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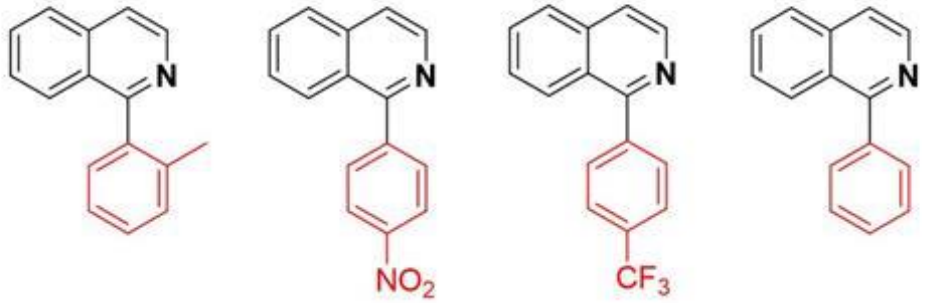
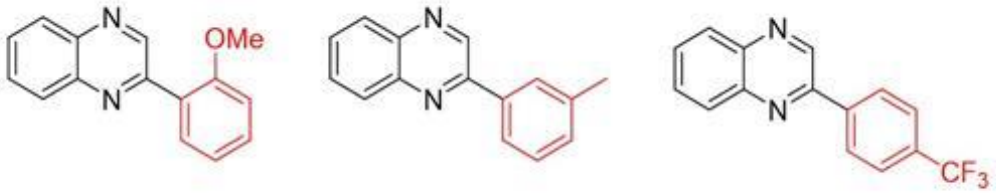
Some examples synthesized



Some examples synthesized



P-343

Vicinal Amino Alcohols Synthesis from Allyl Amines via in Situ Tether Formation and Pd-Catalyzed Carboetherification

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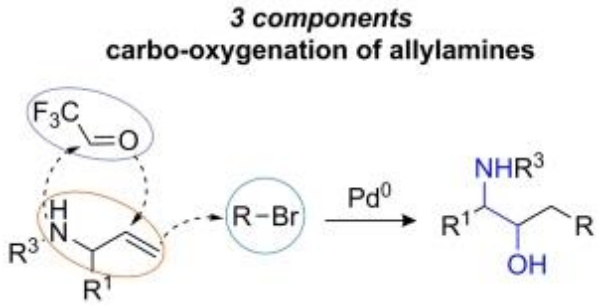
Poster Session 2

Vicinal amino alcohols are common stuctural units both in drugs and natural products.

Herein, we report an unprecedented 3-component tethered carbo-etherefication of allylamines for their synthesis, using trifluoroacetaldehyde as in situ tether. Alkynyl, aryl and vinyl groups could be successfully introduced in good yield and diastereoselectivity and with high functional group tolerance.

The products obtained could be readily and selectively deprotected to access either the free amine or alcohol, thus demonstrating their usefulness.



P-344

Getting More Value from your Catalyst; Towards Tandem and Sequential Cross-Coupling Processes

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Poster Session 2

The need for atom economy as well as efficient catalysis is majorly impacting on the manufacturing of pharmaceutical intermediates and fine chemicals. Tandem catalysis has thus become a very attractive synthetic strategy. A reluctance to work-up and isolate intermediates (especially in long-winded total syntheses) has inspired the establishment of tandem processes, often catalysed by transition metals. This has led us to combine various cross-coupling reactions with procedures that follow in the synthesis, thus trying to improve the efficiency of the overall process.

Selective cross-coupling of dielectrophiles is being studied. This includes exploiting two of the major components from the depolymerisation of lignin; 2-methoxyphenol (guaiacol) and catechol. Since there are relatively few items of commerce consisting of two or more phenolic OH groups, catalytic chemistry to replace C-O bonds with other linkages such as C-C bonds needs to be further developed. This project aims to initiate this challenge (ideally in a tandem manner) and consequently must address the issue of low reactivity of aryl methyl ethers in cross-coupling reactions. Recently, progress has been made using nickel catalysis however very specific nucleophiles have been utilised.

Cross-coupling reactions of guaiacol imidazole-sulfonate using relatively economic nucleophilic partners have been successful. Attempts are now being made to both develop a general solution to “catalytic constructive deoxygenation” of these functionalised aryl methyl ether products, and to investigate if certain classes of nucleophile and adjacent functionality allow reactivity.

Research is also focused on linking cross-coupling reactions with enantioselective additions to alkenes. This methodology could provide chiral building blocks in a very direct and efficient manner. Promising initial steps towards the synthesis of a drug target involving a tandem cross-coupling - enantioselective hydroxycarbonylation reaction will be discussed.

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P-345

Sandmeyer-type Fluoroalkylations

Christian Matheis[1], Dr. Kévin Jouvin[1], Bilguun Bayarmagnai[1], Dr. Grégory Danoun[1], Dr. Matthias F. Grünberg[1], Prof. Dr. Lukas J. Gooßen[1]
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Poster Session 2

Fluorine containing residues are central functionalities imparting unique chemical and physical properties, such as improved metabolic stability, better receptor binding selectivity and higher lipophilicity compared to their non-fluorinated analogs. New, efficient methods for the installation of fluorinated groups into functionalized molecules are constantly sought.
Recent years have witnessed a tremendous progress in fluoroalkylation technology. In this context we developed copper-mediated simple straightforward tri-/ difluoromethyl(thiol)ation methods starting from broadly available halides, boronic esters, amines and mesylates.[sup][1][/sup] We disclosed sustainable concepts for late-stage fluoroalkylations via redox-neutral Sandmeyer-type reactions which converts arenediazonium salts smoothly into the corresponding tri-/difluoromethylated products.[sup][2][/sup] Moreover, the in situ diazotization could be added to the advantageous features of our initial methods (copper-mediated and inexpensive tri-/difluoromethylating reagents).
These protocols open up versatile synthetic entries to important fluoroalkyl structures starting directly from widely available (hetero-)aromatic amines.

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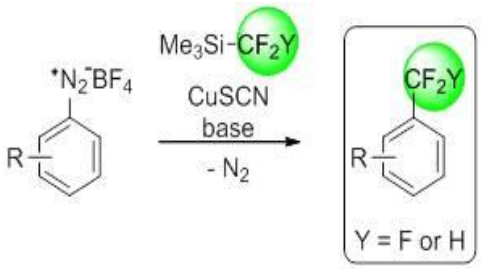

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Sandmeyer-type Fluoroalkylthiolations

Dr. Kévin Jouvin[1], Christian Matheis[1], Bilguun Bayarmagnai[1], Dr. Grégory Danoun[1], Dr. Matthias F. Grünberg[1], Prof. Dr. Lukas J. Gooßen[1]
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Poster Session 2

Fluorine containing residues are central functionalities imparting unique chemical and physical properties, such as improved metabolic stability, better receptor binding selectivity and higher lipophilicity compared to their non-fluorinated analogues.
Based on our knowledge on trifluoromethylation,[1] we recently described a straight-forward Sandmeyer-type fluoroalkylation using inexpensive and easily accessible arenediazonium salts as starting material.[2]
Recent years have witnessed a shift in focus toward trifluoromethylthiol groups as it induce a higher lipophilicity and membrane permeability in comparison of the trifluoromethyl group. We sought that an one-pot Sandmeyer thiocyanation followed by a Langlois type nucleophilic displacement of the cyano group by fluoroalkyl species provide a smooth, versatile and cheap entry to fluoroalkylthiolated molecules starting directly from widely available (hetero-)aromatic amines.[3] This strategy was applicable to the synthesis of alkyl fluoromethyl sulfide starting from alkyl halides or mesylates.[3b, c]

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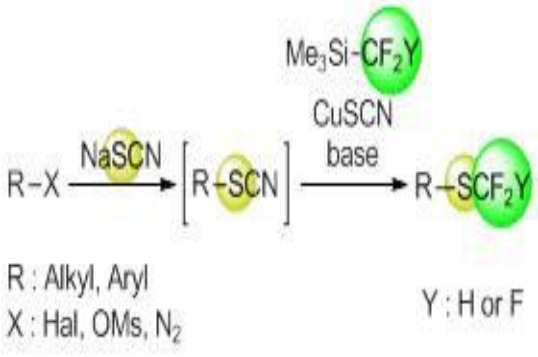

P-468

Regioselective Palladium-Catalyzed Heterocyclization-Sonogashira-Coupling Cascades from 2-Alkynylbenzamides and Terminal Alkynes

Dr. Jose M. Aurrecoechea[1], Aitor Ortega[1], Unai Vilar[1], Dr. Youssef Madich[1], Dr. Belén Vaz[2], Prof. Dr. Rosana Álvarez[2]

[1]*Universidad del Pais Vasco UPV/EHU, Leioa, Spain,* [2]*Universidade de Vigo, Vigo, Spain*

Poster Session 1

The palladium-catalyzed heterocyclization-Heck coupling cascades between C-C triple-bond-tethered heteroatom-based nucleophiles and alkenes has provided an efficient entry into a variety of functionalized heterocyclic derivatives.[1] In contrast, the corresponding use of terminal alkynes as coupling agents (heterocyclization-Sonogashira-type cascade) remains much less developed.[2]

We now report selective heterocyclization-Sonogashira coupling cascades between 2-alkynylbenzamides 3 and terminal alkynes 4, under palladium catalysis, to produce adducts 5. Regeneration of the catalyst from the Pd(0) produced in the coupling is achieved with air as terminal oxidant.

[SCHEME]

Our results show that the cascade reaction is compatible with the use of benzamides derived from both aliphatic and aromatic amines (R^1 group), while substitution at R^2 and R^3 with either alkyl or aryl groups is also similarly effective. As a result, products 5 are obtained with significant structural diversification, emanating from variations in the alkyne 3 and in the starting 2-alkynylbenzamides, themselves prepared by Sonogashira coupling between 2-iodobenzamide substrates 1 and terminal alkynes 2.

In conclusion, an effective heterocyclization-Sonogashira coupling cascade has been developed from simple building blocks 3 and 4. This single-operation procedure provides significant advantages over previously reported two-step alternatives, where appropriately functionalized cyclization intermediates had to be isolated and then submitted to standard Sonogashira conditions.[3]

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We thank the Spanish Ministerio de Economía y Competitividad (Grant CTQ2012-37734, FEDER) and Universidad del País Vasco for financial (fellowship to Y. M.) and technical (SGIker) support.


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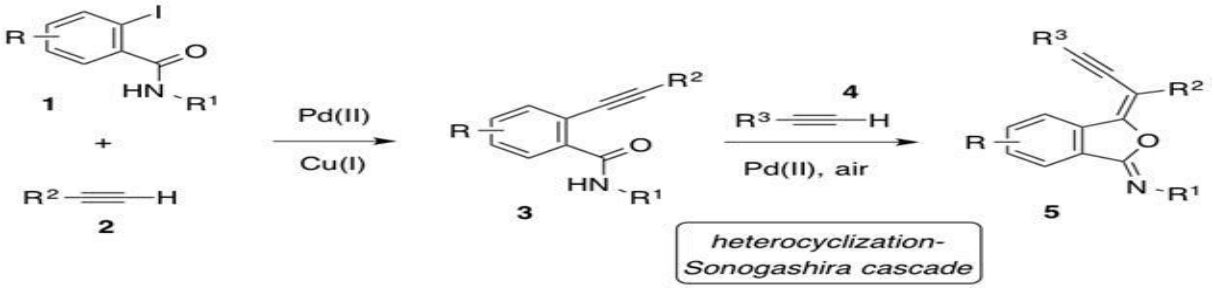
R
I
O
HN
R1
1
+
R2
H
2
Pd(II)
Cu(I)
R2
R
O
HN
R1
3
4
R3
H
Pd(II), air
R3
R2
R
O
N
R1
5
heterocyclization-
Sonogashira cascade

P-348

Pseudo metal generation via catalytic oxidative polymerization supported on reactive template for redox switched off-on photothermal therapy

Jong-Woo Lim[1], Seo Ryung Bae[1], Jihye Choi[3], Hyun-Ouk Kim[1], Byunghoon Kang[1], Myeong-Hoon Kim[1], Yong-Min Huh[2], Seungjoo Haam[1]

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Poster Session 2

Photothermal therapy that employs optical absorbing agents under light irradiation has attracted much attention in recent years as a promising alternative to traditional cancer therapies. Moreover, photothermal therapy researcher primarily focused on achieving a higher standard of biocompatibility and improving the thermal conversion efficacy of the photothermal agents (PTAs). Thus, we fabricated a tailored polyaniline-coated iron oxide nanocluster (PPAM) as photothermal agent via complementary oxidant system (COS) on the correlation between iron oxide nanocluster and ammonium peroxydisulfate using a catalytic redox polymerization. Under physiological pH, PPAM reveals no special features; however under low pH conditions which is a notable characteristic of the cancer microenvironment, PPAM automatically converts into its emeraldine salt (ES) state thus activates as a photothermal therapeutic agent. Furthermore, the external proton gradient-responsive conversion between EB and ES, redox-triggered autonomous conversion in vitro, and photothermal function as PTA in vitro were assessed on HT1080 cells. Finally, systemic regulation of the cell death pathway is studied by controlling the photothermal therapeutic efficacy on HT1080 cancer cells. The results suggest that PPAM, a self-redox-responsive activatable photothermal therapeutic agent, provides a new platform for highly sensitive and specific apoptotic hyperthermia, which may hold promise in future therapeutic fields.

P-349

Synthesis of Pd (II) Schiff Base Complexes Derived From Condensation of Salicylic Aldehyde with Aniline Derivatives for Suzuki Coupling Reactions

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[1]*Chemistry Department, Faculty of Arts and Sciences, Cukurova University, Adana, Turkey*

Poster Session 2

Palladium-catalyzed Suzuki coupling reactions of aryl halides with aryl boronic acids is one of the most powerful and simplest methods for C-C bond formation. Especially, phosphine metal complexes have been used as catalyst in these reactions [1-2].

In spite of significant success of phosphine ligands, they have major disadvantages such as; handling problems, synthetic difficulties, high cost, toxicity and air sensitivity. In this context, nitrogen-based ligands are used as alternatives to phosphine derivative ligands in Suzuki coupling reactions. Among them, Schiff base derivatives are very popular ligands in coordination chemistry because of their easy formation and coordination with variety of metals that allowed their use as catalyst in different asymmetric reactions [3].

This work is described the formation of Schiff bases resulting from condensation of salicylic aldehyde with fluorinated aniline derivatives and their Pd(II) complexes. Elemental analysis, FT-IR, NMR and TGA were used to characterize the synthesized ligands and their metal complexes.

Figure 1

Catalytic activity of metal complexes was tested over Suzuki coupling reactions of aryl bromide with phenyl boronic acid.

Figure 2

From IR analysis of Schiff base ligands characteristic peaks were observed: C-H(Ar) 3005-3060, C=N 1620-1680, C-F 1190-1240 $cm_{-1}$and for palladium complexes, C-H(Ar) 2900-2980, C=N 1580-1620, C-F 1150-1200, Pd-N 550-560 were observed and confirmed the structure. Catalytic activity experiments were realized in DMF within time range of 30-120 min at 313.15 K over Suzuki reaction and analyzed by GC. The results have shown that, maximum conversation obtained at 90 min with %99 yield and the yield be constant when reaction time increased from 90 min to 120 min.

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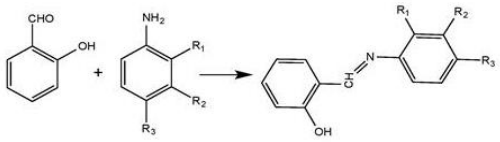

	R_1	R_2	R_3
L1	CF_3	H	H
L2	H	CF_3	H
L3	H	H	CF_3

Figure 1. Preparation of Schiff base ligands

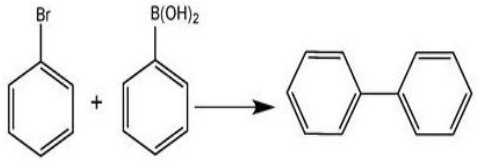

Figure 2. Schematic represantation of Suzuki C-C coupling reaction

P-350

Catalytic enantioselective palladium-catalyzed cascade reaction. Access to lycorane core

Prof. Dr. Esther Lete[1], Dr Estibaliz Coya[1], Mrs Iratxe Barbolla[1], Prof Dr Nuria Sotomayor[1]
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Poster Session 2

Catalytic enantioselective transition metal-catalyzed cascade reactions represent one of the most powerful and efficient methods for the rapid assembly of biologically active and complex chiral molecules from simple substrates. Particularly, enantioselective asymmetric intramolecular Heck reaction has emerged as an excellent tool for the construction of polycyclic frameworks generating tertiary and quaternary stereocenters. In this context, our interest in asymmetric synthesis[1] and in palladium catalyzed reactions[2] led us to study the possibility to apply an enantioselective palladium-catalyzed polyene cyclization to 2,3-dialkenylpyrroles (1) using chiral phospane ligands (L*) for the construction of the structural core of the lycorine class of Amaryllidaceae alkaloids. Because of their unique tetracyclic structure and their pharmacological activity (anticancer, antiviral, antiparasitic, etc.), Lycorane-type alkaloids have attracted numerous synthetic studies. However, relatively few approaches to the asymmetric synthesis of these alkaloids have been reported so far.
In our strategy, the σ-arylpalladium intermediate resulting from the migratory insertion of the arylpalladium to the alkene should be trapped by an adequately positioned internal alkene, thus allowing the sequential formation of two rings in one step. A careful choice of the catalytic systems and reaction conditions is critical to obtain good enantioselectivities (up to 90%).The extension to the formation of larger rings will also be discussed.

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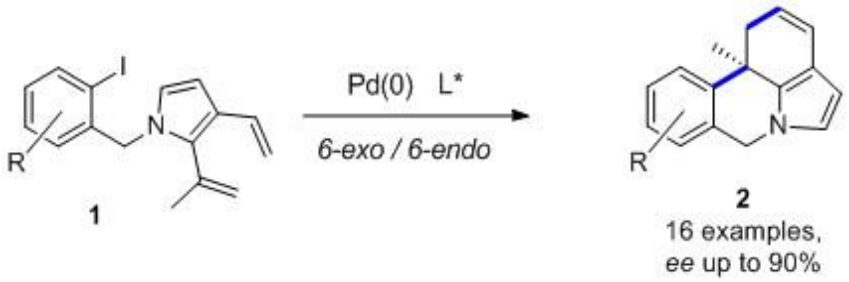

P-351

New P,N-ligands for enantioselective Ir-catalyzed hydrogenation of unfunctionalized olefins

Ms Maria Biosca Brull[1], Dr. Oscar Pàmies[1], Prof. Montserrat Diéguez[1], Mr Alexander Paptchikhine[2], Prof. Pher G. Andersson[2]

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Poster Session 2

The asymmetric hydrogenation of olefins is one of the most powerful transformations for preparing chiral compounds due to its high efficiency, atom economy and operational simplicity. Whereas the reduction of olefins containing an adjacent polar group has been successfully achieved, the hydrogenation of unfunctionalized olefins is less developed and the search for more efficient ligands is still needed.[1] In this area, a small but structurally important family of Ir-phosphoramidite-oxazoline/thiazole precatalysts has been synthetized by changing the nature of the N-donor group (either oxazoline or thiazole) and the configuration at the biaryl phosphoroamidite moiety (Scheme 1). This study identifies a series of Ir-catalytic systems that can hydrogenate a wide range of minimally functionalized olefins (including E- and Z-tri- and disubstituted substrates, vinylsilanes, enol phosphinates, tri- and disubstituted alkenylboronic esters, and α,β-unsaturated enones) in high enantioselectivities (ee values up to 99%) and conversions.[2]

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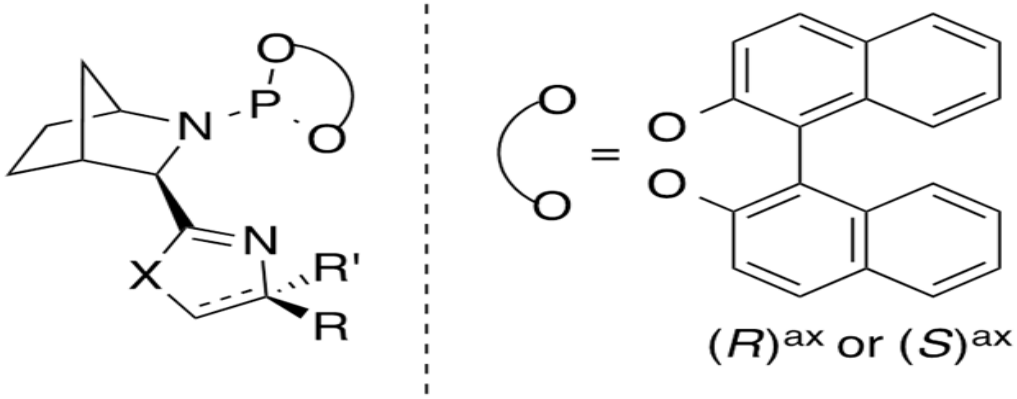

Scheme 1. Phosphoroamidite-thiazole/oxazoline (**L1-2a-b**) ligands

P-352

Selective formation of cis-Platinum(II)-NHC-Pnictogen complexes by ligand exchange & Evaluation as Potential Anticancer Platinum-Drugs

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Poster Session 2

Since the discovery of cisplatin by Rosenberg in 1965 and its approval by the FDA in 1978, the potential anticancer activity of platinum complexes has been highlighted. Nevertheless, the latter suffers severe side effects, which lead to the research of novel active complexes offering lower toxicity and resistance.

Among these, platinum N-Heterocyclic Carbene (NHC) complexes have demonstrated very promising results as anticancer agents.[1] Recently interesting biological activity have been depicted using metal-complex bound to a phosphorus atom.[2] The lability of a trans pyridine ligand in an NHC-Pt(II)-pyridine complex can be exploited giving an access to a wide diversity of platinum complexes. Indeed, pyridine can be substituted with various nitrogen-based ligands[sup]3,4[/sup] to yield the corresponding Pt-complexes and few examples were reported using phosphine ligands.[5]

Thus we developed a modular, simple and high-yielding method allowing the introduction of a range of pnictogen-based ligands (Pn = PPh_3, $AsPh_3$ and $SbPh_3$) . The a trans NHC−Pt(II) precursor complex 1, allowed the simple preparation of exclusive cis-configurated neutral complexes. Using an excess of ligand provide the formation of bis-Pn cationic platinum complexes again with a cis-geometry.

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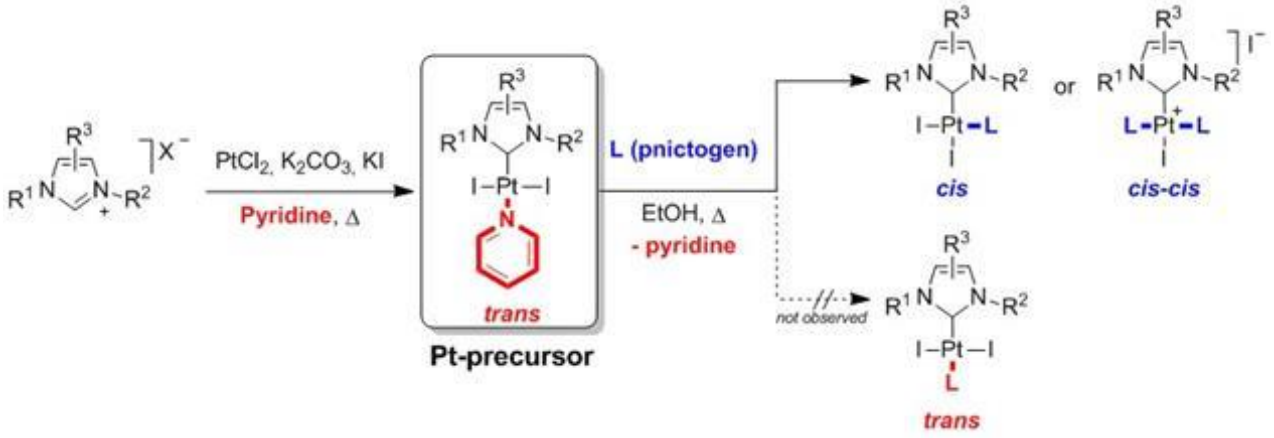
PtCl2, K2CO3, KI
Pyridine, Δ
trans
Pt-precursor
L (pnictogen)
EtOH, Δ
- pyridine
not observed
cis
or
cis-cis
trans

P-353

Copper complexes bearing non-innocent ligands : towards trifluoromethylation

Mr Jeremy Jacquet[1], Ms Elise Salanouve[1], Dr Maylis Orio[2], Dr Hervé Vezin[2], Dr Sébastien Blanchard[1], Dr Etienne Derat[1], Dr Marine Desage-El Murr[1], Prof. Louis Fensterbank[1]

[1]Institut Parisien de Chimie Moléculaire, Université Pierre et Marie Curie, Paris, France, [2]Laboratoire de Spectrochimie Infrarouge et Raman, Villeneuve d'Ascq, France

Poster Session 2

Because of their unusual electronic behaviour, non-innocent (or redox) ligands have long sparked the interest of spectroscopists and inorganic chemists, and their potential in catalysis has only later been considered. Their efficiency has now been shown in many synthetic applications, such as cycloisomerisations and oxidations.[1] However, these ligands have never been developed for trifluoromethylation reactions. We focused on the development of a trifluoromethylated copper complex bearing non-innocent ligands, in view to study the potential influence of the ligands on the reactivity of the complex.

Iminosemiquinonate radical ligands are well-established non-innocent ligands and have been previously used with several metals.[2] The copper complex bearing two iminosemiquinonate radical ligands is air-stable and can undergo two successive monoelectronic oxidations or reductions, without modification of the copper oxidation state. Upon reaction with Umemoto's reagent, an electrophilic source of CF_3, a new complex was formed.[3]

Pulsed EPR spectroscopic measurements and electrochemistry, together with DFT calculations allowed to confirm a ligand-centered oxidation associated with the formation of a Cu(II)-CF_3 bond. The observed reactivity of the isolated complex demonstrates an ability to perform a transfer of CF_3 on electrophilic sites of the ligand, with or without the presence of a substrate. Considering the initial electrophilic nature of the CF_3, this can be overall interpreted as a formal umpolung of the CF_3 moiety, sustained by the redox ligands.

The initial bis(iminosemiquinonate)copper complex is also able to induce radical trifluoromethylation in the presence of an electrophilic trifluoromethylating agent and unsaturated moieties. Indoles, silyl enol ethers and alkynes were tested.

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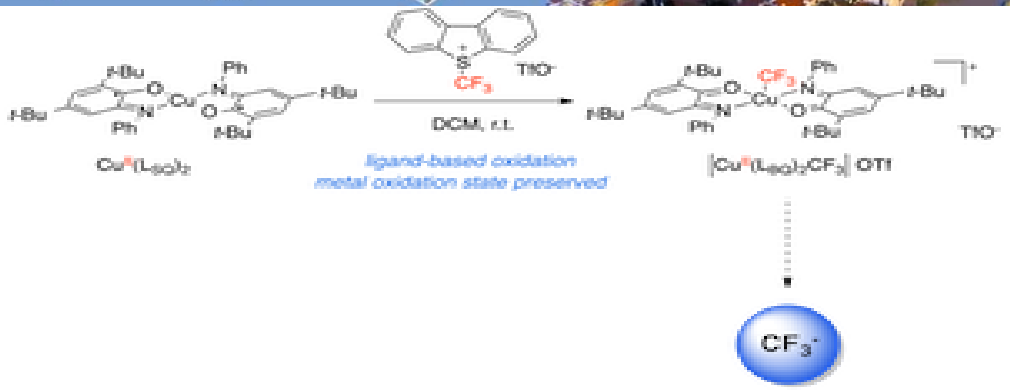
t-Bu
Ph
O
N
Cu
TfO⁻
CF3
DCM, r.t.
ligand-based oxidation
metal oxidation state preserved
CF3⁻

P-354

Palladium catalyzed diaryl sulfoxide generation from aryl benzyl sulfoxides and aryl chlorides

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Poster Session 2

Aryl sulfoxides are important structural motifs in bioactive compounds and marketed therapeutics. Significant effort, therefore, has been devoted to their preparation. The most popular mehods for the synthesis of sulfoxides are oxidation of sulfides and nuclephilic substitution of sulfinamides or sulfinate esters.

Transition-metal catalyzed cross-coupling reactions are powerful method to form C-S bonds[1] and offer an alternative approach to construct aryl sulfoxides. Recently we communicated[2] diaryl sulfoxide formation from aryl benzyl sulfoxides and aryl bromides using a palladium catalyst based on van Leeuwen's NiXantPhos ligand.[3] Given the scarcity of aryl chlorides that have been successfully employed in the sulfenate anion arylation, and the reduced costs and greater abundance of aryl chlorides relative to aryl bromides, we viewed the inclusion of aryl chlorides in this reaction as important.

Herein, we report a palladium-catalyzed diaryl sulfoxide formation from aryl benzyl sulfoxides and aryl chlorides.[4]

Diaryl sulfoxides are synthesized from aryl benzyl sulfoxides and aryl chlorides via three sequential catalytic cycles all promoted by a NiXantPhos-based palladium catalyst. The key step is S-arylation of a sulfenate anion. An air- and moisture-stable precatalyst derived from NiXantPhos efficiently facilitates the transformation. Various functional groups, including those with acidic protons, were tolerated. This method can also be extended to methyl and dibenzyl sulfoxides substrates.

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P-355

Sequential Palladium(II)-catalyzed C-H activation reactions for the synthesis of substituted quinolones and coumarins

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Poster Session 2

Transition-metal-catalyzed direct alkenylation of Csp^2-H bonds (Fujiwara-Moritani reaction) has emerged as an efficient, atom-economical, and environmentally friendly synthetic tool for the preparation of highly functionalized aromatic molecules. Our interest in catalytic C-H activation chemistry (1) led us to study this reaction with the aim of developing efficient and practical procedures to prepare polysubstituted quinolones and coumarins, which important structural motifs embedded in a wide variety of bioactive natural products and pharmaceuticals.

Herein, we describe an efficient approach to the synthesis of biologically active 3-alkenyl-4-substituted quinolin-2(1H)-ones that involves two sequential C-H alkenylation reactions. First, a Pd(II) catalyzed selective 6-endo intramolecular C-H alkenylation of N-phenylacrylamides has allowed the construction of quinolone core, which could be further functionalized in C-3 through a second intermolecular C-H alkenylation reaction (2). This method is a significant advance over the existing procedures that require preactivatated reaction partners. Furthermore, these reactions can also be carried out in aqueous media at room temperature, using a 2% aqueous solution of PTS, or even in water, with good yields. Details of these transformations will be given. The extension of this procedure to to the synthesis of the corresponding coumarins, quinolines or chromanes will also be discussed.

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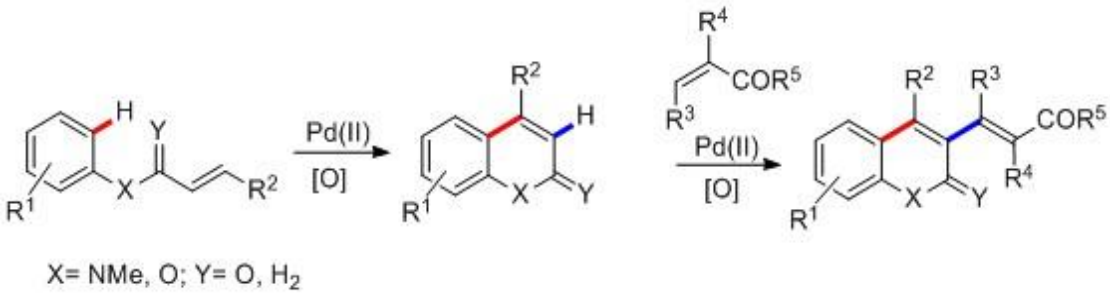

P-356

Rhodium complexes containing quinone moiety in oxidation and cross-coupling reactions.

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Poster Session 2

Quinones, owing to their unique characteristics, play important roles in living organisms, in photosynthesis, aerobic cellular respiration, blood coagulation, and bone metabolism.[1,2] What is more, thanks to their biological and pharmacological activity, they are widely used in medicine.[3] They are also commonly known as oxidants, however little is known about their influence on the catalytic properties of metal complexes.
In modern organic synthesis oxidation and cross-coupling reactions catalyzed by transition metals complexes are of high importance because they enable the synthesis of numerous molecules under relatively mild conditions.[4] Although there are a number of known protocols used in the above mentioned reactions, intensive research aimed at synthetizing of better catalysts is still ongoing.
Herewith the synthesis of new rhodium complexes containing quinone moiety will be presented as well as their utilization in the oxidation and cross-coupling reactions.

Figure 1: Examples of studied quinones.

Acknowledgement:
This work has been supported by FNP, HOMING PLUS/2013-7/6.

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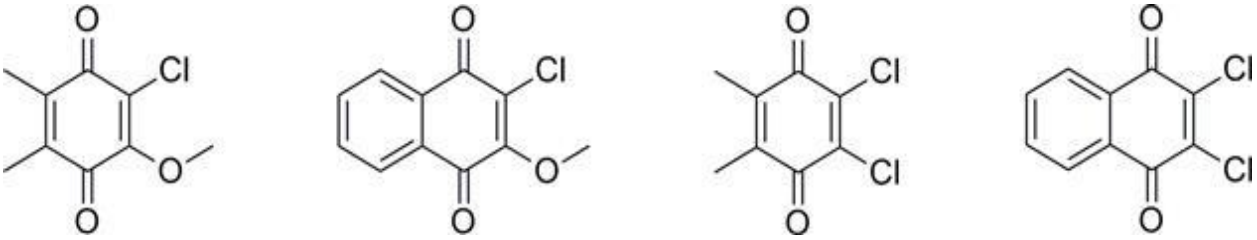

P-357

Electrophilic Gold(I) Carbenes via Decarbenation of Cycloheptatrienes

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Poster Session 2

We have recently demonstrated that aryl gold(I) carbenes [LAu=CHAr][sup]+[/sup], formed by a retro-Buchner reaction of 7-aryl 1,3,5-cycloheptatrienes (decarbenation reaction), give rise to cyclopropanes by reaction with electron-rich olefins.[1] Alternatively, indenes and fluorenes have been formed by the intramolecular reaction of alkenes or arenes in the ortho position of the aryl moiety, respectively.[2] The scope of these reactions has now been extended by using alkenyl-substituted cycloheptatrienes, as well as by trapping the gold(I) carbenes by 1,3-dipoles, to access to a broad range of small molecules under mild conditions.

Acknowledgments:
We thank MINECO (project CTQ2010-16088/BQU, Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319), the European Research Council (Advanced Grant No. 321066), Cellex Foundation, and the ICIQ Foundation for financial support.

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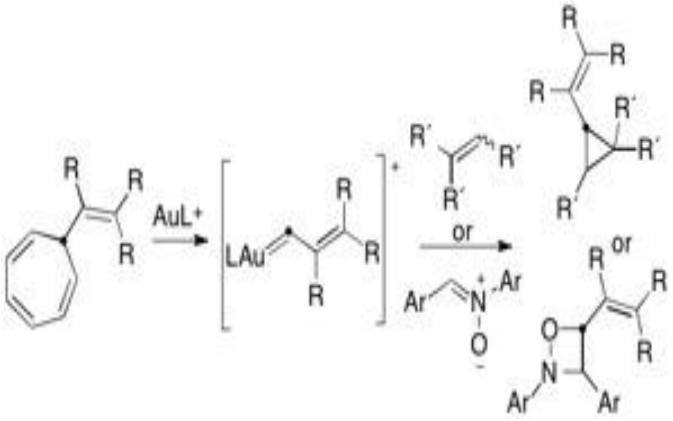

P-358

Ru-catalyzed C-H functionalization of aminoacid derivatives: an effective strategy for the synthesis of N-hetero-bicyclic compounds.

Sara Ruiz Morte[1], Esteban P. Urriolabeitia[1]
[1]*Instituto de Síntesis Química y Catálisis Homogénea (ISQCH, CSIC-Universidad Zaragoza), Zaragoza, Spain*

Poster Session 2

C-H bond activation catalyzed by transition metals is a very useful tool for the synthesis of high added value molecules. It allows the introduction of countless fragments in otherwise inactive C-H bonds.[1] Furthermore, the presence of a directing group allows the reaction to occur regioselectively. We have reported the use of primary amines as efficient directing groups, enabling the regioselective synthesis of N-heterocycles such as (benzo)isoquinolines and fused pyridines.[2] This process is catalyzed using non-expensive Ru complexes, which have shown an increasing number of applications in catalytic C-H functionalizations along last years.

Aminoacids are biologically important molecules and, due to the presence of the amino moiety, they are adequate candidates for directed metal-catalyzed C-H functionalization. Up to now, however, the N atom must be protected before the functionalization takes place in order to achieve efficient transformations, and this complicates the synthetic sequence.[3] Therefore, the functionalization of N-unprotected aminoacid derivatives is still challenging. Herein we report the oxidative coupling of unprotected N-free phenylglycinates with unsaturated hydrocarbons (alkynes and alkenes), catalyzed by a Ru (II) complex.

The reaction between methylphenylglycinate derivatives and a range of alkynes affords 3,4-substituted methylisoquinoline-1-carboxylates, while the coupling between N-free or N-substituted methylphenylglycinate derivatives and widely available alkenes gives substituted methylisoindoline-1-carboxylates (see Figure 1). The interest of isoquinoline- and isoindoline-1-carboxylate skeletons resides in the fact that they are often found in compounds with pharmacological and biological activity, and they are also key synthetic intermediates.

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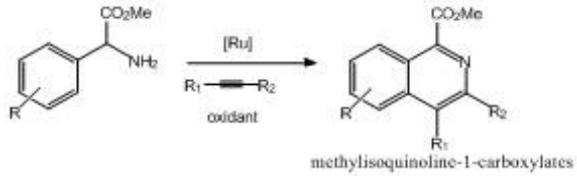
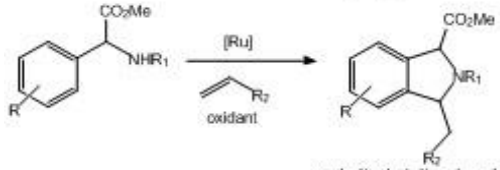


methylisoquinoline-1-carboxylates



methylisoindoline-1-carboxylates

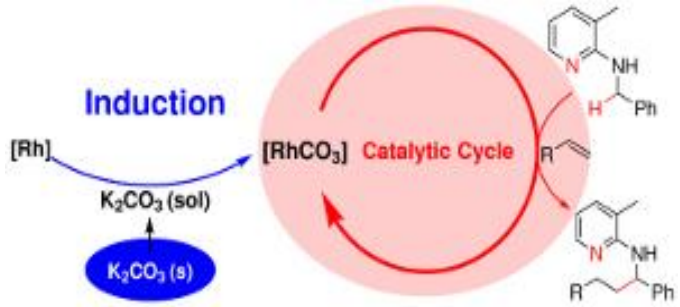
P-359

Investigations into the Kinetic Modelling of the Direct Alkylation of Benzylic Amines: Potassium carbonate is responsible for the Observation of an Induction Period

MSc Robert Pollice[1], Dr. Michael Schnürch[2]
[1]*ETH Zürich, Zurich, Switzerland,* [2]*TU Wien, Vienna, Austria*

Poster Session 2

Within this work a Rh(I)-catalyzed direct C-H alkylation of benzylic amines with alkenes co-catalyzed by potassium carbonate was studied as a benchmark reaction to gain insight into the main kinetic influence factors associated with heterogeneous bases in metal-catalyzed reactions and to elucidate one of the associated underlying reaction mechanisms. Detailed investigations into the kinetic behavior of this transformation revealed that potassium carbonate, which is effectively insoluble in the reaction mixture under the reaction conditions, is only needed in the beginning of the reaction. During the concomitant induction period potassium carbonate is proposed to dissolve to a vanishingly small extent and the Rh-precatalyst irreversibly reacts with dissolved potassium carbonate to form the catalytically active species. The duration of this induction period is dependent on the molar loading, the specific surface area and the water content of potassium carbonate and on the agitation of the reaction mixture and all these dependences can be rationalized on the basis of a detailed kinetic model which also explains the kinetic behavior of the catalytic cycle during the initial reaction period.



P-360

A catalytic multicomponent coupling reaction for the enantioselective synthesis of spiro and fused bicyclic acetals.

Lara Cala Álvarez[1], Patricia Fernández Fernández[1], Dr. Abraham Mendoza Valderrey[2], Dr. Félix Rodríguez Iglesias[1], Dr. Francisco Javier Fañanás Vizcarra[1]
[1]*University of Oviedo, Oviedo, Spain,* [2]*Stockholm University, Stockholm, Sweden*

Poster Session 2

Natural products are an exceptional source of drug leads and a continuous inspiration for the design of small-molecule libraries for drug discovery.[1] Spiroacetals have been found as a key structural unit in many biologically active and structurally diverse natural products.[2] It should be stressed that despite the unquestionable interest of optically active spiroacetals, very few strategies for the enantioselective synthesis of these compounds from achiral substrates have been reported before we became interested in the development of a “reagent-controlled” asymmetric synthesis of spiroacetals.[sup]3[sup]

We developed the first multicomponent catalytic asymmetric synthesis of hybrid molecules which comprises a spiroacetal scaffold and an α-amino acid motif. These molecules are easily available through a gold phosphate-catalysed one-pot three component coupling reaction alkynols, arylamines and glyoxylic acid.[4]

As spiroacetals, fused bicyclic acetals are also present in several bioactive molecules.[sup]5[sup] In this context, we extended our strategy to obtain [3.3.0] and [4.3.0] bicyclic compounds in an enantioselective fashion by using alkynols of different chain lengths.

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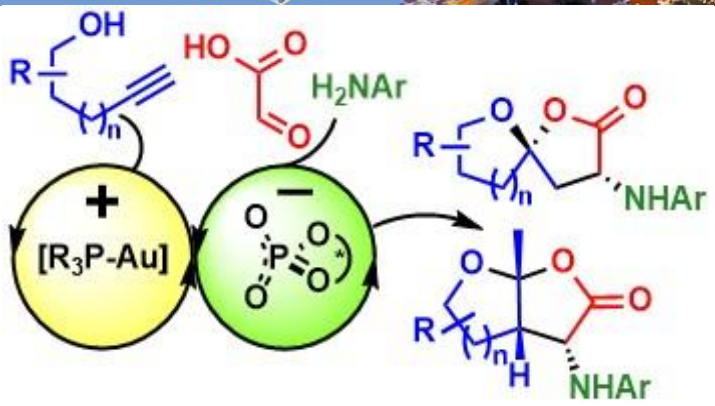
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P-361

Mechanistic Studies on the Rh(III)-Mediated Amido Transfer Process Leading to Robust C–H Amination with a New Type of Amidating Reagent

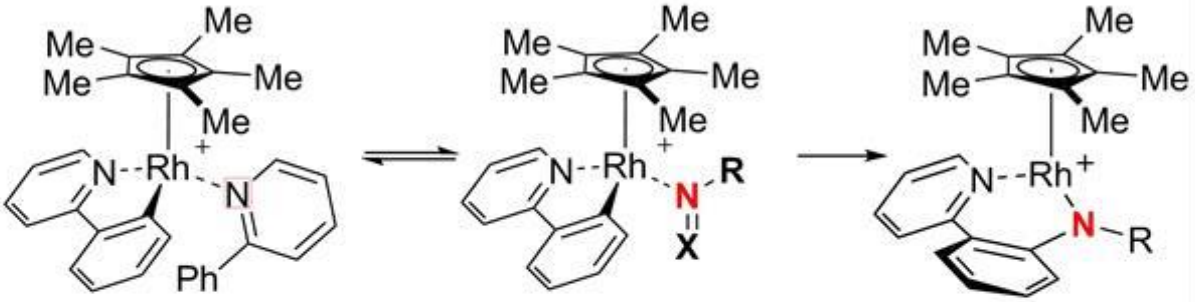
Mr. Yoonsu Park[1,2], Mr. Kyung Tae Park[1,2], Dr. Jeung Gon Kim[2,1], Prof. Dr. Sukbok Chang[2,1]

[1]*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea, Daejeon, South Korea,* [2]*Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon, Republic of Korea, Daejeon, South Korea*

Poster Session 2

Mechanistic investigations on the Cp*Rh(III)-catalyzed direct C–H amination reaction led us to reveal the new utility of 1,4,2-dioxazol-5-one and its derivatives as highly efficient amino sources. Stepwise analysis on the C–N bond-forming process showed that competitive binding of rhodium metal center to amidating reagent or substrate is closely related to the reaction efficiency. In this line, 1,4,2-dioxazol-5-ones were observed to have a strong affinity to the cationic Rh(III) giving rise to dramatically improved amidation efficiency when compared to azides. Kinetics and computational studies suggested that the high amidating reactivity of 1,4,2-dioxazol-5-one can also be attributed to the low activation energy of an imido-insertion process in addition to the high coordination ability. While the characterization of a cationic Cp*Rh(III) complex bearing an amidating reagent was achieved, its facile conversion to an amido-inserted rhodacycle allowed for a clear picture on the C–H amidation process. The newly developed amidating reagent of 1,4,2-dioxazol-5-ones was applicable to a broad range of substrates with high functional group tolerance, releasing carbon dioxide as a single byproduct. Additional attractive features of this amino source, such as they are more convenient to prepare, store, and use when compared to the corresponding azides, take a step closer toward an ideal C–H amination protocol.

Mechanistic Clarification



New Class of Amidating Reagents

- *Strong Coordination*
- *Low Activation Barriers*
- *External Oxidant-Free*
- *Low Catalyst Loading*

P-362

Pd-Catalyzed Autotandem C-C/C-C bond-forming reactions with tosylhydrazones: Synthesis of Spirocycles with extended π-conjugation

Dr María-Paz Cabal[1], Miss Raquel Barroso[1], Dr Carlos Valdés[1]
[1]*Universidad De Oviedo, Oviedo, Spain*

Poster Session 2

According to our interest in the Pd-catalyzed cross-coupling reactions employing tosylhydrazones [1,2], we have reported the first autotandem process through a C-C/C-N sequence[3] and the first autotandem C-C/C-C process with participation of tosylhydrazones as a coupling partner[4]. We envisioned a different approach by designing a reaction cascade in which the funcionality generated in the first step would react again in a second step. In particular, considering the cross-coupling reaction of tosylhydrazones, the double bound formed in the first Pd-catalyzed cross-coupling might participate in an intramolecular Heck reaction to render spirocycles through a C-C/C-C autotandem sequence[5].

Some of these rigid spirocyclic structures with extended π-conjugation have shown fluorescent properties and would be employed in the development of electroluminiscent and optoelectronic materials[6].

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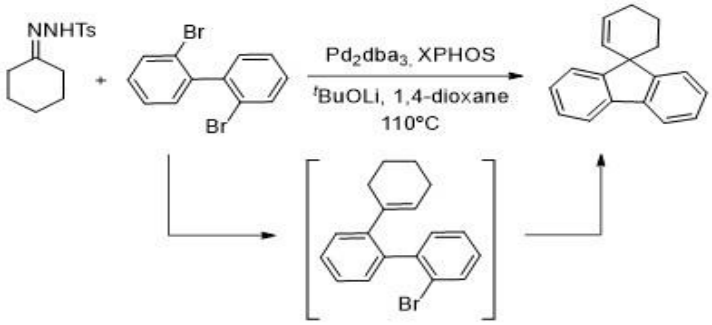


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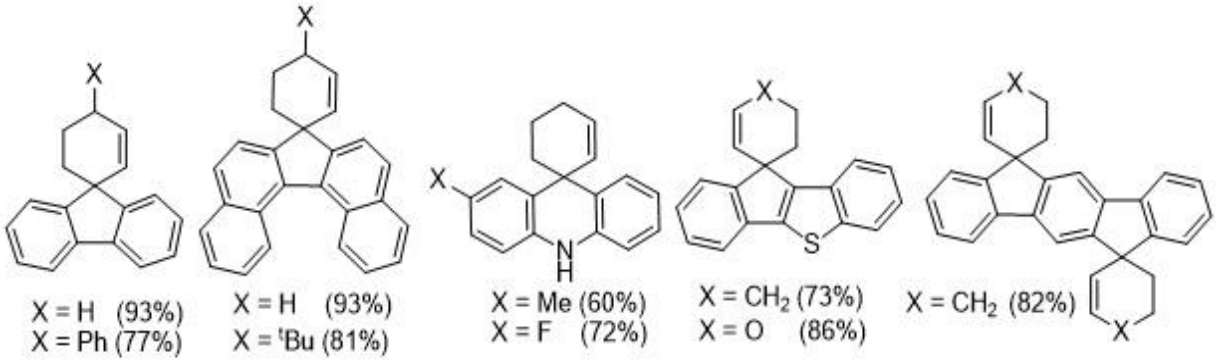
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X = H (93%)
X = tBu (81%)
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N
H
X = Me (60%)
X = F (72%)
X
S
X = CH2 (73%)
X = O (86%)
X
X
X = CH2 (82%)

P-364

Synthesis of pyrene-functionalized cholesterol derivatives via Copper (I) catalyzed "click" reaction

Sevinc Ilkar Erdagi[1], Erdinc Doganci[2,3], Cavit Uyanik[1], Faruk Yilmaz[2]
[1]Kocaeli University, Department of Chemistry, Kocaeli, Turkey, [2]Gebze Technical University, Department of Chemistry, Gebze/Kocaeli, Turkey, [3]Kocaeli University, Deparment of Science Education, Kocaeli, Turkey

Poster Session 2

It is well known that cholesterol (Chol) is an essential molecule for humans as a component of cell membrane and as a precursor of steroid hormones and bile acids. In recent years, interest in cholesteric (or chiral nematic) liquid crystalline materials has increased chiefly because of their particular optical properties, including a large optical rotation and selective light reflection [1, 2]. Pyrene (Py) is a widely used fluorescence probe for such studies [3]. Because pyrene has long fluorescence lifetime, ability to form excimers, and a well-defined fluorescence spectrum [4].

The "Click" chemistry technique based on the the Cu(I)-catalyzed alkyne-azide cycloadditon (CuAAC) reaction invented by Sharpless as a versatile tool for functional group modifications in organic synthesis. It provides high reaction yields and excludes time-consuming purification processes [3].

In this study, novel pyrene end-capped cholesterol derivatives (Chol-Py) with different methylene spacers were synthesized by using "click" chemistry techniques. Firstly hydroxyl functionality of cholesterol was converted to bromide and azide end groups in turn. Further end-group modification of azide functional cholesterol derivative was achieved quantitatively via the Cu (I) catalyzed "click" reaction between azide and 1-ethynyl pyrene in the final step [3] (Fig. 1).

Figure 1 –Synthesis of pyrene-functionalized cholesterol derivatives (Chol-Py).

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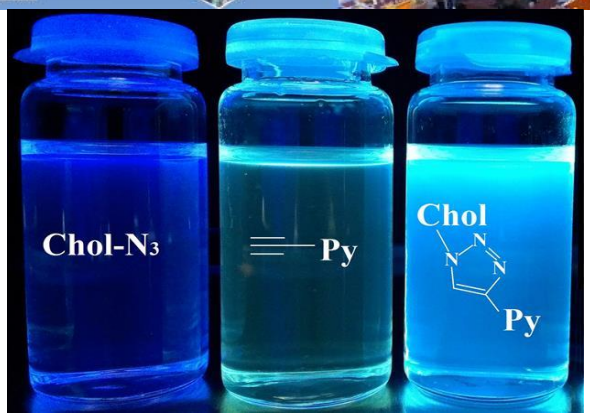
Chol-N3
Py
Chol
Py

P-365

A Rhodium-Catalysed Hydroacylation Approach to the Synthesis of Highly Functionalised Quinolines

Mr James Neuhaus[1], Miss Sarah Morrow[1], Mr Michael Brunavs[2], Prof Michael Willis[1]
[1]*University of Oxford, Oxford, UK* [2]*Eli Lilly, Windlesham, UK*

Poster Session 2

Rhodium catalysed hydroacylation is an extremely efficient and 100% atom economical process, enabling the construction of enones and ketones from simple aldehydes and alkynes.[1] Highly active catalytic systems have lead to high functional group tolerance, benign reaction conditions and the ability to use low catalyst loadings, all of which are attractive attributes for any synthetic protocol. The application of hydroacylation towards the synthesis of various heterocyclic precursors has previously been demonstrated, with both furans and benzofurans readily accessible.[2] This work looks to apply high activity bisphosphine Rh complexes to the synthesis of quinolines, via hydroacylation of substituted 2-ethynylaniline derivatives with various β-chelating aldehydes. Once a simple Boc-protection strategy was employed to prevent imine formation the coupling was observed to proceed with high efficiency at ambient conditions, achieving excellent yields. Pleasingly, these Friedländer-type intermediates were found to undergo a simple Boc-deprotection-cyclisation sequence to generate highly functionalised quinoline products. This sequence has proven extremely effective for a range of electron neutral and electron poor alkynes, whilst for electron rich alkynes an alternative sequence, starting from 2-nitrophenylacetylenes and involving a reductive cyclisation afforded access to not only quinolines, but by varying the conditions also tetrahydroquinolines and quinoline N-oxides. In conclusion, this work has demonstrated the applicability of Rh-catalysed hydroacylation to the formation of highly regiocontrolled Friedländer-type intermediates, leading to highly functionalised quinolines and quinoline derivatives.

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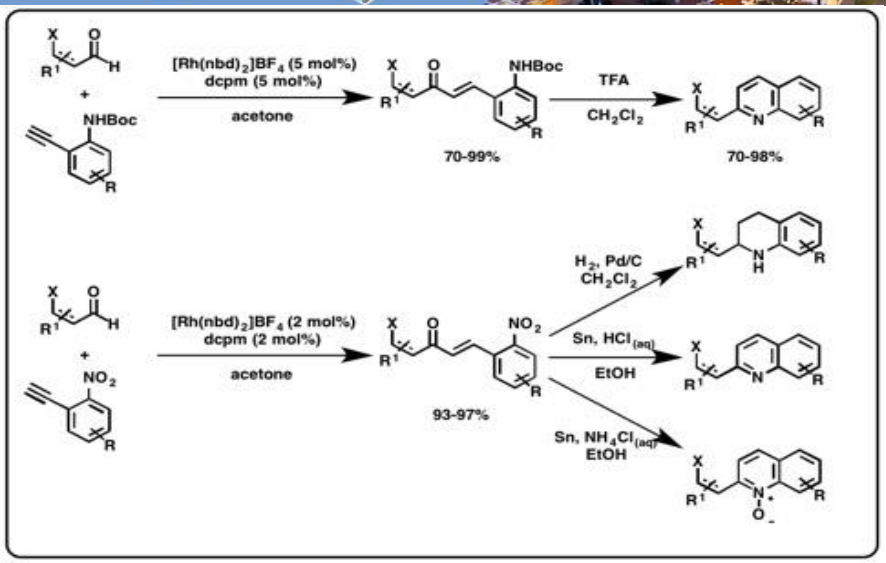
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dcpm (5 mol%)
acetone
NHBoc
TFA
CH2Cl2
70-99%
70-98%
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dcpm (2 mol%)
acetone
NO2
H2, Pd/C
CH2Cl2
Sn, HCl(aq)
EtOH
Sn, NH4Cl(aq)
EtOH
93-97%

P-366

Synthesis of Biaryls via Decarboxylative Hiyama Coupling

Dr. Dmitry Katayev[1], Benjamin Exner[2], Prof. Dr. Lukas Gooßen[3]
[1]Technische Universität Kaiserslautern, Kaiserslautern, Germany, [2]Technische Universität Kaiserslautern, Kaiserslautern, Germany, [3]Technische Universität Kaiserslautern, Kaiserslautern, Germany

Poster Session 2

Transition metal-catalyzed cross-coupling reactions are established tools for the construction of carbon–carbon bonds. Within recent years, decarboxylative cross-couplings involving broadly available carboxylic acids have emerged as an environmentally benign alternative to traditional methodologies, as they release carbon dioxide as the only by-product.

Redox-neutral decarboxylative cross-couplings, often mediated by bimetallic catalyst systems, allow the formation of carbon–carbon bonds starting from aromatic carboxylates and numerous carbon electrophiles, however with the drawback of elevated reaction temperatures. Milder conditions can be applied in the oxidative version of this reaction, in which a carbon nucleophile is coupled with the carboxylic acid.[sup][1][/sup] Among the many nucleophilic reagents, organosilicon compounds remain particularly challenging substrates due to the relative stability and low polarity of the C–Si bond. Thus their conversion has so far only been achieved in moderate yields.[sup][2,3][/sup]

We now developed a trimetallic Pd/Cu/Ag system which allows the decarboxylative Hiyama coupling of ortho-substituted aryl carboxylates with trialkoxyarylsilanes in high yields. The meticulous investigation of the transformation revealed that a Pd-N-heterocyclic carbene complex efficiently catalyzes the cross-coupling with silver carbonate supporting its re-oxidation, while copper(II) fluoride acts as a decarboxylation catalyst, stoichiometric oxidant and fluoride source to activate the silicon based substrate. The protocol was applied to the synthesis of 22 biaryl compounds, among them examples bearing halogen substituents that remained intact during the reaction enabling further transformations. The synthetic utility of the biaryl products was demonstrated by their conversion into pharmaceutically meaningful carbazoles and 1H-indazoles.[sup][4][/sup]

References:

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– CO2
NO2
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R1
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N
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Ph
R1
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H
N
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P-367

Skeletal diversity in Gold(I) and Platinum(II) Catalyzed Cycloadditions of Allenedienes

Mr. Ronald Nelson[1], Mr. Jaime Fernández-Casado[1], Dr. Hélio Faustino[1], Mr. Iván Varela, Dr. Jose Luis Mascareñas[1], Dr. Fernando López[1,2]

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidad de Santiago de Compostela, Santiago De Compostela, Spain, [2]Instituto de Química Orgánica General (CSIC), Madrid, Spain

Poster Session 2

Cycloaddition reactions are among the most practical and efficient methods to construct cyclic products from relatively simple, acyclic starting materials.[1] Our group has developed intramolecular [4C+3C] cycloadditions of allenedienes promoted by Platinum (II) chloride or N-heterocyclic carbene-gold (I) complexes,[2] and [4C+2C] cycloadditions promoted by phosphite-gold (I) complexes.[3] We show herein further details of the scope of this process and demonstrate that subtle modifications in the catalyst change the outcome of the reaction. Some of the transformations allow the assembly of different carbocyclic skeletons that form the basic core of natural sesquiterpenes.

[Figure]

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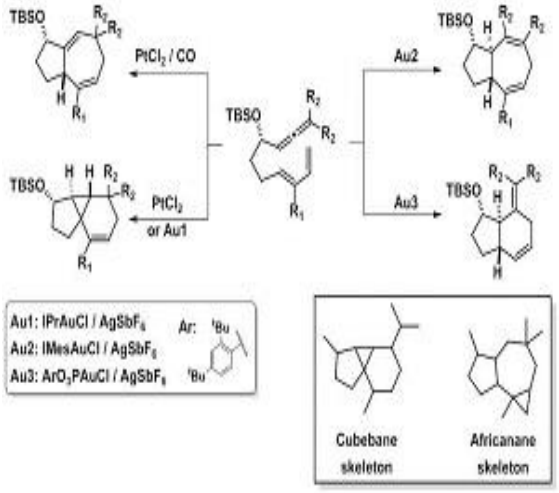
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Ar:
tBu
tBu
Cubebane
skeleton
Africanane
skeleton

P-368

Oxidations catalyzed by an imine-based nonheme iron (II) complex: a mechanistic perspective

Mr. Giorgio Olivo[1], Miss Martina Nardi[1], Dr. Stefano Di Stefano[1], Prof. Osvaldo Lanzalunga[1], Prof. Miquel Costas[2]

[1]*University La Sapienza of Rome, Roma, Italy,* [2]*Universitat de Girona, Girona, Spain*

Poster Session 2

Nonheme iron complexes represent a promising synthetic methodology for reliable aliphatic C-H bond oxidation.[1] Catalyst's activity and selectivity are highly dependent on ligand properties, with elaborated ligand structures usually required to achieve good regioselectivities. This feature often leads to expensive and difficult to obtain complexes, which can limit the diffusion of this synthetic methodology.[2]
In this context we studied a simple nonheme iron complex (3) which can be prepared in situ from cheap and commercially available reagents. Complex 3 shows an activity in C-H bond oxidation comparable to the one of several amine-based Fe complexes.[3] From a mechanistic point of view, complex 3 acts as a pentadentate, metal-based oxidant without involvement of free radical species, and the only oxygen source is H2O2. The first step of the catalytic cycle is the oxidation of Fe(II) complex 3 into Fe(III). Then, the Fe(III) complex loosens the coordination of a pyridine arm in order to host and activate H2O2 (Fig. 1). Eventually the oxidative degradation pathway of the catalytic species has been studied.[4]
Catalytic activity of complex 3 in some hydrocarbon oxidations together with the full mechanistic investigation of complex 3 will be here reported.

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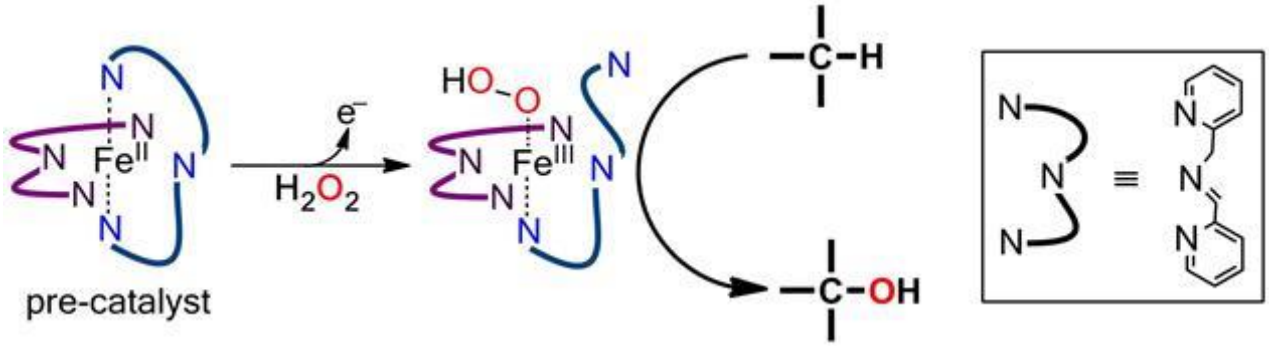

P-369

Rhodium (III)-catalyzed formal cycloadditions between hydroxystyrenes and alkynes

Mr. Andrés Seoane[1], Ms. Noelia Casanova[1], Dr. Noelia Quiñones[1], Mr. David Fernández[1], Dr. Moisés Gulías[1], Prof. Jose Luis Mascareñas[1]

[1]*Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago De Compostela, Spain*

Poster Session 2

Recent years have witnessed an increasing number of reports on synthetic transformations that rely on the functionalization of traditionally inert C-H bonds [1]. Some of these reactions involve formal cycloadditions processes, therefore providing for new and practical alternatives to construct highly valuable cyclic molecules from readily available starting materials.

In this context, we have demonstrated that readily available ortho-vinylphenols undergo a formal [5+2] hetero-cycloaddition to alkynes when treated with catalytic amounts of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$ [2]. The reaction, which involves the cleavage of the terminal C-H bond of the alkenyl moiety, generates highly valuable benzoxepine skeletons. If the substrates are substituted in the internal position of the alkene, the reaction generates interesting spirocyclic skeletons that can rearrange to valuable azulenones [3]. Herein we present details of these annulations, including mechanistic aspects, synthetic scope, as well as preliminary results using alkenylanilides instead of alkenylphenols.

[Figure 1]

References:

[1] For selected recent reviews of metal-catalyzed C−H functionalizations, see: (a) Wencel-Delord, J.; Glorius, F. Nat. Chem.2013,5, 369−375. (b) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. Acc. Chem. Res.2012,45, 788−802. (c) Yeung, C. S.; Dong, V. M. Chem. Rev.2011,111, 1215−1292. (d) Wencel-Delord, J.; Droege, T.; Liu, F.; Glorius, F. Chem. Soc. Rev.2011,40, 4740−4761

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[3] Seoane, A.; Quiñones, N.; Casanova, N:;Mascareñas, J. L.; Gulías, M. J. Am.Chem. Soc. 2014, 136, 7607-7610.


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OH
2.5 mol% [Cp*RhCl2]2
Cu(OAc)2·H2O 0.5 equiv
air, CH3CN, 40 °C
Δ

P-370

Incorporation of Carbon Dioxide based on Alkyne Activation by Silver Catalysts

Mr. Kohei Sekine[1], Yuta Sadamitsu[1], Tohru Yamada[1]
[1]*Keio University, Yokohama/Kohoku-Ku/Hiyoshi, Japan*

Poster Session 2

Carbon dioxide has received much attention as C1 feedstock, due to its low toxicity, an abundant supply and easy handling. Our group reported that the silver-catalyzed incorporation of carbon dioxide into alkyne derivatives, such as propargylic alcohols and propargylic amines, to afford the corresponding exo-Z-alkenyl cyclic carbonates and carbamates[1]. It was assumed that silver catalysts effectively activate C-C triple bond as π-Lewis acid to promote the cyclization reactions of intermediates. It was also found that the silver catalytic system could be applied to ketone derivatives to give the corresponding lactones[2] or furans having a carboxyl group[3] in good-to-high yields with new C-C bond generation between substrates and carbon dioxide. As a next step for C-C bond forming reaction with carbon dioxide, the reaction of organosilane compounds as nucleophile was examined. Recent results will be discussed.

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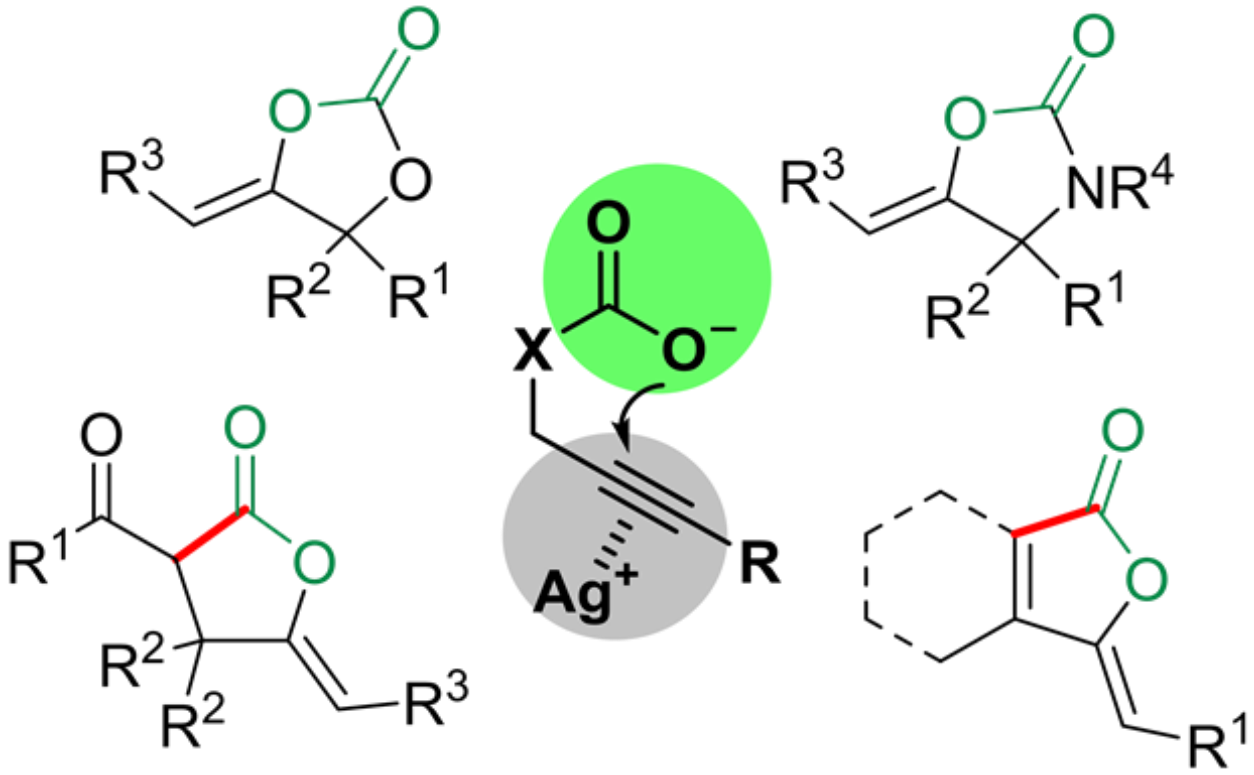

R3
R2
R1
X
Ag+
R
NR4

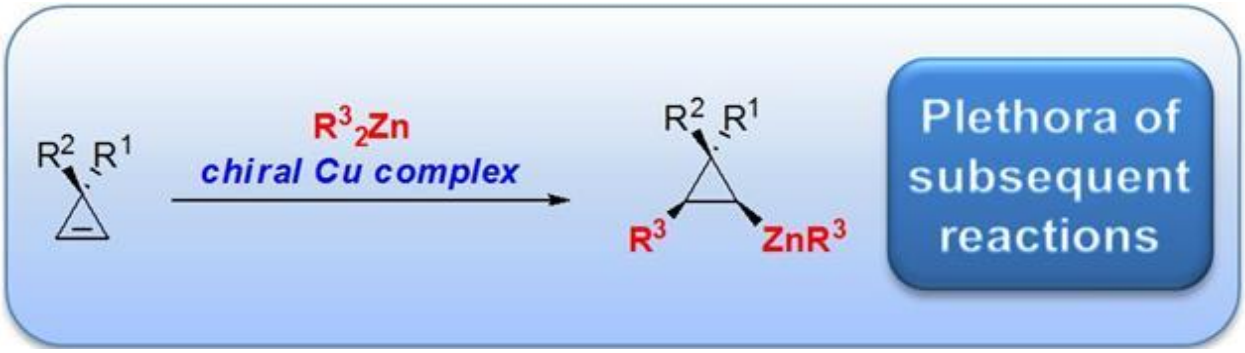
P-371

Asymmetric carbocupration of unfunctionalized cyclopropenes

Dr. Daniel Muller[1]
[1]*Technion, Haifa, Israel*

Poster Session 2

The asymmetric carbocupration of cyclopropenes represents an attractive alternative for the synthesis of enantioenriched cyclopropanes. In particular the synthesis of unfunctionalized enantioenriched cyclopropanes requires a multi-step synthesis and is limited in the choice of substituents on the cyclopropane ring. We recently found that unfunctionalized cyclopropenes in the presence of a chiral copper catalyst react smoothly with organometallic reagents such as diorganozinc reagents to furnish highly substituted enantioenriched cyclopropyl zinc reagents in high yield and good enantioselectivity. Moreover, we demonstrate the synthetic use of the corresponding cyclopropylmetals for a great variety of subsequent reactions such as allylic substitutions, 1,4-additions and many other. This unprecedented synthesis of cyclopropanes is also very practical proceeding efficiently with low catalyst loading and mild reaction conditions.



P-372

Gold(I)-Catalyzed, Stereocontrolled Enamide Synthesis from Primary Amides and Propargyl Aldehydes Using a Tandem Strategy

Mr. Sang Min Kim[1,2], Ms. Dabon Lee[1,2], Dr. Soon Hyeok Hong[1,2]

[1]Center for Nanoparticle Research, Institute for Basic Science (IBS), Gwanak-gu, Republic of Korea, [2]Department of Chemistry, College of Natural Sciences, Seoul National University, Gwanak-gu, Republic of Korea

Poster Session 2

Enamides are very common organic compounds and encompass numerous natural products and drug candidates. In addition, enamides are highly valuable synthetic intermediates for the synthesis of chiral amines, heterocycles, and cross-coupling reagents. Recently, diverse transition metal-catalyzed reactions for synthesizing enamides have been developed utilizing Ru, Rh, Fe, Pd, Au, and Cu, which provide significant advantages over traditional synthetic methods. Nevertheless, these reactions are also limited due to difficulty to prepare the necessary starting materials, requirement of particular reaction conditions, and confined scope of the enamide products.

We reported a novel strategy for enamide synthesis from primary amides and propargyl aldehydes via Au(I)-catalyzed tandem amide addition and Meyer-Schuster rearrangement. This method provides an atom-economical way to produce enamides from simple and versatile starting materials. This is the first example of transition metal-catalyzed Meyer-Schuster rearrangement of inherently unstable substrates with a carbon-heteroatom bond at the propargyl position. In situ generated hemiaminals were successfully converted to the desired products under the optimized conditions. Enamide stereochemistry was controlled simply by changing solvents and adding a catalytic amount of acid. The developed synthetic strategy provides a new method to synthesize various β-substituted-α,β-unsaturated carbonyl compounds.

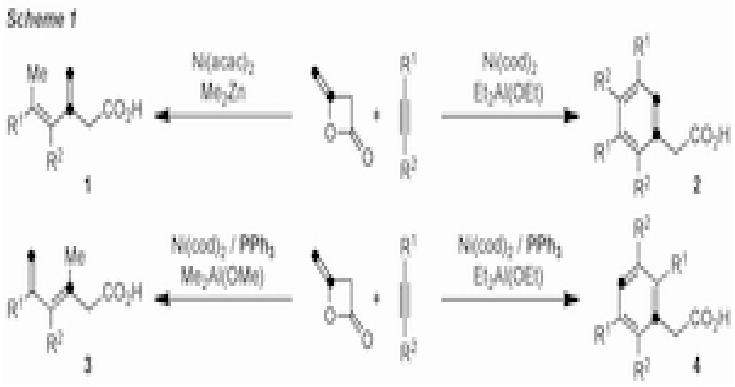
P-373

Ni-Catalyzed Selective Formation of Unsaturated Carboxylic Acids and Phenylacetic Acids from Diketene

Mr. Ryo Ninokata[1], Dr. Takamichi Mori[1], Dr. Gen Onodera[1], Dr. Masanari Kimura[1]
[1]*Nagasaki University, Nagasaki, Japan*

Poster Session 2

Nickel-catalyzed coupling reactions are attractive and efficient synthetic method for the construction of useful and complex molecules in modern organic chemistry. We reported the Nickel(0)-catalyzed multicomponent coupling reaction of unsaturated hydrocarbon and organometal to accomplish the C–C bond formation with high regio- and stereoselectivity. In this research, Ni-catalyzed three-component coupling reaction of diketene, alkyne, and Me_2Zn provided 3-methylene-4-hexenoic acid 1 with excellent regio- and stereoselectivity (Scheme 1). By use of $Et_2Al(OEt)$ instead of Me_2Zn, [2+2+2] cycloaddition reaction of diketene and two equivalents of alkynes proceeded to give phenylacetic acid 2. These reactions seem to proceed via C–O bond cleavage of diketene. Furthermore, in the presence of PPh_3, the regio- and stereoselective multicomponent coupling reaction of diketene, alkyne, and $Me_2Al(OMe)$ proceeded to give 3,5-hexadienoic acid 3. On the other hand, by use of $Et_2Al(OEt)$ instead of $Me_2Al(OMe)$ under the similar reaction conditions, [2+2+1+1] cycloaddition reaction of diketene and two equivalents of alkynes provided phenylacetic acid 4. These reactions might proceed via C–C double bond cleavage of diketene.



P-374

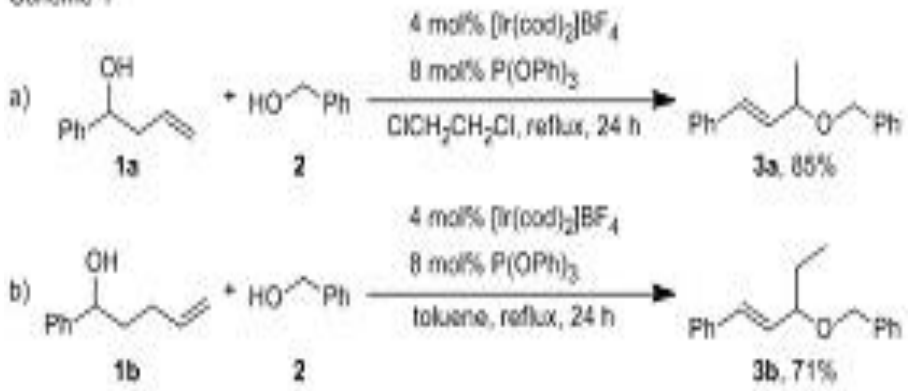
Olefin Isomerization and Successive Allylic Etherification Catalyzed by Cationic Iridium Complex

Dr. Gen Onodera[1], Mr. Takanao Seike[1], Mr. Goki Hirata[1], Dr. Masanari Kimura[1]
[1]*Nagasaki University, Nagasaki, Japan*

Poster Session 2

Cationic iridium complex is one of the most useful catalysts for the isomerization of terminal olefin to internal olefin with high E-selectivity. On the other hand, Takeuchi and his co-workers reported that the iridium catalyst was effective for the allylic substitution reactions, and then many other groups have studied the iridium-catalyzed allylations involving the enantioselective reactions. We have directed our attention to these catalytic activities of iridium complex and developed the novel etherification of homoallyl alcohol. The reaction of homoallyl alcohol 1a with benzyl alcohol 2 proceeded to give α-methylcinnamyl ether 3a in high yield with excellent regioselectivity in the presence of a catalytic amount of cationic iridium complex (Scheme 1, a)). In this reaction, π-allyliridium complex seemed to be generated by an oxidative addition of allyl alcohol provided by an isomerization of terminal olefin moiety of homoallyl alcohol 1a. Then, the electrophilic allylation of benzyl alcohol gave α-methylcinnamyl ether 3a. Furthermore, bishomoallyl alcohol 1b reacted with benzyl alcohol 2 to give α-ethylcinnamyl ether 3b in good yield (Scheme 1, b)).

Scheme 1



P-375

Electron Deficient Triaryl Boranes as Efficient Lewis Acidic Additives for Palladium Catalyzed C-H Activation: a Case Study

Ms Orsolya Tischler[1], Ms Zsófia Bokányi[1], Dr. Zoltán Novák[1]
[1]*Eötvös Loránd University, Budapest, Hungary*

Poster Session 2

In the past few years, Pd-catalyzed C(sp^2)-H activation reactions of arenes bearing diverse ortho-directing groups were widely studied. In continuation of our recent research[1] on C-H activation we aimed to examine the effect of Lewis acids on the palladium-catalyzed cross-dehydrogenative coupling of anilides and aldehydes, as a conceptually new approach for the activation of the catalytic system. We hypothesize that Lewis acidic additives in the reaction may trigger the formation of a 'more cationic' Pd-catalyst with enhanced electrophilicity.
In our study, we examined the applicability of electron deficient boron compounds as Lewis acidic additives in palladium catalyzed C-H activation reactions. Their beneficial effect was demonstrated in the palladium catalyzed reaction of aldehydes and anilides through mild, directed oxidative couplings producing ortho-acylated N-aryl acetamides.

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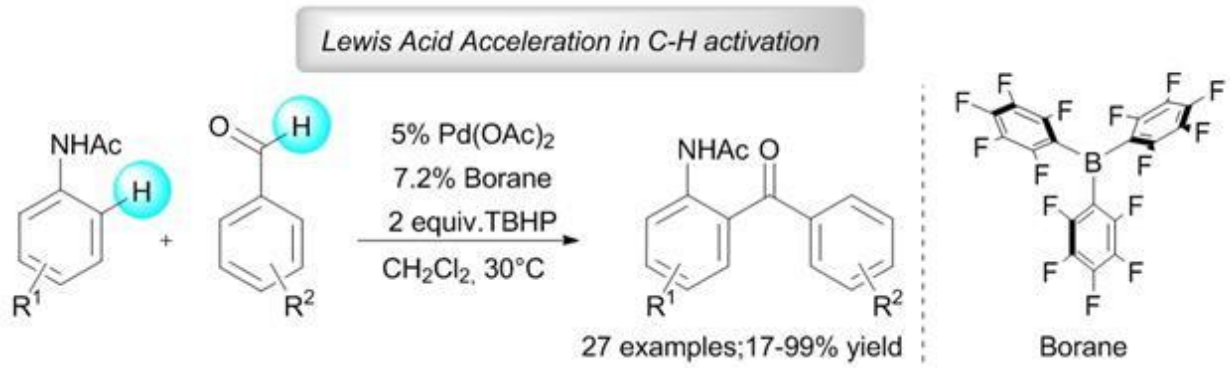

P-376

N-Heterocyclic Carbene Catalyzed Switchable Reactions of Enals with Azoalkenes: Formal [4+3] and [4+1] Annulations for the Synthesis of 1,2-Diazepines and Pyrazoles

Dr. Chang Guo[1]
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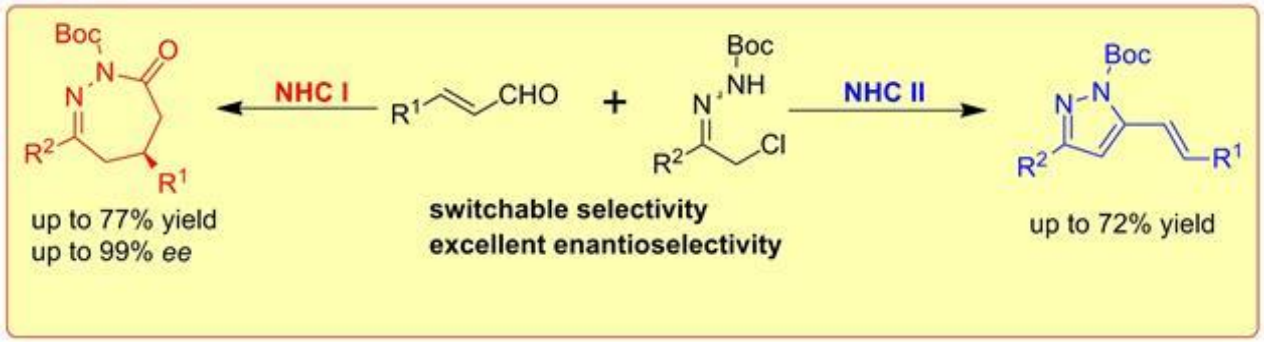
Poster Session 2

A regio- and enantioselective formal [4+3] annulation reaction between enals and in situ formed azoalkenes has been achieved. A diverse set of 1,2-diazepine derivatives were synthesized in good yields with excellent enantioselectivities (up to 99% ee). Alternatively, modifying the standard NHC catalyst switched the reactivity toward a formal [4+1] annulation to afford functionalized pyrazoles. The electronic and steric properties of the N-heterocyclic carbene organocatalyst play a vital role in controlling the reaction pathway (homoenolate vs acyl-anion reactivity of enal), allowing selective access to diverse 1,2-diazepine and pyrazole derivates from identical substrates.



P-377

Phosphane-Functionalized η^7-Cycloheptatrienyl-η^5-Cyclopentadienyl Titanium Complexes

Sabrina Troendle[1], Dr. Matthias Freytag[1], Prof. Dr. Peter George Jones[1], Prof. Dr Matthias Tamm[1]
[1]*TU Braunschweig, Institute for Inorganic and Analytical Chemistry, Braunschweig, Germany*

Poster Session 2

Phosphane ligands of type A are widely used for cross-coupling reactions in combination with palladium precursors.[1] Moreover the application of ferrocenyl mono- and di-functionalized phosphanes B as ligands was thoroughly investigated in catalytic reactions.[2] Based on these results, cycloheptatrienyl-cyclopentadienyl complexes of group IV elements bearing phosphanes have been synthesized and characterized in our group.[3 4]
The complexes 1a and 1b showed high activity in Suzuki-Miyaura coupling reactions.[4] Interestingly, further investigations involving the use of rhodium and iridium precursors led to isolation of the corresponding monophosphane complexes which are interesting starting materials for further investigations.[4]

Furthermore we are interested in synthesizing sterically demanding diphosphane-substituted troticene complexes ($ChtPR_2TiCpR_2$; Cht = Cycloheptatrienyl, Cp = Cyclopentadienyl) and their use as new ligands for heterobimetallic complexes and in homogeneous catalysis.

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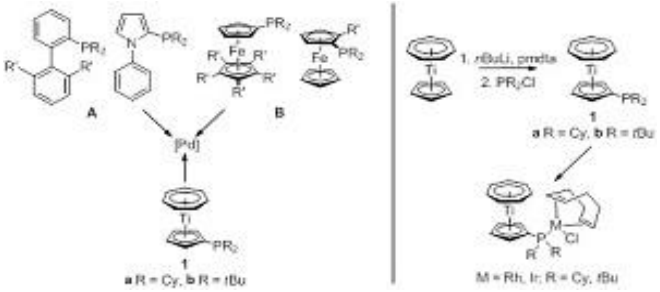


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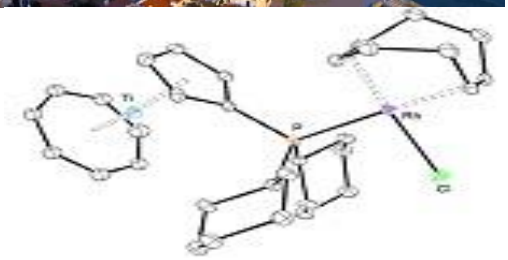


P-378

C-N Bond Formation via Catalytic Activation of Isocyanides

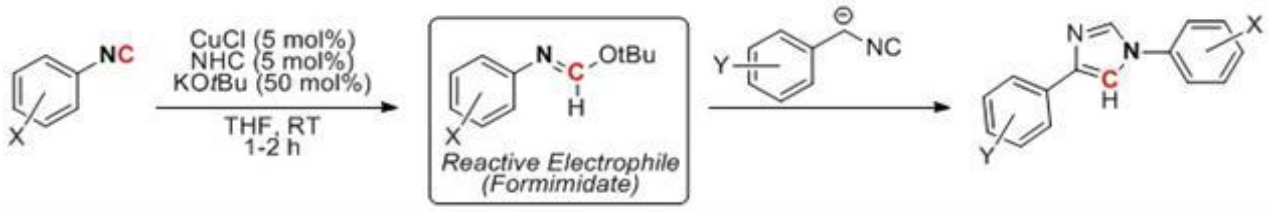
Mr. Jungwon Kim[1,2], Prof. Soon Hyeok Hong[1,2]

[1]*Center for Nanoparticle Research, Institute for Basic Science (IBS), Gwanak-gu, Gwanak-gu, South Korea,* [2]*Department of Chemistry, College of Natural Science, Seoul National University, Gwanak-gu, South Korea*

Poster Session 2

Isocyanide is one of the reactive building block for the synthesis of several heterocycles. Based on unique reactivity of isocyanide, a lot of strategies to utilize terminal carbon as 'reactive nucleophile' have been developed. However, applications of innate electrophilicity of isocyanide are limited to a few examples, including introduction of strong carbon nucleophiles or participation of transition-metal catalyst. Therefore, development of new strategy to activate the terminal carbon without strong reagents would widen the scope of substrates and products.

Previously our group reported mild conditions for the in-situ generation of reactive electrophile, formimidate, from aryl isocyanides to produce biaryl imidazoles within short time, suggesting the high electrophilicity of reaction intermediate. Based on this strategy, we proposed a novel activating mode of isocyanide, which is analogue to the previously reported intermediates from metal catalysts. Sequential attack of nucleophile can produce useful intermediates, which can be transformed into other complex nitrogen-heterocycles.



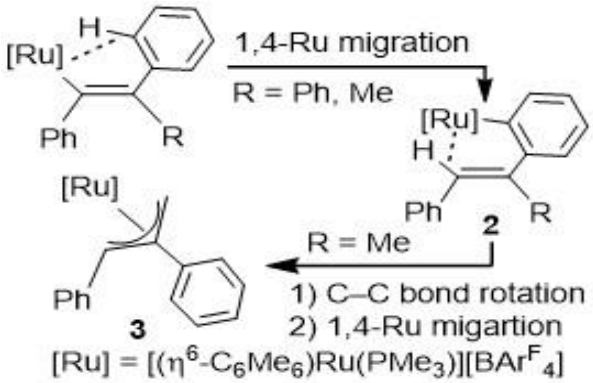
P-379

1,4-Migration of the Metal Center in (η^6-arene)Ru(II) Complexes

Mr. Koichi Takano[1], Dr. Yousuke Ikeda[1], Dr. Shintaro Kodama[1], Dr. Youichi Ishii[1]
[1]*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-Ku, Japan*

Poster Session 2

We have recently disclosed that the metal centers of the vinyl complexes $[Cp^*M\{C(R^1)=CPh(R^2)\}(PMe_3)]^+$ (M = Rh, Ir), which are formed from the reactions of group 9 d^6 metal complex $[Cp^*M(Ph)(PMe_3)]^+$ with internal alkynes, take part in the 1,4-metal migration to form the corresponding o-vinylaryl complexes. Although C–H bond activation by intramolecular 1,4-metal migration has recently attracted considerable attention as the key step in transition metal catalyzed synthetic reactions, only groups 9 and 10 metal centers have been considered to serve as an effective reaction site. To broaden the scope of the 1,4-metal migration to group 8 metal complexes, we focused our attention on the reaction of d^6-Ru(II) complex $[(\eta^6\text{-}C_6Me_6)RuCl(Ph)(PMe_3)]$ (1) with internal alkynes. When 1 was allowed to react with PhC≡CR in the presence of NaBAr[sup]F[/sup]$_4$ (Ar[sup]F[/sup] = 3,5-$(CF_3)_2C_6H_3$), o-(vinyl)aryl complexes $[(\eta^6\text{-}C_6Me_6)Ru\{o\text{-}C_6H_4C(R)=CHPh\}(PMe_6)][BAr[sup]F[/sup]_4]$ (2a; R = Ph, 2b; R = Me) were formed through the initial insertion of the alkyne into the Ru–Ph bond and the subsequent 1,4-Ru migration. The present reaction provides the first experimental evidence of 1,4-metal migration in a structurally well-defined group 8 metal complex. While complex 2a is stable even at 50 °C, 2b was further isomerized at room temperature to the η^3-allyl complex $[(\eta^6\text{-}C_6Me_6)Ru\{\eta^3\text{-}CH_2C(Ph)CHPh\}(PMe_3)][BAr[sup]F[/sup]_4]$ (3). A deuterium labeling experiment using $[(\eta^6\text{-}C_6Me_6)RuCl(C_6D_5)(PMe_3)]$ disclosed that 3 was formed through the rotation of the C_{aryl}–C_{vinyl} bond in 2b and the second aryl-to-allyl 1,4-Ru migration. This result is in stark contrast to a related reaction of an iridium complex, in which a similar η^3-allyliridium complex is formed by the sequential C=C bond rotation-direct 1,3-Ir migration process form the vinyliridium complex $[Cp^*Ir\{C(Ph)=C(Me)Ph\}(PMe_3)][BAr[sup]F[/sup]_4]$. On the other hand, η^6-p-cymene analog of 1 was found to undergo second alkyne insertion accompanied by dissociation of the p-cymene ligand to produce the tether-type complex $[Ru\{(\eta^6\text{-}C_6H_5)C(=CHPh)\text{–}C_6H_4\text{–}CPh=(\eta^3CC_6H_5)\}(PMe_3)][BAr[sup]F[/sup]_4]$ (4).

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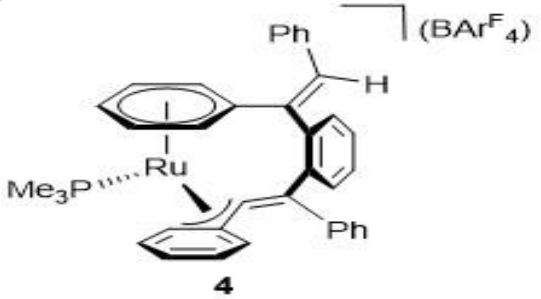
Ph
H
Me3P
Ru
Ph
(BArF4)

4

P-380

Direct Conversion of Ketoxime Esters into α-Acyloxy Imines in an Ir(III) Complex

Mr. Hiroyuki Takahashi[1], Dr. Shintaro Kodama[1], Dr. Youichi Ishii[1]
[1]*Chuo University, Tokyo, Kasuga, Bunkyo-Ku, Japan*

Poster Session 2

Oxime esters are known to be converted readily into the corresponding amides because of the good leaving ability of the carboxylate group (Beckmann Rearrangement). On the other hand, House et al. reported that a multistep conversion of ketoxime acetates into α-acetoxy ketones, which involves N-methylation by $Me_3O^+BF^{4-}$, deprotonation by NEt_3, [3,3]-sigmatropic rearrangement of the N-oxyenamine intermediates, and hydrolysis. If the formation of N-oxyenamines from ketoxime acetates can be induced by coordination of a Lewis acid, this transformation is expected to be achieved without N-methylation step. However, use of hard Lewis acids such as $AlCl_3$ ends in Beckmann rearrangement as the result of the coordination to the ester oxygen atom. In this study, we envisioned that introduction of a directing group to ketoxime ester substrates leads to direct transformation to the corresponding α-acyloxy imines on coordination to a Lewis acidic transition metal complex.

As expected, 2-acetylpyridine oxime acetate (1) with $[(Cp^*IrCl)(\mu\text{-}Cl)]_2$ at 25 ºC in dichloromethane resulted in the formation of 2-(α-acyloxyacetyl)pyridine imine complex $[Cp^*Ir\{C_5H_4NC(=NH)(OCOCH_3)\}]Cl$ (2Cl) in 82% yield, whose structure was further confirmed by an X-ray diffraction study of $2BF_4$. The imine-enamine tautomerization involved in this process was confirmed by a deuterium exchange reaction using 2-acetylpyridine O-methyloxime complex $[Cp^*Ir\{C_5H_4NC(=NOCH_3)CH_3\}]Cl$ (3Cl) in the presence of a catalytic amount of NEt_3. Similar reactions with 2-acetylpyridine oxime benzoate, tosylate and carbonate proceeded smoothly, whereas the pyridyl group in the substrates is essential for the reaction. From these results, coordination of the Ir(III) center to the imino nitrogen atom of oxime esters is deduced to promote tautomerization leading to the corresponding N-oxyenamines, and the subsequent [3,3]-sigmatropic rearrangement takes place in the Ir complex.

P-381

CYCLIZATION OF THIOPHENES BY DUAL GOLD CATALYSIS

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Poster Session 2

In the last two decades, homogenous gold catalysis has evolved into an active field of modern organic chemistry. In 2012, a new pattern of reactivity in gold catalysis was discovered: a diyne system is activated by two gold centers simultaneously.[1] Dual catalysis consists of one gold center activating an alkyne, acting as a π-acid, and a second forming a gold-acetylide. Exploring this type of reactivity applied to substituted thiophenes showed some interesting trends: the mode of cyclization (5-endo or 6-endo) depends on the position of the alkynes on the thiophene and on the substituents of the alkynes.[2]

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P-382

Synthesis and Activity of PEPPSI-Type Palladium Complexes With Quinone Ligands

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Poster Session 2

Palladium-catalyzed cross-coupling reactions are widely used in organic chemistry because they facilitate the synthesis of C–C bonds in targeted positions under relatively mild conditions.[1-2] PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization, and Initiation), designed by Organ et al, is one of the example of a Pd-catalyst in which the usually used phosphine ligand was replaced by an NHC carbene. With this structural modification the PEPPSI catalyst is not only very stable but it also exhibits broad catalytic activity in such cross-coupling reactions as Suzuki–Miyaura, Negishi, and Stille–Migita, among others, as well as in amination and sulfination.[3]
Herewith a synthesis and application of a series of new PEPPSI-type palladium(II) complexes containing quinone moiety in their structure will be presented.

Figure 1: Examples of new PEPPSI catalysts.

Acknowledgement:
This work has been supported by FNP, HOMING PLUS/2013-7/6.

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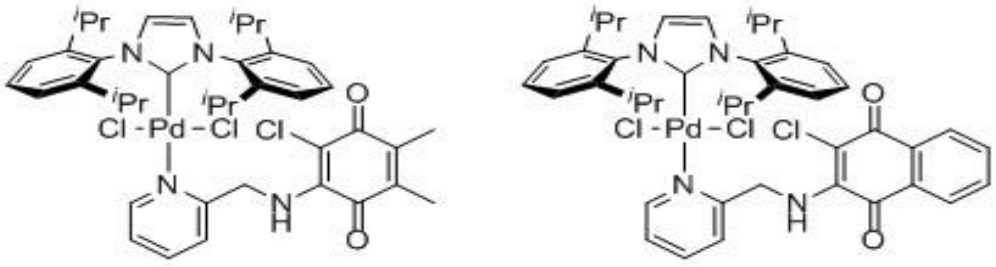

P-383

Ni(0)/NHC Catalyzed Highly Enantioselective Synthesis of Benzoxasiloles via Ligand Controlled Switching from Inter- to Intramolecular Aryl-Transfer Process

Dr. Ravindra Kumar[1], Dr. Yoichi Hoshimoto[2], Dr. Masato Ohashi[3], Dr. Sensuke Ogoshi[4]
[1]Osaka University, Suita, Japan, [2]Osaka University, Suita, Japan, [3]Osaka University, Suita, Japan, [4]Osaka University, Suita, Japan

Poster Session 2

Unlike the catalytic enantioselective activation of aldehyde via η¹ coordination to metal of high oxidation states η² coordination to low valent transition metals are very few, despite of abundant examples in co-ordination chemistry. In continuation of original work, reported from the laboratory for racemic synthesis of benzoxasilole[1] via activation of organosilanes by (η²-aldehyde)Nickel(0) complex, its asymmetric version has been developed. Here, a highly enantio- and diastereoselective synthesis of 3-arylbenzoxasiloles has been achieved in excellent selectivities (er and dr >98%) for the first time. The synthetic utilities of chiral benzoxasiloles to variable chiral building blocks and antihistaminic drug molecules such as (S)-neobenodine and (R)-orphenadrine were also demonstrated. The crossover experiment showed complete switch of reaction pathway from intermolecular to intramolecular aryl-transfer process by changing the ligand from IPr to chiral NHC ligand.

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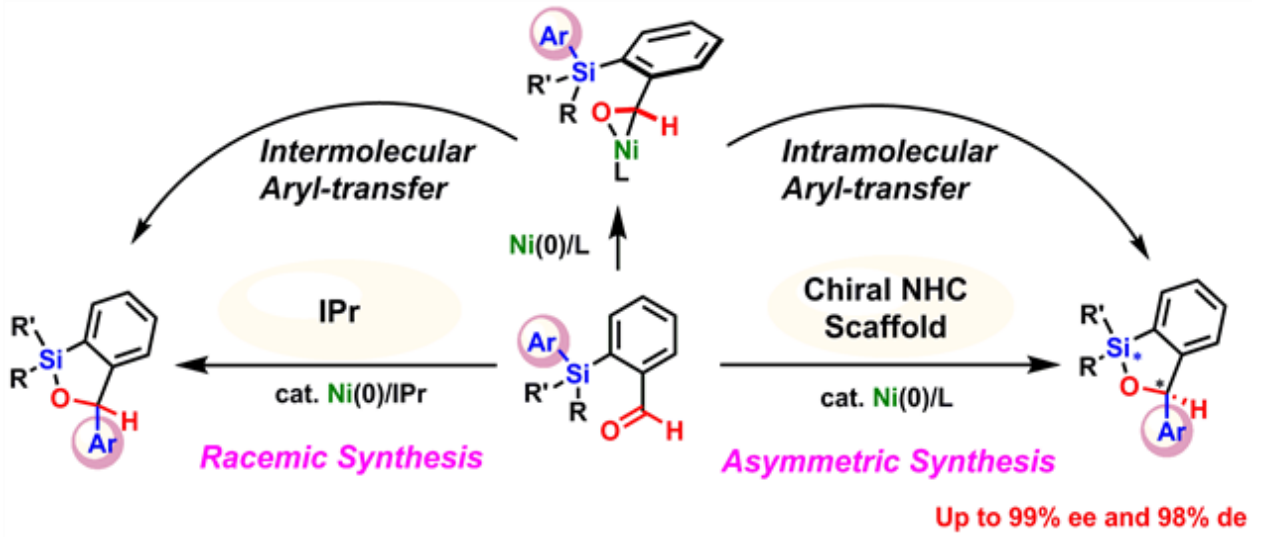

P-384

Anti-Selective Iron-Catalyzed Carbosilylation of Alkynes

Assistant Prof. Takahiro Iwamoto[1,2], Student Tatsushi Nishikori[1,3], postdocs Naohisa Nakagawa[1,2], Prof. Masaharu Nakamura[1]

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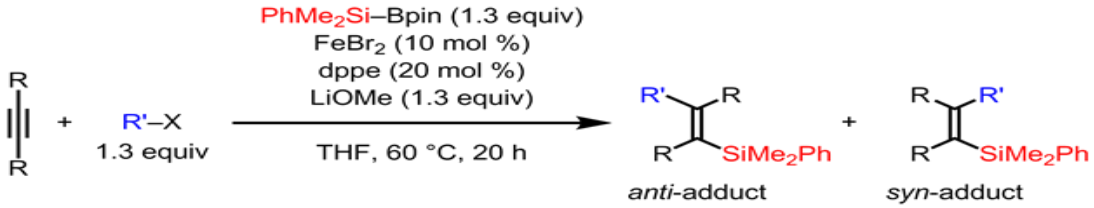
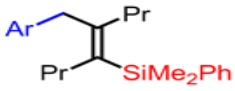
Poster Session 2

With investigation of various transformation reactions of silyl groups, tetrasubstituted vinylsilanes are versatile synthetic intermediates for tetrasubstituted alkene, which are often observed in medicinal products. The most effective synthetic method for accessing these structural motifs is transition metal-catalyzed carbosilylation of alkyne. Since the Fleming's pioneering work by using stoichiometric amount of silyl-cuprate reagent, it is reported that a variety of transition metals, such as Cu, Pd and Rh, catalyze silylmetallation of alkyne, affording vinyl metal species, which react with some electrophiles to give vinylsilanes. However, there still remain some limitations of substrate scope of electrophiles, and in particular alkylation reagents such as alkyl halide have never been utilized in carbosilylation reactions of alkyne. Herein we found the iron-catalyzed carbosilylation of alkynes by using alkyl halides as electrophiles.

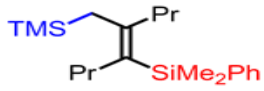
Reaction of 4-octyne with benzyl chloride and silylborane proceeded in the presence of FeBr2 and dppe (1,2-bis(diphenylphosphino)ethane) ligand, providing vinylsilane 1a in 70% yield and with 93% anti-selectivity (Table 1). Although the reaction proceeded even in the absence of any ligand, bidentate phosphine ligands such as dppe obviously increased anti-selectivity. Furthermore both electron-rich and deficient benzyl chlorides underwent the carbosilylation reaction giving the vinylsilane 1b and 1c in highly anti-selective fashion. In addition, (trimethylsilyl)methyl iodide, which should be less active in the iron-catalyzed coupling reaction, was reacted smoothly. Diphenyl alkyne also participated in the reaction to afford anti-adducts 3 in 70% yield. These are the first transition iron-catalyzed carbosilylation reactions using alkyl halides as electrophiles. In the presentation, reaction mechanism will be discussed focusing on the anti-selectivity.

Table 1. Iron-Catalyzed Carbosilylation of Alkynes Using Silylborane[a]

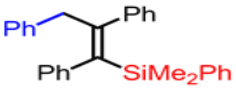




(*E*)-**1**
1a: Ar = C_6H_4, 70% (*E*/*Z* = 93 : 7)
1b: Ar = 4-$MeOC_6H_4$, 49% (*E*/*Z* = 96 : 4)
1c: Ar = 4-CNC_6H_4, 67% (*E*/*Z* = 96 : 4)



(*E*)-**2**, 66%
(*E*/*Z* = 97/ 3)[b]



(*Z*)-**3**, 70%[a]
(*E*/*Z* = 3 : 97)

[a]Total yields of *E* and *Z* isomers were determined by NMR analysis using pyradine as an internal standard. [b]The reaction was conducted with (trimethylsilyl)methyl iodide as an alkyl halide.

P-385

Towards the Gold-Catalyzed Synthesis of Cannabimovone and Anhydrocannabimovone

Dr. Javier Carreras[1], Mariia S. Kirillova[1], Prof. Antonio M. Echavarren[1]
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Poster Session 2

Gold-catalysis has emerged as a powerful tool in total synthesis for the construction of complex structures.[1] As an application of gold-catalyzed enyne cycloisomerization, we decided to target cannabimovone and anhydrocannabimovone (Figure 1).[2] These compounds have strong affinity for the cannabinoid receptors with a biological profile similar to that of tetrahydrocannabinol. Gold catalysis leads to the cyclopentene core structure of these molecules in a concise manner (Figure 2).

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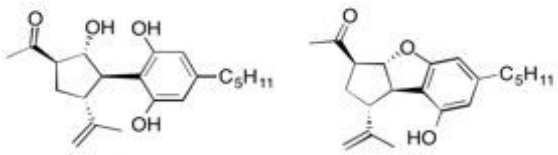

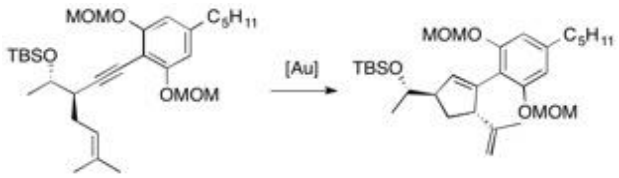

P-386

Towards the Gold-Catalyzed Synthesis of Echinopines A and B

MSc. Ruth Dorel[1], Dr. Estíbaliz Coya[1], Prof. Antonio M. Echavarren[1]
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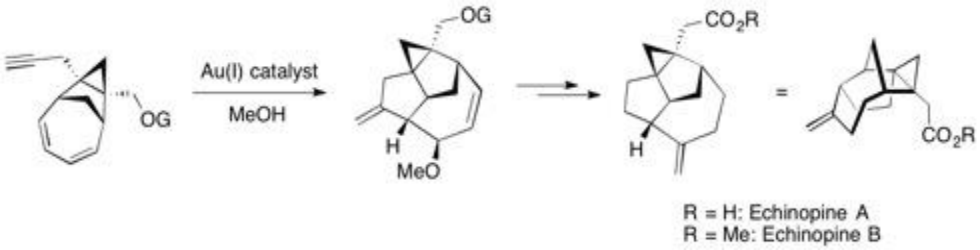
Poster Session 2

Gold(I)-complexes have emerged as one of the most powerful tools to construct molecular complexity due to their unique ability for electrophilic activation of multiple bonds under mild reaction conditions. We envisioned a ready access to the carbon skeleton of sesquiterpenoids echinopine A and B by using a gold(I)-catalyzed cycloisomerization reaction as the key step. Thus, the unique 3,5,5,7-tetracyclic core of these natural products was stereoselectively obtained in a very efficient transformation from the corresponding enyne in the presence of gold(I) and MeOH as an external nucleophile via 5-exo-dig cyclization.



P-387

Synthesis of enol esters by addition of carboxylic acids to internal alkynes catalyzed by gold(I) complexes in water and under MW irradiation

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[1]*Departamento de Química Orgánica e Inorgánica (IUQOEM), Laboratorio de Compuestos Organometálicos y Catálisis (unidad asociada al CSIC) and Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universidad de Oviedo, Oviedo, Spain*

Poster Session 2

The addition of carboxylic acids to alkynes catalyzed by different transition metals constitutes an efficient methodology to prepare enol esters which has been extensively studied in the literature with special emphasis on ruthenium complexes[1]. Otherwise, gold complexes have been demonstrated an extraordinary reactivity associated with carbon-carbon multiple bonds. For example, the synthesis of lactones promoted by the gold(I)-catalyzed intramolecular addition of carboxylic acids to terminal alkynes was reported previously by several groups, although scarce examples of the intermolecular version are known to date.

Terminal alkynes usually present a high regioselectivity regarding on nucleophilic additions due to the big differences between the two carbons of the triple bond. However, internal alkynes do not always provide such regioselectivity and, in consequence, there are really few examples of regio- and stereoselective synthetic protocols to obtain internal enol esters[2].

With this situation in mind, we decided to deal whit this challenge in order to design a new methodology to obtain these interesting compounds using gold(I) complexes as catalysts. Moreover, the reactions described here occur employing water as solvent and microwave irradiation as an alternative energy source.

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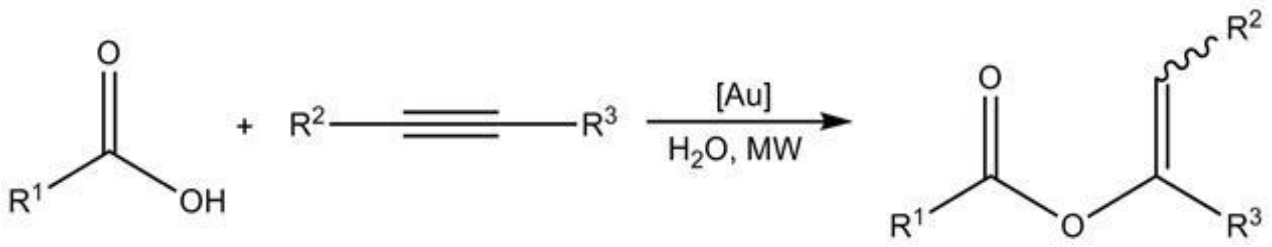

P-388

The Versatility of Gold(I)-Catalysis Applied to the Total Syntheses of (–)-Nardoaristolone B and Lundurine C

Dr. Michael Muratore[1], Mariia Kirillova[1], Anna Homs[1], Ruth Dorel[1], Prof. Dr. Antonio Echavarren[1,2]
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Poster Session 2

The breadth of reactions catalyzed by electrophilic gold(I) complexes and salts[1] and the versatility of intermediates accessible through these transformations have been utilized to develop expedient and efficient total syntheses of the natural products (–)-nardoaristolone B and lundurine C. Notably, the first enantioselective synthesis of nardoaristolone B has been accomplished implementing for the first time an oxidative gold(I)-catalyzed cyclization of 1,5-enyne in the context of total synthesis, in 7 steps and 11–13% overall yield (Scheme 1).[2]

Scheme 1. First enantioselective total synthesis of (–)-nardoaristolone B.

Furthermore, with a distinct strategy, an intramolecular gold(I)-catalyzed hydroarylation of alkyne has proved successful to efficiently prepare the polycyclic core of the lundurines and complete the synthesis of lundurine C. Our 11-step longest linear synthetic sequence provides a rapid entry towards this architecturally complex natural product and related analogues (Scheme 2).

Scheme 2. Total synthesis of lundurine C.

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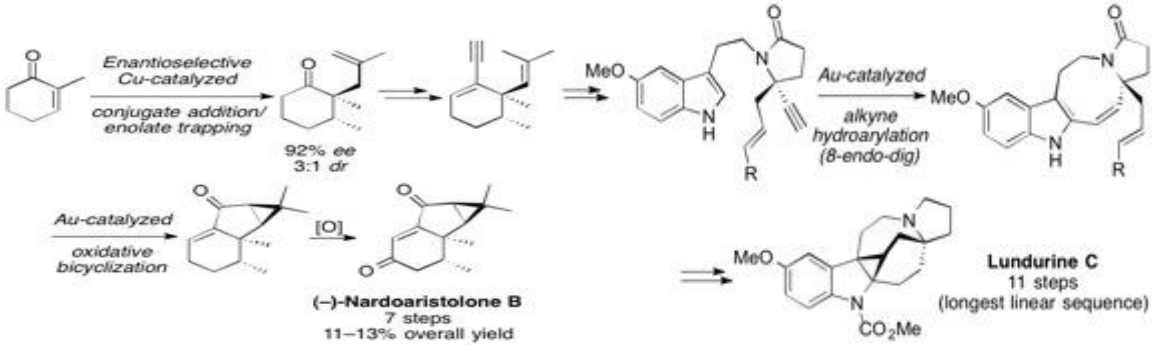

P-389

Rhodium-Catalyzed [5+2] Cycloisomerizations of Ynamide-Vinylcyclopropanes

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[1]*University of Oxford, Oxford, UK*

Poster Session 2

The widespread nature of azacycles in biologically active compounds has made them key targets for the synthetic community. Of great importance is the ability to construct these systems in an atom economical and stereocontrolled fashion. In this context the generation of organic ring scaffolds via transition metal-catalyzed cycloisomerisation of acyclic substrates has attracted much attention.[sup]1,2[/sup] A useful extension of this methodology is the formation of heterocyclic systems containing larger ring sizes through higher-order cycloisomerisations. This poster will illustrate the first rhodium-catalysed [5+2] cycloisomerisation of ynamide-vinylcyclopropanes 1 to heterobicyclic products 2.

These reactions proceed in excellent yield, are complete in under an hour at room temperature, and tolerate a variety of substituents and protecting groups. An investigation into the influence of tether substituents reveals high levels of diastereo- and regioselectivity. In addition, it is possible to achieve absolute stereocontrol in the synthesis of single enantiomer products (+)-2 with the use of chiral ligands. The development of a novel ligand results in a greatly increased rate of reaction and an increased enantioselectivity.

In summary, we have developed a highly efficient method for the preparation of diversely substituted hetereocycles. These transformations occur with complete regio-, diastereo-, and enantioselectivity, factors which are essential for the application of synthetic methodology to biomedical targets.

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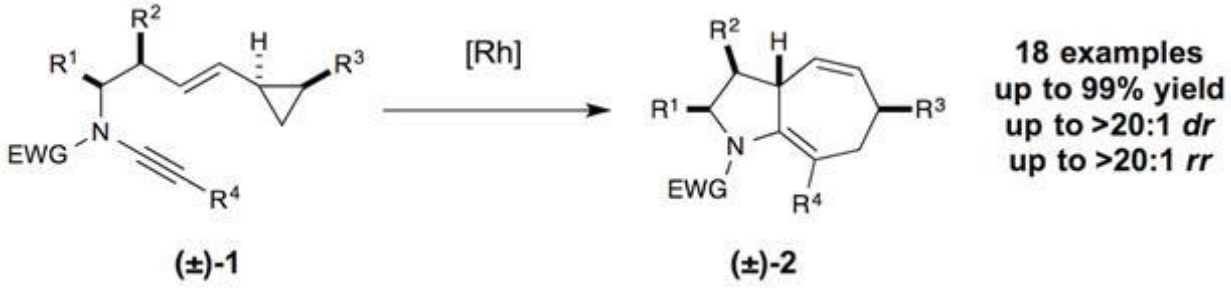


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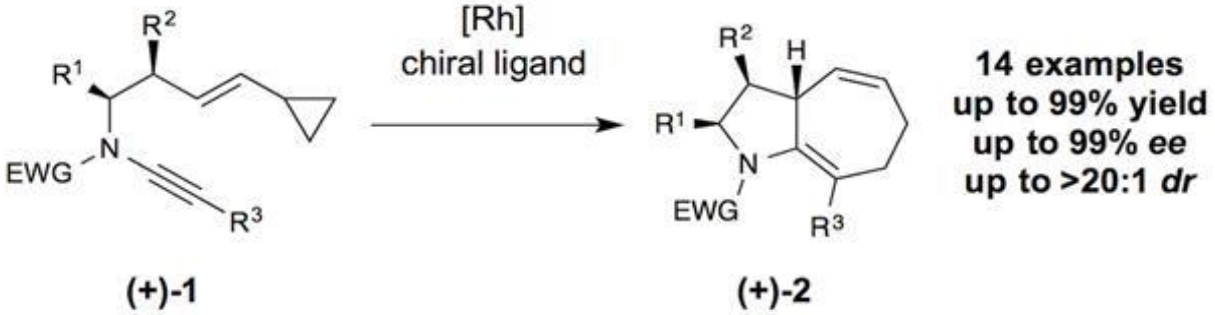
R2
R1
N
EWG
R3
[Rh]
chiral ligand
R2
H
R1
N
EWG
R3
14 examples
up to 99% yield
up to 99% ee
up to >20:1 dr

(+)-1 **(+)-2**

P-390

Palladium Catalysed Decarboxylative Rearrangement of N-Alloc Ynamides and Enamines

Miss Juliana Alexander[1], Dr. Matthew Cook[1]
[1]*Queen's University Belfast, Belfast, UK*

Poster Session 2

The palladium catalysed allylation of enolates and enamines, such as the Tsuji allylation, can be a powerful tool with high levels of enantioselectivity available. These methods can have major drawbacks in their substrate scope due to poor levels of E:Z selectivity in the reactive enolate or enamine leading to poor stereoselectivity. Previous work has focused on cyclic or sterically biased systems which negates these problems however also limits the substrate scope[1]. Our approach is to utilise geometrically defined N-alloc enamines (3) as rearrangement precursors which will form a single geometric isomer of the enamine intermediate thus opening up a much larger substrate scope.

We have developed a rapid synthesis of these enamines through a copper catalysed amination reaction of bromoacetylenes(1) to form alloc ynamines(2) followed by a copper mediated addition of a Grignard reagent across the alkyne to form the N-alloc enamine as a single geometric isomer. We have developed conditions for the rearrangement of (3) to form chiral neo-pentyl amine(4) in a racemic manner and are currently optimising the enantioselectivity.2 We have also explored the rearrangement of ynamine(2) which upon decarboxylative rearrangement provides allenamine(5). These reactive compounds are difficult to synthesis when non-stabilising groups are present and this method provides a very direct and facile entry to these moieties. Allenamines(5) can undergo a variety of reactions including cycloadditions and act as electrophiles such as their reaction with aqueous acid to form secondary amides (6)[2].

We have developed new robust allylation methods which allows for a much greater substrate scope and reactivity profile to be used in both the rearrangement of N-alloc enamines and ynamines.

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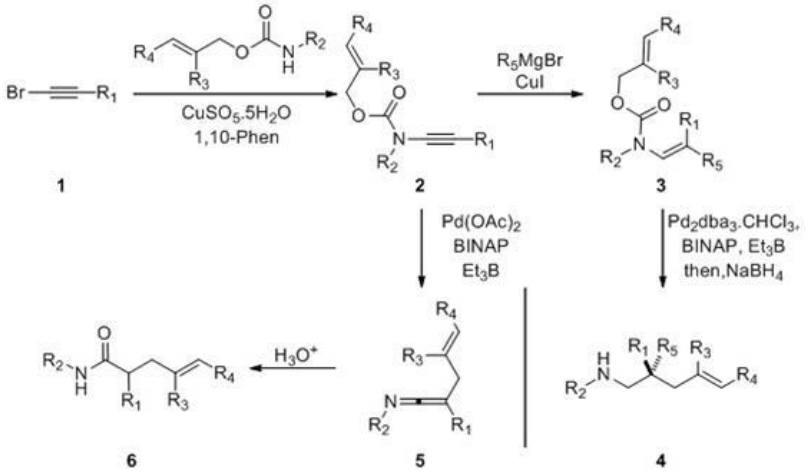
CuSO5.5H2O
1,10-Phen
R5MgBr
CuI
Pd(OAc)2
BINAP
Et3B
Pd2dba3.CHCl3,
BINAP, Et3B
then,NaBH4
H3O+
1
2
3
4
5
6

P-391

Functionalization of heterocycles nitriles using the organometallic base TMPMgCl.LiCl

MsC Fernanda Moraes Dos Santos[1], MsC João Henrique Carvalho Batista[1], Dr Giuliano Cesar Clososki[1]
[1]*University of São Paulo, Ribeirão Preto, Brazil*

Poster Session 2

Heterocyclic compounds are often highlighted for being of great importance in the chemical and pharmaceutical areas, due to their broad spectrum of biological and pharmacological activities.[1] Thus, the search for new methodologies to achieve functionalized hetero-aromatic rings is of great importance. In this work, we investigated the use of the TMPMgCl.LiCl base in the functionalization of furan-, thiophene- and pyrazine-containing heterocyclic nitriles.[2] Methodological studies were performed for each substrate in order to obtain the appropriate reaction conditions. After direct metalation reaction using the organometallic base, the corresponding organometallic intermediates were reacted with several electrophiles leading to a number of heterocycle nitriles functionalized in good yields. In order to improve the isolated yields, some alternative conditions were studied such as the use of TMPMgCl.LiCl base in the presence of $ZnCl_2$ and microwave-mediated reactions.[3] After reaction with electrophiles, the expected ortho-functionalized derivatives were obtained in yields ranging from 48% to 92%.

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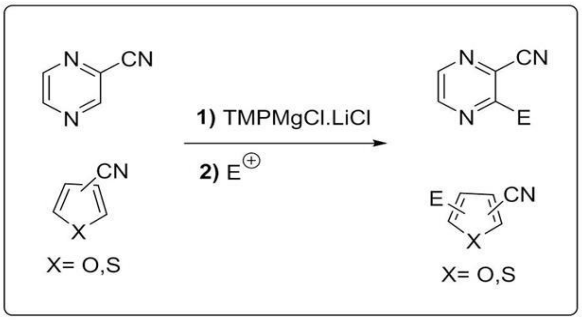

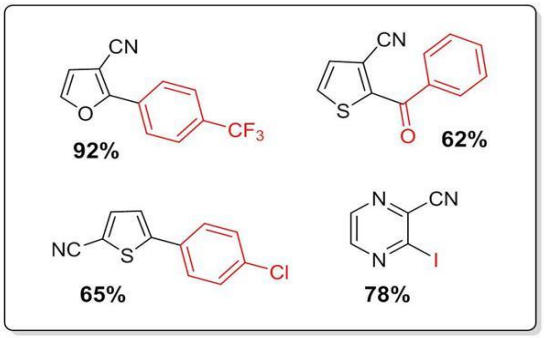

P-392

A Search for Active First-Row Transition Metal Alkylidene Complexes.

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[1]*Massey University at Auckland, Auckland, New Zealand*

Poster Session 2

High-powered computing facilities and high level calculations allow fully optimised structures to be obtained for organometallic complexes which have very good physical parameter comparisons to X-ray structures. Simplified models of complexes no longer need to be used, and energy-minimised structures can be obtained for complexes which have not been actually prepared. This ideology removes the need for bench syntheses which may be complicated or produce compounds which are difficult to handle. The computational approach gives much more information about a complex and allows a more complete understanding of fundamental characteristics than the normal bench synthesis would provide. We have used this 'synthesis by computation' approach [1] to obtain information on first row transition metal alkylidene complexes which might be more suitable olefin metathesis catalysts than the Grubbs or Schrock complexes and provide a cheaper entry into this type of catalysis. Energy minimised structures were found for the cobalt and iron complexes [(PPh3)2M(=CHCMe2Ph)] and [(PPh3)2M(=CHCMe2Ph)Cl] and their ability to act as olefin metathesis catalysts probed by the computational approach.

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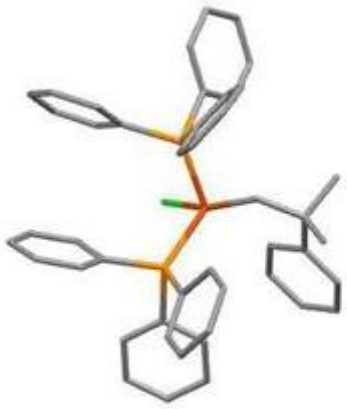

P-393

Metallacylic Complexes of Pd(II) and Pt(II)with Bulky Phosphine Ligands

Dr. Riccardo Peloso[1], Mr Práxedes Sánchez-Mellado[1], Dr Joaquín López-Serrano[1], Prof. Ernesto Carmona[1]
[1]*Universidad De Sevilla, Sevilla, Spain*

Poster Session 2

Recent studies from our group led to the synthesis of new bis(platinacyclic) platinum complexes by facile activation of benzylic C-H bonds of the bulky phosphine ligands, P[sup]i[/sup]Pr_2Xyl and $PMe(Xyl)_2$ (Xyl = 2,6-dimethylphenyl).[1,2] Hydride abstraction from a Pt-CH_2 fragment permitted the identification and characterization of a highly electrophilic Pt(II) alkylidene, whose reactivity with Lewis bases, dihydrogen, and diazocompounds was described. In this contribution we further investigate the reactivity of this cationic Pt(II) carbene with CO, XylNC,[2] and alkynes (Scheme 1a), which results in different types of C-C bond formation involving the alkylidene Pt=CH unit.
On the other hand, preliminary studies on related Pd(II) bis(metallacycles) allowed for the isolation of a stable agostic complex (Scheme 1b), which was characterized by NMR spectroscopy and X-ray diffraction analyses, together with some adducts resulting from the replacement of the agostic interaction by CO and acetonitrile. At variance with the behaviour of the analogous bis(platinacycle), the palladium(II) complex did not afford any carbene structure by treatment with Ph_3C[sup]+[/sup]. A C-C coupling between the metallated CH_2 group and the triphenylmethyl cation was observed, instead.

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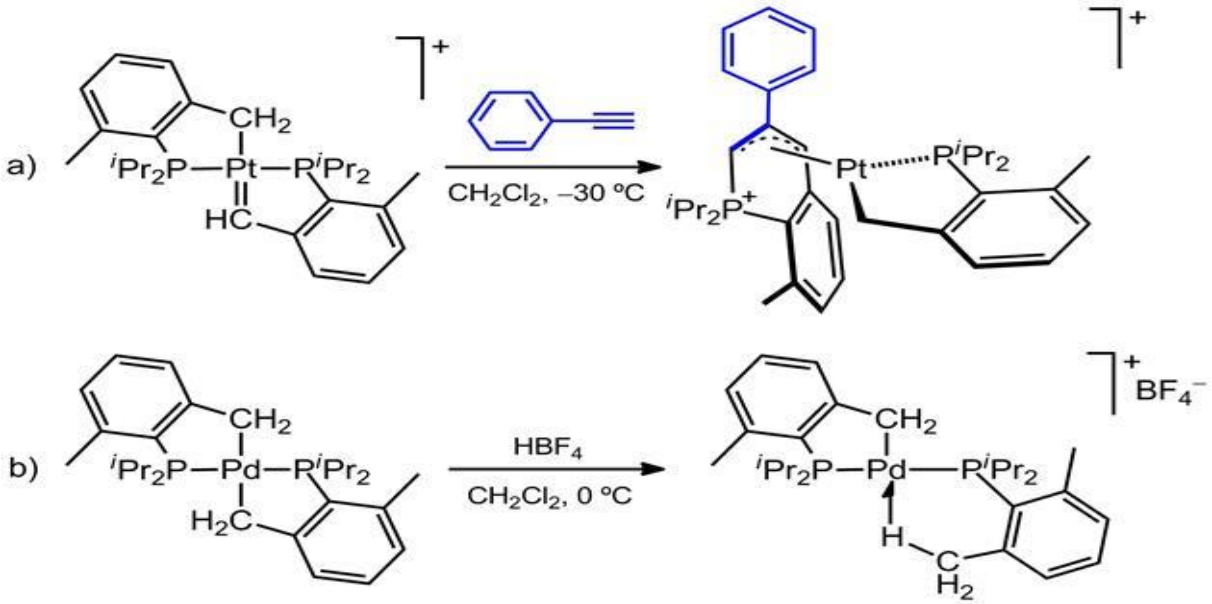

Scheme 1

P-394

The Catalytic Oxidative Synthesis of Ortholactones and their Applications in Synthesis

Miss Kate Baddeley[1], Dr Matthew Cook[1]
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Poster Session 2

Ortholactones are synthetically useful electrophilic compounds which could have many potential uses in organic synthesis. These can act as both mono and divalent electrophiles with a range of nucleophilic partners reacting at the C1 position. Despite this, the formation of these synthetically useful reagents is not facile and is plagued by low yields and functional group incompatibility. Common methods involve highly atom inefficient alkylative, acidic or basic methods that are not amenable to a wide range of functionality and are not particularly efficient methods, especially on a large scale.

We have circumvented many of the issues alluded to above by developing an aerobic, palladium catalysed, oxidative synthesis of ortholactones (2) which proceeds via a Wacker type mechanism from readily accessible dihydropyrans (1). [1] This method uses a palladium and copper co-catalytic system with atmospheric air as the terminal oxidant and enables the synthesis of a wide variety of highly functionalised ortholactones in good to high yields. The reaction is tolerant to a broad scope of both substrates and alcohols.

The synthetic utility of these compounds is demonstrated with an intermolecular Sakurai type reaction to form spiroketals (3), and the formation of complex and highly stereospecific γ-lactones (4) via an acid mediated rearrangement. [2]

This work has developed a new functional group tolerant method for the synthesis of functionalised ortholactones and provided a facile route to previously inaccessible compounds. This will allow the further use of ortholactones in the synthetic arena, namely in the synthesis of complex natural products.

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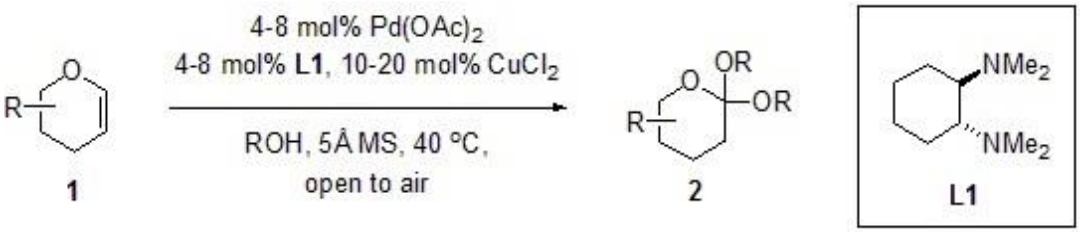


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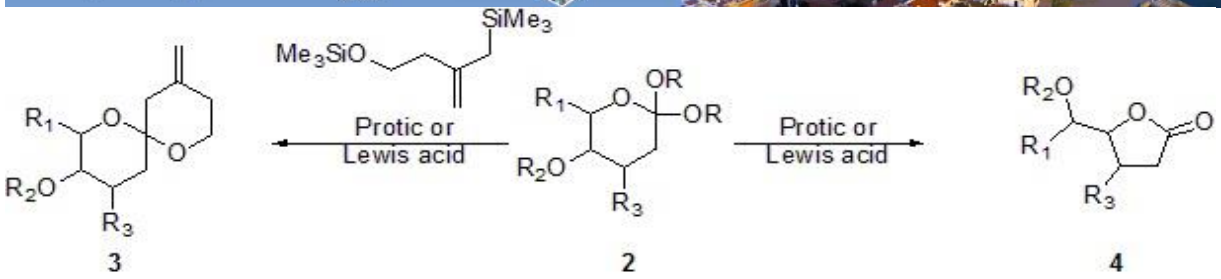
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P-395

Transition-metal-Catalyzed Csp2–Csp3 Coupling of Aryl Methyl Ethers via Direct Alkylation of Inert C–O Bond

Xiangqian Liu[1], Chien-Chi Hsiao, Matthias Leiendecker, Guo Lin, Prof. Dr. Magnus Rueping
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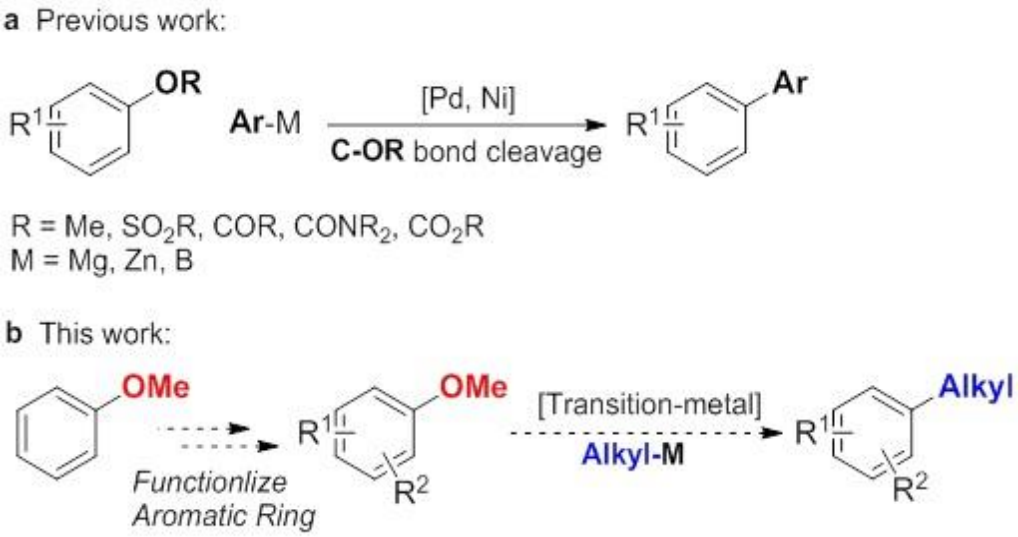
Poster Session 2

Phenol derivatives are emerging aryl electrophiles in catalytic cross-coupling reactions as alternatives to aryl halides due to lower costs…. However, only few existing methodologies employ the simplest, most atom-economical aryl methyl ethers as coupling courterparts. Due to the remarkable activation energy for aryl C–OMe bond cleavage and beta-hydrogen elimination associated, the alkylation of aryl C–OMe bonds has remained a significant challenge. We herein developed a new strategy to facilitate the alkylation of aryl C–OMe bonds. A variety of aryl methyl ethers and metal alkyls were cross-coupled under transition-metal catalytic system. The methodology to alkylate aryl C–OMe bonds and the strategies of using temporary directing/activating ability combining with orthogonal activity of aryl methoxy groups are expected to find applications in the more efficient construction of valuable targets.



P-396

SILICA SUPPORTS FUNCTIONALIZED BY SILSESQIOXANES IN NUCLEIC ACID SYNTHESIS

PhD Karol Szubert[1,2], PhD Emilia Frydrych-Tomczak[2], PhD Magdalena Jankowska-Wajda[1], PhD Karol Pasternak[3], Prof. Marcin K. Chmielewski[3,4], Prof. Hieronim Maciejewski[1,2]

[1]Adam Mickiewicz University in Poznań, Poznań, Poland, [2]Poznan Science and Technology Park, A. Mickiewicz University Foundation, Poznań, Poland, [3]FutureSynthesis, Poznań, Poland, [4]4The Institute of Bioorganic Chemistry, Polish Academy of Sciences, Poznań, Poland

Poster Session 2

Although many molecular reactions involving synthetic oligonucleotides (ONs) are carried out in the homogenous, liquid phase (e.g. PCR or DNA sequencing) there is still a great number of techniques which require an oligonucleotide attached to the solid phase (e.g. oligonucleotide synthesis or microarrays). The reactions of this type exhibit many advantages: the target molecule is easily accessible to the chemical/target molecules, there is no need of using reagents in great excess, small reaction volumes are needed, thanks to the immobilization of ON it is easy to remove unused reagents or purify the reaction centre[1].

Development of new chemical modifications used in automated nucleic acid synthesis has brought about the need for new types of solid supports [2]. Generally, most commonly used and commercially available supports are based on CPG (Controlled Pored Glass) or (PS (Polystyrene).

In this communication we present the synthesis of highly efficient modified supports, based on CPG, and their application in chemical biomolecule synthesis oriented at nucleic acids. To generate an active site on the supports surface we used polyhedral oligomeric silsesquioxane (POSS) containing amino group.

The project “High efficient solid support for biomolecules synthesis” (no. PBS1/B9/7/2012) was funded by the National Centre for Research and Development.

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P-398

Amidato complexes of ruthenium, rhodium and iridium from concise N-H bond activation: exploration in catalysis

Ms. Laura Fra[1], Mr. R.Martín Romero[1], Dr. Claudio Martínez[1], Prof. Dr. Kilian Muñiz[1,2]
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Poster Session 2

Acceptor-substituted N-H groups as found in carbamides and sulfonamides are readily activated through suitable unsaturated metal complexes applying the concept of metal-ligand bifunctionality. This process generates chiral-at-metal amidato complexes of ruthenium, rhodium and iridium. An enantioselective catalytic aza-Michael reaction was developed on the basis of this process, which uses the reversible addition of N-H bonds to the unsaturated metal fragments within an enantioselective N-H transfer to prochiral alkenes. It gives rise to indoline β-amino acids.[1] The amidato metal complexes from N-H activation can also be employed as catalyst precursors for transferhydrogenation.[2]

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P-399

Alkali Metal Amide-Catalyzed Allylic C(sp^3)–H Bond Activation[1]

Hanno Kossen[1], Wei Bao[1], Uwe Schneider[1]
[1]*The University of Edinburgh, Edinburgh, UK*

Poster Session 2

Alkali metal amides have not been reported as Brønsted base catalysts in C–H bond activation.[2] They are usually encountered as stoichiometric bases or precursors to form different catalytically active species in situ.[3]
Here, we propose alkali metal amide-catalyzed C–C bond formations between aldimines and unbiased olefins through allylic C(sp3)–H bond activation (Scheme 1). This atom-economic method provides an unprecedented catalytic pathway to form linear homoallylic amines with excellent selectivity.

Common methods for the preparation of these products rely on the use of allylic silanes or halides.[4] Allylations of imines with unbiased allylic substrates are rare and usually require transition metal Lewis acid catalysts.[5] Our concept also proved to be applicable to functionalized allylic substrates (X = SiR3, Bpin, SPh, PPh2), where the functional handle is retained in the product for subsequent modification.

The poster will focus on the recent advances in the first use of alkali metal amides as Brønsted base catalysts in C–C bond formations. Functional group tolerance and scope are explored and first insights into the mechanistic details will be presented. We will also include results of functionalized C–C bond formations and their applications in cross-coupling reactions. Finally, we will demonstrate the first example of asymmetric alkali metal amide catalysis.

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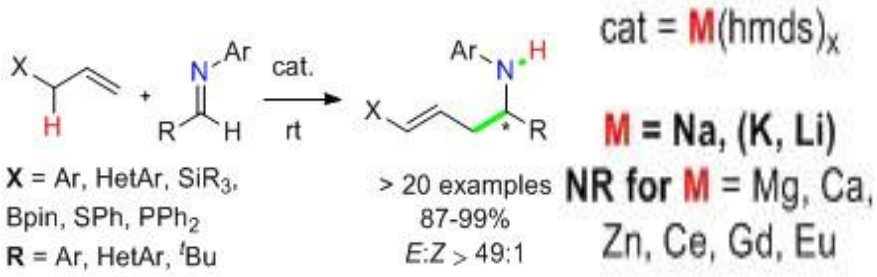

P-400

Palladium High Oxidation State Catalysis: Intermolecular Diamination and Aminoacetoxylation of Alkenes

Mr. Nicola Lucchetti[1], Dr. Claudio Martínez[1], Prof. Dr. Kilian Muñiz[1,2]
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Poster Session 2

Diamines represent an ubiquitous functional group in organic chemistry, which commonly is not conceived in a direct manner, but rather through a sequential combination of several synthetic steps. An attractive route to vicinal diamines consists of the direct oxidative transformation of alkenes.[1] In 2010, we reported the first general intermolecular 1,2-diamination of unactivated alkenes employing high-oxidation-state palladium catalysis,[2] which uses two commercially available nitrogen sources and proceeds with complete regioselectivity under mild conditions.[3] First results on the corresponding diamination of internal alkenes were also developed.[4] This approach again relies on high-oxidation-state palladium catalysis using a defined iodine(III) species as terminal oxidant. At the same time, it represents a rare example of a palladium catalysed difunctionalization of an internal alkene. Gratifyingly, the reaction proceeds with complete chemo-, regio- and diastereoselectivity. The conditions are also applicable to related aminooxygenation reactions.[5]

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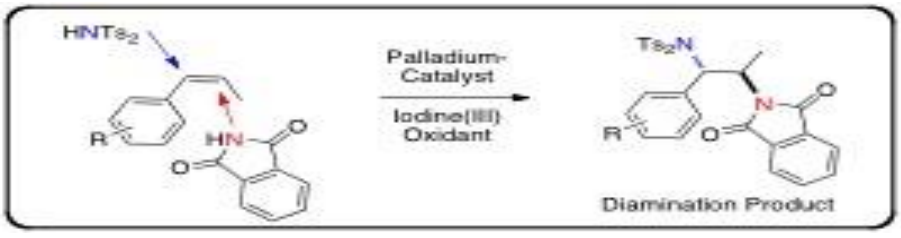

P-401

New Hypervalent Iodine(III) Reagents Incorporating Transferable Nitrogen Groups

Dr. Stefan Haubenreisser[1], Dr. Jose A. Souto[1], Dr. Claudio Martínez[1], Dr. Irene Velilla[1], Prof. Dr. Kilian Muñiz[1,2]

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Poster Session 2

Hypervalent iodine reagents represent versatile synthetic tools for a series of selective oxidative transformations.[1] Such an approach is of particular synthetic value where reactions are concerned that enable entirely new transformations. We have been particularly interested in the development of new synthetic methodology for direct amination of hydrocarbon molecules such as alkenes, alkanes, acetylenes, arenes and allenes.[2] We have recently found that simple protonolysis events enable incorporation of nitrogenated groups into the coordination sphere of common iodine(III) complexes, as for example, in case of the previously described compound A, which contains a rare iodine-nitrogen single bond.[2][sup]a[/sup] Further protonolysis furnishes the new iodine(III) compound $PhI(NTs_2)_2$ B containing two defined iodine-nitrogen single bonds.[3] It is of utmost synthetic importance that the new compound B contains iodine-nitrogen entities, which upon solution dissociation lead to electrophilic iodine centres and nucleophilic nitrogen groups.

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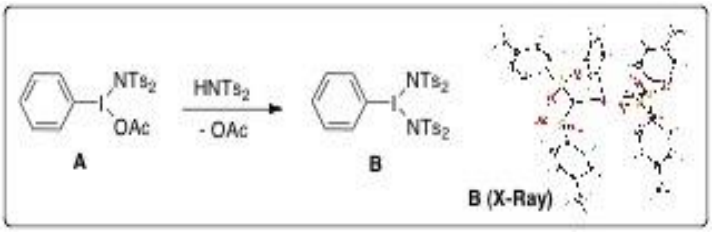

P-402

Metal Catalysed Intramolecular Diamination of Alkenes

Dr Matilde Aguilar-Moncayo[1], Dr Claudio Martínez[1], Prof Dr Kilian Muñiz[1]
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Poster Session 2

Vicinal diamines constitute important functional entities in a variety of fields ranging from life science to general organic chemistry and homogeneous catalysis. Despite this fact, efficient synthetic approaches toward this class of compounds are rare, and their direct construction within oxidative nitrogen transfer reactions remains challenging. In 2005, we pioneered the application of palladium catalysis in high oxidation state[1] for the intramolecular construction of vicinal diamines from alkenes.[2] In the following years, we have significantly broadened the synthetic scope of this particular approach towards 1,2-diamines and have introduced different protocols based on palladium, nickel and gold catalysis. We here provide an overview on available protocols for the intramolecular diamination of alkenes developed by our group.[3]

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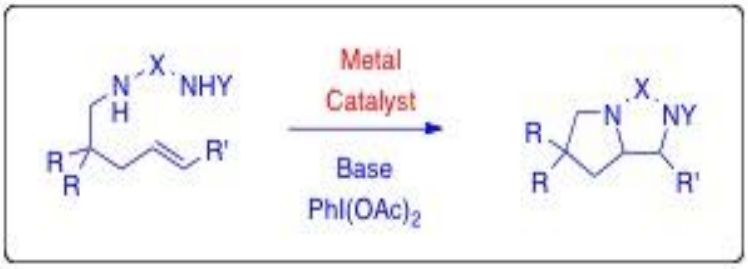

P-403

A Carboxylic Acid Mediated Phthalimide-Shuttling in the Aminopalladation of Alkenes

Dr Claudio Martínez[1], Prof. Dr. Rosana Álvarez[3], Prof. Dr. Kilian Muñiz[1,2]

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Poster Session 2

A mechanistic scenario is presented for the aminopalladation with phthalimide that is involved in the oxidative difunctionalization of alkenes.[1] The work identifies new bisphthalimidato palladium(II) complexes as catalysts for this transformation. On the basis of stoichiometric control reactions and quantum chemical calculations, a new pathway for aminopalladation of alkenes is proposed. It is based on a carboxylic acid that improves proton release and mediates an unprecedented phthalimide shuttling between free phthalimide and the bisphthalimidato palladium catalyst.[2]

References
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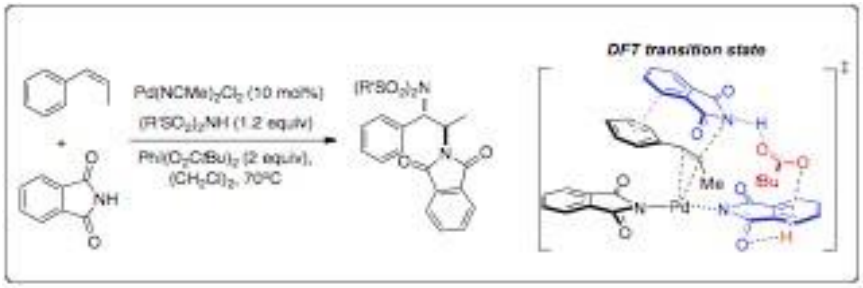


P-538

Palladium-catalyzed reaction of 2-fluoroallyl esters with phenols and succinimide

Mr. Masaki Kogawa[1], Mr. Hirotaka Watanabe[1], Mr. Mitsuaki Yamamoto[1], Ms. Maki Minakawa[1], Mr. Motoi Kawatsura[1]

[1]*Nihon University, Japan*

Poster Session 2

The palladium-catalyzed reaction of allyl esters with nucleophiles is one of the most useful processes in organic synthesis. In these reactions, one equivalent of the nucleophile was introduced into the allyl unit, and allylic compounds or cyclopropane derivatives were provided as the major reaction product. On the other hand, as an alternative reaction process for the palladium-catalyzed reaction, the reaction of 2-haloallyl esters with nucleophiles provides doubly-substituted products under the appropriate reaction conditions. Based on these backgrounds, we examined the reaction of 2-fluoroallyl acetates with the phenoxide anions and succinimide, then succeeded to obtaining the desired allylpyrrolidine-2,5-dione analogues in good yields with a perfect regioselectivity and a high Z-selectivity.

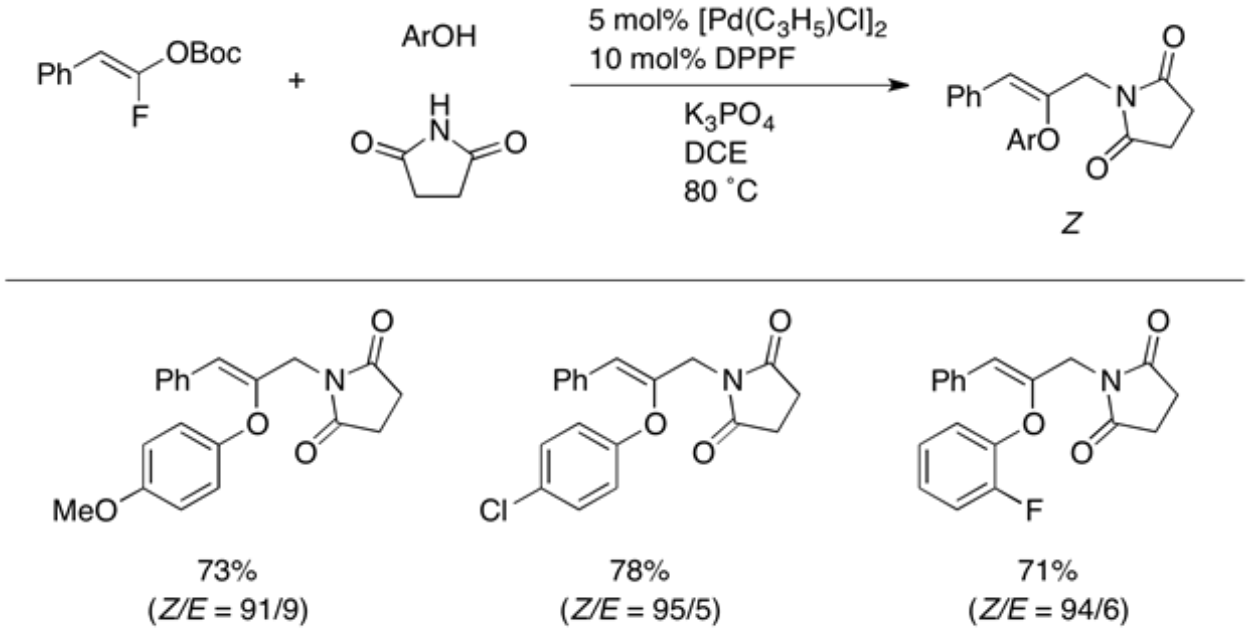


Figure. The palladium-catalyzed reaction of 2-fluoroallyl esters with phenols and succinimide.

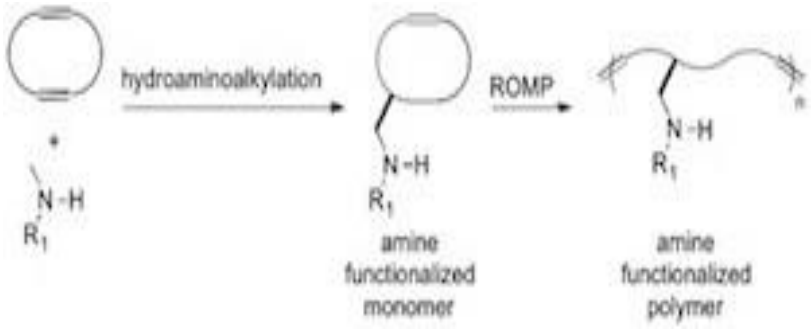
P-404

Hydroaminoalkation for the Catalytic Synthesis of Amine Functionalized Polymers: Variable Hydrogen-bonding for Tunable Rheological Properties

Mitchell Perry[1], Erin Morgan[1], Peter Edwards[1], Tannaz Ebrahimi[2], Savvas Hatzikiriakos[2], Laurel Schafer[1]
[1]Department of Chemistry, University of British Columbia, Vancouver, Canada, [2]Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, Canada

Poster Session 2

Hydroaminoalkylation, a carbon-carbon bond forming reaction alpha to an amine, has been shown to selectively generate mono-alkylated strained amino alkenes. The desired products can be fashioned in a one-step, atom economic protocol, starting from norbornadiene or 1,5-cyclooctadiene, and a variety of commercially available secondary amines. These amino alkenes have been used as monomers in ring opening metathesis polymerization (ROMP) to afford novel amine containing polymers with controlled characteristics. Synthetic targets of this nature are often inaccessible due to the incompatibility of common initiators with secondary nitrogen moieties. Polymers with a range of predictable molecular weights and low dispersities were easily generated using Grubbs second generation catalyst. Macromolecules derived from norbornene exhibit glass transition temperatures ranging from 61-75 °C and could offer a more processable material relative to unsubstituted poly(norbornene). Furthermore, by incorporating pendant secondary amines capable of hydrogen bonding, the thermal stability of these materials is markedly improved, up to 386 °C, as indicated by the thermogravimetric analysis.



P-405

Preparation of new push-pull chromophores with thiophene moiety

Ing. Jana Kousalova[1], prof. Ing. Jiri Kulhanek[1]
[1]*University of Pardubice, Pardubice, Czech Republic*

Poster Session 2

Organic π-conjugated molecules with intramolecular charge transfer (ICT) from donor (D) to acceptor (A) [1] are one of the fastest growing parts of organic chemistry. Dipolar character and also possibility of application of these molecules as active molecules in optoelectronic devices (for example date memory, OLED, OPVC, etc.) is their main reason. The presence of polarized π-conjugated system causes nonlinear optic properties of second and third order. The most common configuration of push-pull system is linear [2], branched [3] or Y-shaped [4,5].
The objective of this work is synthesis and study of properties of new push-pull chromophores on the base of ferrocene, which was used as donor part. Thiophene with combination with double or triple bond was used as π-linkage. As acceptor were used 1-methylimidazol-4,5-dicarbonitrile, 5-cyanothiophene or 3,4-dicyanothiophene (Fig. 1).

Fig. 1: Structure of prepared chromophores.

Three series of push-pull chromophores were prepared which different acceptor group. Synthesis was carried out three to five steps with the use of Suzuki-Miyaura, Sonogashira or Heck cross-coupling reaction. The electrochemistry properties of prepared push-pull chromophores were measured. Potential nonlinear optical properties of target compounds were calculated.

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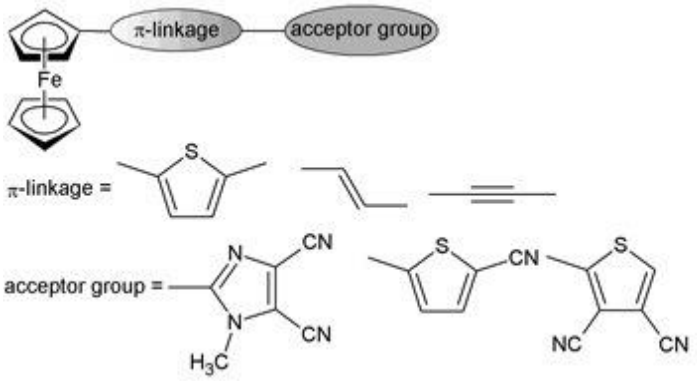

P-406

Nano-a-nano. Fe nanoparticle-catalyzed reactions in aqueous nanomicelles.

Prof. Bruce Lipshutz[1]
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Poster Session 2

Highly reactive nanoparticles of iron can be readily formed from a commercially available, inexpensive iron salt. These reagents have been found to be especially effective at mediating both cross-coupling reactions, such as Suzuki-Miyaura and Sonogashira reactions, as well as highly valued reductions of nitro-aromatics and –heteroaromatics, in water under very mild conditions. The key to success lies in the application of micellar catalysis using “designer” surfactants, where the combination of these in situ-formed aqueous nano-reactors deliver the substrate(s) to the metal nanoparticles.

P-407

Iridium-Catalyzed Single-Step N-Substituted Lactam Synthesis from Lactones and Amines

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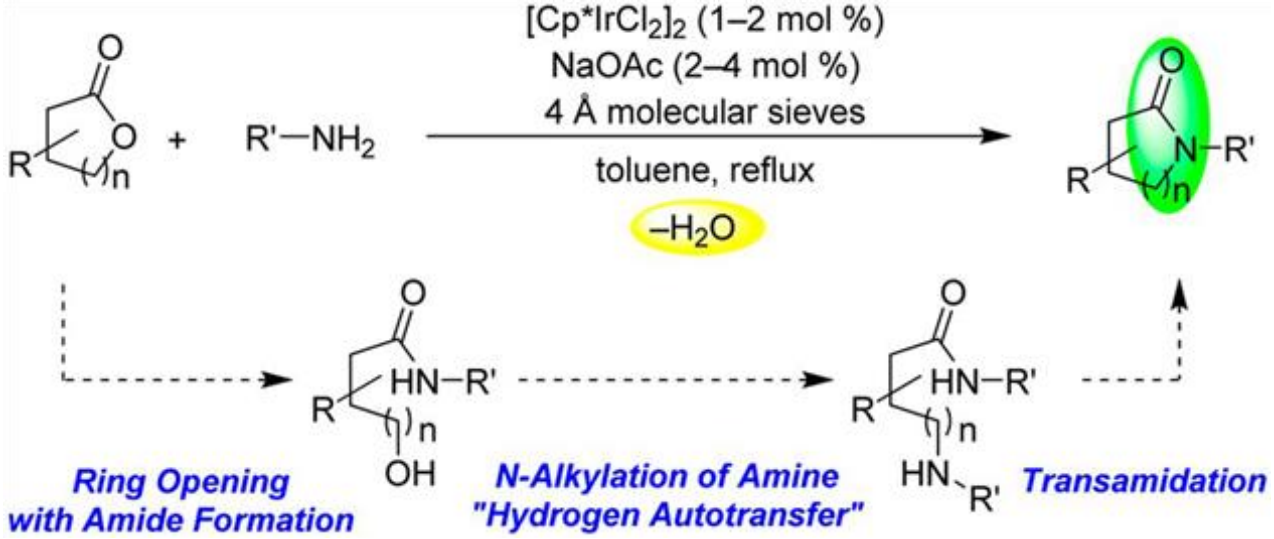
[1]*Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul, South Korea*

Poster Session 2

Lactams are one of the fundamental functional groups in pharmaceutical, polymer, and organic chemistry. There have been a number of synthetic methods for lactams developed, but most methods suffer harsh reaction conditions and/or require reactive reagents. Herein, a novel catalytic lactam synthesis was achieved directly from lactones and amines with commercially available iridium complex and sodium acetate. In the method, amide bond and C-N bond formation occurred in a single-step reaction. Two reaction intermediates, hydroxyamide and aminoamide, were observed during 1H NMR kinetic study. Each catalytic reaction of two intermediates gave the corresponding lactam in good yield. On the basis of the mechanistic investigation, an interesting mechanism via three sequential transformations was proposed; aminolysis of lactone, N-alkylation of amine with hydroxyamide, and intramolecular transamidation of aminoamide affording the corresponding lactam. This catalytic method in milder condition will be an environmentally benign alternative for lactam synthesis.



P-408

Metal–Ligand Cooperative Catalysts of Niobium and Tantalum for Radical Addition Reaction

Metal–Ligand Cooperative Catalysts of Niobium and Tantalum for Radical Addition Reaction Haruka Nishiyama[1], Teruhiko Saito[1], Hayato Tsurugi[1], Kazushi Mashima[1]
[1]*Osaka University, Toyonaka, Japan*

Poster Session 2

Transition metal complexes with redox-active ligands have attracted recent interests in terms of their unique capability to enable the electron transfer process of base metal complexes through the redox events within the supporting ligand in any catalytic reactions. We have focused our attention to the preparation and reactivity of group 5 metal complexes bearing redox-active N,N'-diaryl-1,4-diaza-1,3-butadiene (α-diimine) ligands, and we already found that tantalum complexes with the dianionic α-diimine ligand mediated the reductive cleavage of carbon-halogen bonds of polyhaloalkanes to form carbon radicals.1 In this contribution, we report catalytic application of (α-diimine)MCl3 (M = Nb, Ta) for radical addition reactions of polyhaloalkanes to alkenes, in which reversible redox behavior of the metallacyclic moiety plays an important role for reductively cleaving carbon-halogen bonds as well as regenerating the catalytically active metal species.

We investigated catalytic radical addition reaction of CCl4 to 1-octene using a catalytic amount (3 mol%) of niobium and tantalum complexes 1a,b and 2a,b. Among all complexes examined, niobium complex 1b showed the highest catalytic activity to produce 1,1,1,3-tetrachlorononane in up to 85% yield (Scheme 1). Niobium complex 1a had low activity for reductive cleavage for the carbon-halogen bond. Thus, 1a afforded a product in low yield. Though tantalum complexes 2 were active for the carbon-halogen bond cleavage, they showed only low reactivity in this reaction.

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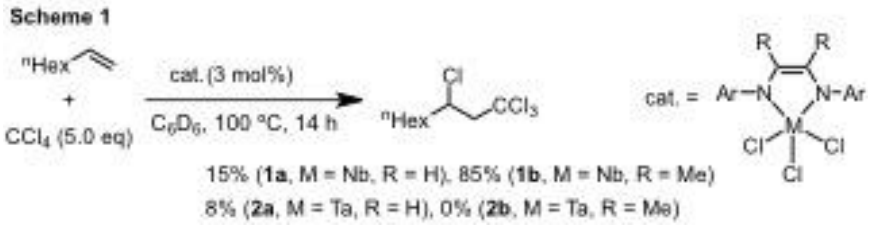


P-409

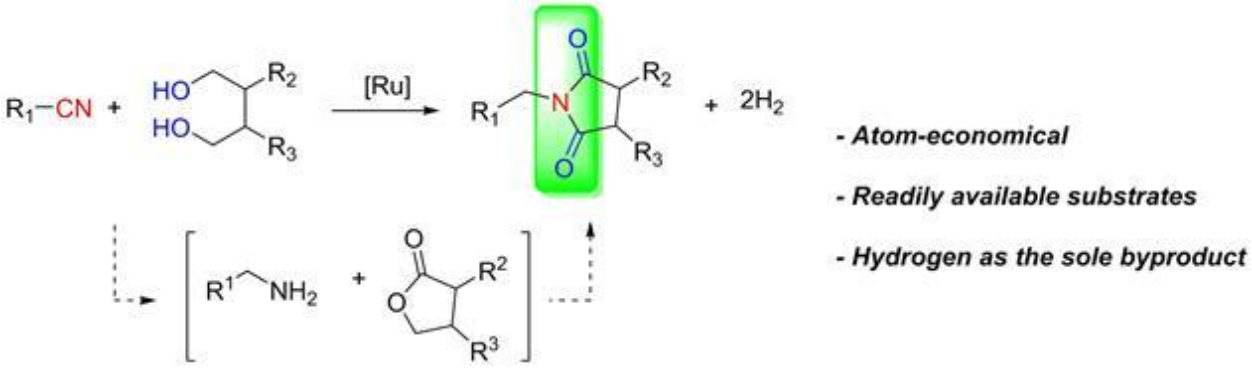
Synthesis of Cyclic Imides from Nitriles and Diols Using Hydrogen Transfer as a Substrate-Activating Strategy

Mr. Jaewoon Kim[1], Prof. Soon Hyeok Hong[1]
[1]*Seoul National University, Seoul, South Korea*

Poster Session 2

Cyclic imide is a key functional group in synthetic, biological, medicinal, and polymer chemistry. In particular, the cyclic imide group is found in several drugs such as thalidomide, phensuximide, buspirone, and lurasidone, and several derivatives have been recently evaluated as attractive new drug candidates with high bioactivities. Despite their utility, the conventional methods for the preparation of cyclic imides have many limitations such as harsh thermal reaction conditions and harmful waste generation from the activating reagents used.

We herein present an atom-economical and versatile protocol for the synthesis of a cyclic imide from a nitrile and a diol, which is readily available and easy to handle. Initially, we hypothesized that first a direct amide bond formation would occur between one of the alcohol groups of diol and nitrile in the same manner as described in our previous study. However, we observed that nitrile is fully reduced to amine by taking hydrogen from diol along with generation of lactone. Notably, this reaction adopts redox-neutral hydrogen transfer as the substrate-activating strategy to generate both the reactive nucleophile and electrophile in the reaction mixture. This operationally simple protocol provides an efficient route to diverse cyclic imides.



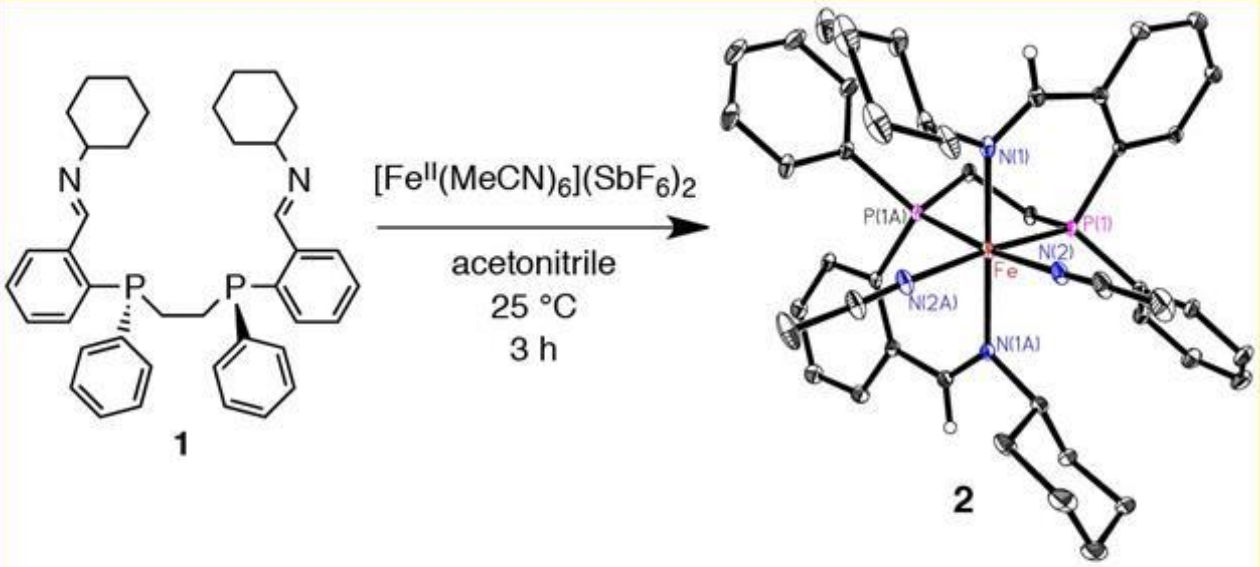
P-410

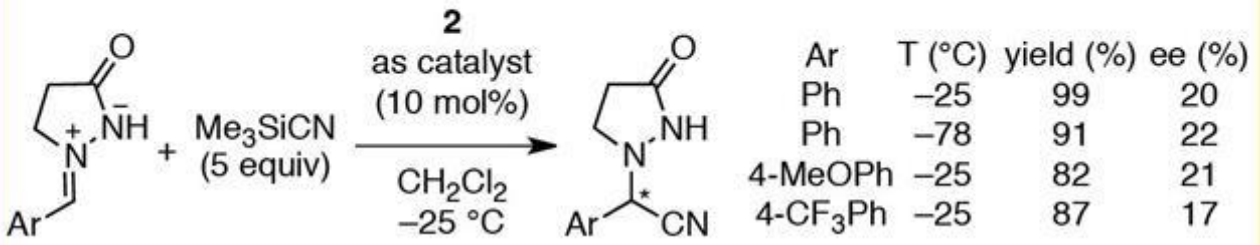
Iron(II) Catalysts with a P-Stereogenic NPPN Ligand for the Enantioselective Strecker Reaction of Azomethine Imines

Raffael Huber[1], Prof Antonio Mezzetti[1]
[1]*ETH Zurich, Zurich, Switzerland*

Poster Session 2

Replacing precious metals with iron has several advantages - iron is abundant, cheap, relatively non-toxic and environmentally benign. However, iron complexes are inherently less stable than their fourth and fifth row analogues. Multidentate ligands can, at least in part, compensate for this by virtue of their chelate effect. We used the enantiomerically pure, P-stereogenic synthon (1S,1'S)-2,2'-(ethane-1,2-diylbis(phenylphosphanediyl))dibenzaldehyde to prepare the tetradentate NPPN ligand 1 by condensation with cyclohexylamine. Ligand 1 reacts with $Fe(MeCN)_6](SbF_6)_2$ to give $[Fe(MeCN)_2(1)](Y)_2$ (2) as a stable, diamagnetic complex, which can be further transformed into its carbonyl, bromocarbonyl, [sup]t[/sup]Bu-isonitrile, and trimethylsilyl cyanide derivatives. All dicationic complexes analyzed by X-ray crystallography feature a Λ-cis-α geometry. Complex 2 catalyzes the enantioselective Strecker reaction of azomethine imines with up to 22% ee. [sup]31[/sup]P{^{1}H} NMR spectroscopy reveals that the product displaces the NPPN ligand from the metal, which explains the low enantioselectivity.





Ar	T (°C)	yield (%)	ee (%)
Ph	–25	99	20
Ph	–78	91	22
4-MeOPh	–25	82	21
4-CF_3Ph	–25	87	17

P-411

Intramolecular Carbolithitaion of Heterosubstituted Alkynes

Miss Maha Ahmad[1], Dr. Rudy Lhermet[1], Dr. Muriel Durandetti[1], Dr. Jacques Madalluno[1]
[1]*COBRA UMR CNRS 6014 - University of Rouen , mont-saint-aignan, France*

Poster Session 2

For the past 30 years, carbometallation methodologies using organolithium reagents have been greatly developed. [1] Recently, we have described a method providing highly functionalized heterocycles by intramolecular carbolithiation of an acetylenic triple bond. [2] Based on this process, a series of heterosubstituted alkynes was successfully submitted to the intramolecular carbolithiation of their triple bond. We show that the addition is stereoselective thanks to the control exerted by the terminal substituent Y on the geometry of the transition state. [3]

Scheme 1

In the case of chloro-alkynes, the intramolecular carbolithiation leads to exocyclic alkylidene carbenoids of which both electrophilic and nucleophilic characters can be used. [4] The resulting vinyl lithium intermediates were engaged in reactions with various electrophiles, allowing in particular to obtain vinyl metalloid. These intermediates were then involved in Suzuki or Stille reactions. Similarly, the chlorinated derivative could be employed in pallado-catalyzed coupling reactions. The cyclization-coupling sequence has yielded various polycyclic structures.

Scheme 2

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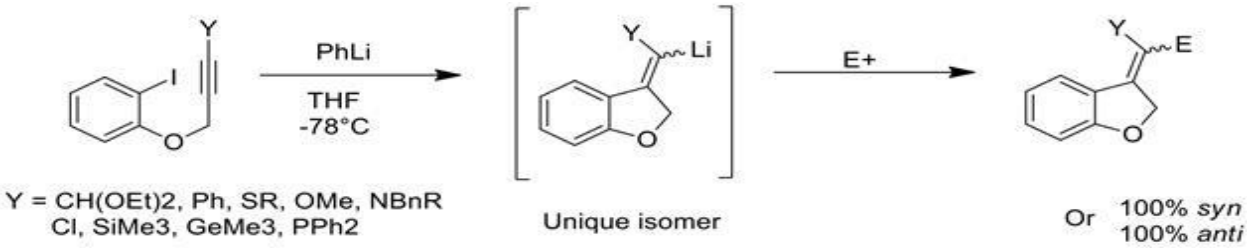


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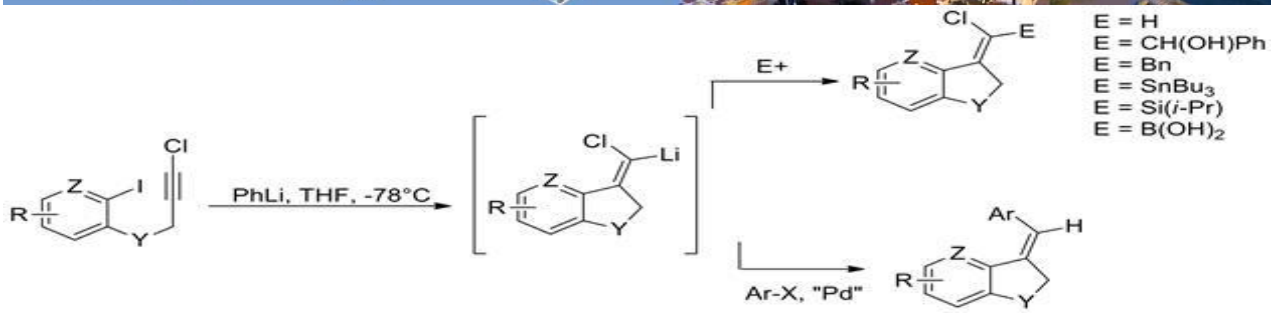
PhLi, THF, -78°C
E+
Ar-X, "Pd"
E = H
E = CH(OH)Ph
E = Bn
E = SnBu3
E = Si(i-Pr)
E = B(OH)2

P-413

Palladium nanoparticles supported on Graphene and Graphene oxide as efficient catalysts for the oxidation of azides to nitriles and the Suzuki coupling.

Dr. Abbas Khoshnood[1], MS. Melania Gómez-Martínez[1], Mr. Xavier Marset Gimeno[1], Dr. Diego J. Ramón[1], Dr. Isidro M. Pastor[1], Dr. Diego A. Alonso[1]
[1]*Alicante University, Alicante, Spain*

Poster Session 2

In recent years, solid nanocatalysts have been of experimental interest because of their advantages such as easier workup, compliance with green-chemistry protocols and more often with enhancement of the regio- and stereoselectivity of the reactions. Furthermore, transition metal nanomaterials such as Palladium nanoparticles (PdNPs) have a high surface to volume ratio providing more active sites per unit area compared with regular bulk catalysts.

We have used Palladium nanoparticles supported on Graphene and Graphene oxide [1] as efficient catalysts for an experimentally simple Suzuki synthesis of biaryls from potassium aryltrifluoroborates as well as nitriles from benzylic azides using low palladium loadings (0.1 mol%). The reactions afford the corresponding products in good to high yields and the nanocatalysts can be easily recover and reused.

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P-414

Copper-Mediated ortho-Nitration of (Hetero)Arenecarboxylates

Timo Wendling[1], Dr. Dmitry Katayev[2], Kai F. Pfister[1], Prof. Dr. Lukas J. Goossen[1]
[1]*TU Kaiserslautern, Kaiserslautern, Germany,* [2]*ETH Zürich, Zürich, Switzerland*

Poster Session 2

Aromatic nitro compounds have a long tradition as synthetic valuable intermediates in organic chemistry. Traditionally, they are synthesized by electrophilic aromatic nitration of arenes, which is, even today, the almost exclusively applied synthetic method. In contrast, only a few chelation-assisted ortho-C-H nitration reactions are known, but their synthetic value suffers from high reaction temperatures and, most notably, by the application of pyridine-based directing groups that are hard to remove or to derivatize.
Here we report a copper-mediated chelation-assisted C-H nitration of (hetero)arenes possessing a carboxylate-based 8-aminoquinoline directing group under unprecedentedly mild reaction conditions (Scheme 1)[1]. Various aromatic Daugulis amides were nitrated selectively in the ortho-position in the presence of $CuNO_3(PPh_3)_2$ and $AgNO_2$ at 50 °C. Saponification under microwave conditions allows regeneration of the carboxylate group within only seven minutes, which can further be tracelessly removed by a copper-catalyzed protodecarboxylation or aryl-[2] or alkoxy-[3] substituted via decarboxylative cross-couplings.

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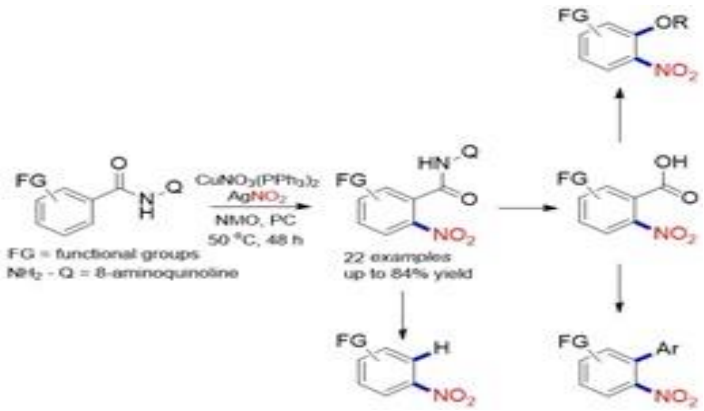

P-415

Spectroscopic and Catalytic Investigations of Different Pd(0)dibenzylideneacetone-Species

Agostino Biafora[1], Philip Weber[1], Prof. Dr. Lukas J. Gooßen[1]
[1]*TU Kaiserslautern, Kaiserslautern, Germany*

Poster Session 2

Bis(dibenzylideneacetone)palladium(0) and tris(dibenzylideneacetone)dipalladium(0) are widely used precursors for the generation of catalytic palladium species.[1] However, the use of $Pd_x(dba)_y$ in transition metal catalyzed reactions often results in different catalytic activities depending on supplier and batch, causing poor reproducibility. For this reason, we tested different $Pd_x(dba)_y$-species (from different suppliers) on their physical (mass analysis, melting point, etc.), spectroscopic (IR, NMR, XRD, etc.) and chemical properties (studies on catalytic activities).[2][sup],[/sup][3] We intend to find a parameter to predict the catalytic activity, which has not been investigated so far. Different $Pd_x(dba)_y$-species from different suppliers (A, B, C, and D) not only show different catalytic activities within the performed test-reactions (diagrams above), but they alter also in regard of their physical and spectroscopic properties. However, at this stage we could not detect a clear parameter to draw connections towards the observed catalytic activity. We are currently investigating: contaminations(-amount), different Pd-distribution within the material and, in collaboration with MPI Mülheim, examination of the samples towards nanoparticles using highly advanced TEM and SEM techniques.

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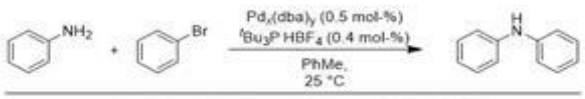
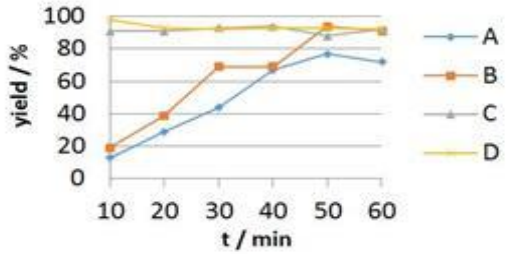
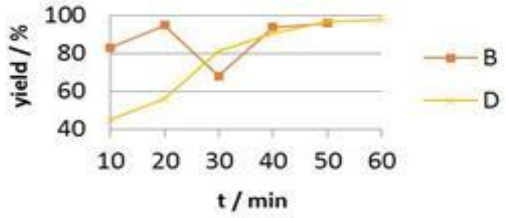
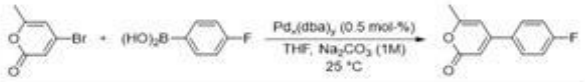


amination test-reaction with $Pd_2(dba)_3$

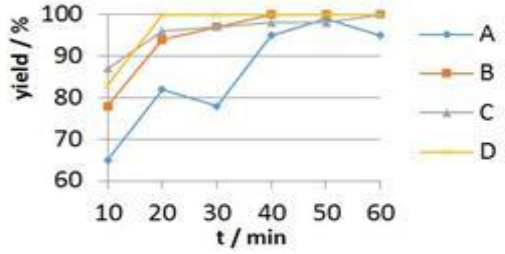


amination test-reaction with $Pd_2(dba)_3 \bullet (CHCl_3)$

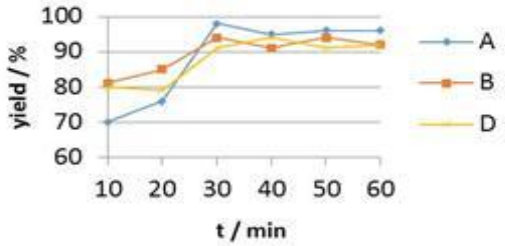




arylation test-reaction with $Pd_2(dba)_3$



arylation test-reaction with $Pd(dba)_2$



P-416

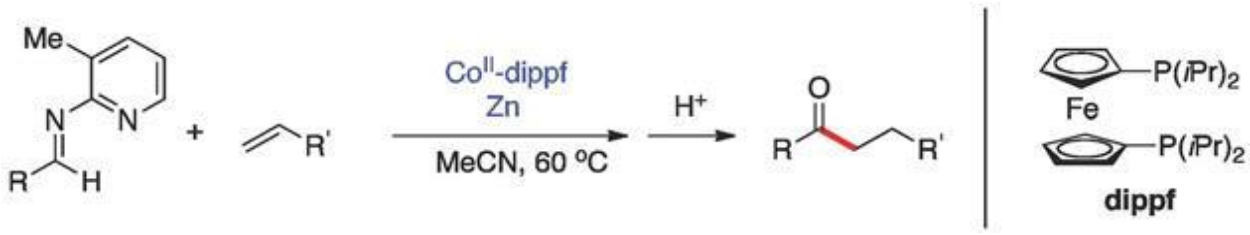
Cobalt-Catalyzed Intermolecular Hydroacylation of Olefins through Chelation-Assisted Imidoyl C–H Activation

Dr JUNFENG YANG[1], Mr Yuan Wah Seto[1], Prof Naohiko Yoshikai[1]

[1]*Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore, Singapore*

Poster Session 2

The catalytic hydroacylation of unsaturated hydrocarbons offers an atom- and step-economical route to ketones from readily available aldehyde substrates. While rhodium(I) catalysts have been most extensively used in such transformations in both inter- and intramolecular settings, the use of analogous cobalt catalysts has been rare. Recently, we demonstrated the competence of low-valent cobalt-diphosphine catalysts in hydroacylation through the development of enantioselective intramolecular hydroacylation reactions of olefins and ketones. Herein we report that a low-valent cobalt catalyst generated from cobalt(II) bromide, 1,1'-bis(diisopropylphosphino)ferrocene (dippf), and zinc powder promotes intermolecular hydroacylation of olefins using N-3-picolin-2-yl aldimines as aldehyde equivalents, affording ketone products in moderate to good yields with high linear selectivity. The reaction is applicable to styrenes, vinylsilanes, and aliphatic olefins as well as to various aryl and heteroaryl aldimines. The present catalytic system features a distinctively lower reaction temperature (60 °C) than typically required in the same type of chelation-assisted hydroacylation promoted by rhodium catalysts (130–150 °C).



P-417

Remote and modulably selective cleavage of ω-alkenyl spiropentane derivatives

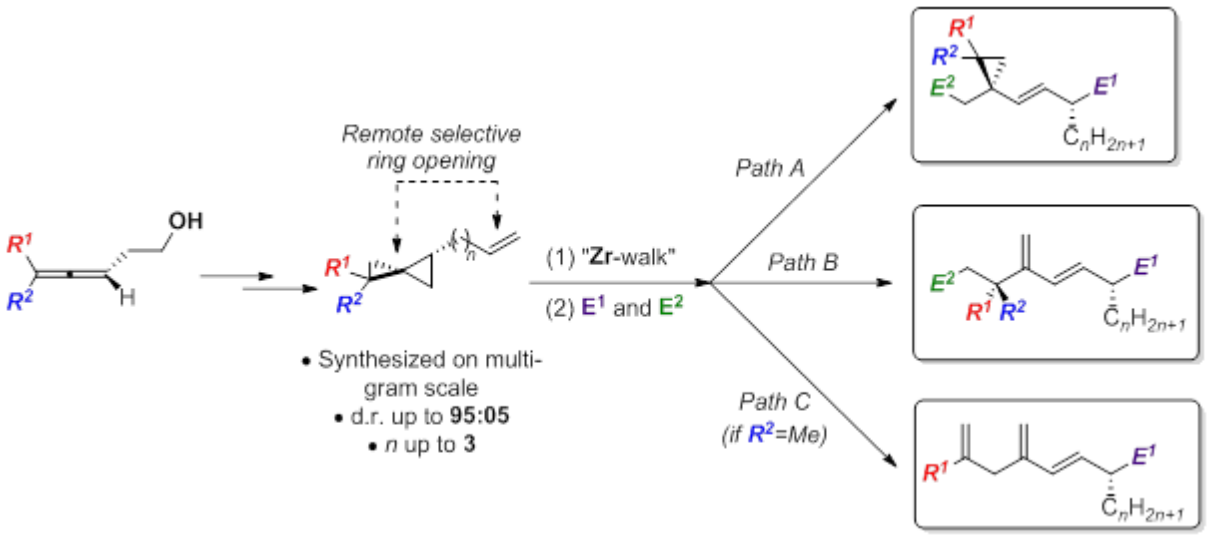
Jeffrey Bruffaerts[1], Sukhdev Singh, Ilan Marek

Poster Session 2

Remote functionalization has becoming an emerging and increasingly popular concept in synthesis. Indeed, customizing a molecule on any desired position, even its least reactive, would represent a new pinnacle in organic chemistry, as virtually any derivative could be accessed in a versatile manner. In this context, a series of pioneering publications have highlighted the transition-metal assisted remote functionalization of alkenes through tandem reactions involving olefin isomerization or chain-walking process.

In our research group, we have achieved so far distant activations of alkenes using a low-valent zirconocene-butene complex generated in situ, namely the Negishi reagent. More specifically, we have reported the remote cleavage of ω-alkenyl cyclopropanes in one-pot procedures involving successively zirconium-walk (migration of the metal on a hydrocarbon chain), selective ring-opening of a three-membered ring, followed by a double functionalization reaction.

In the present context, we hereby report the modulable and selective cleavage of ω-alkenyl spiropentane derivatives, which are chemically accessible starting from allenes. Using organozirconium chemistry, we have set divergent methodologies for the synthesis of vinylcyclopropane, diene and triene derivatives in good yields with excellent stereoselectivities. This work contributes to promote spiropentanes as versatile and useful intermediates in synthesis.



P-418

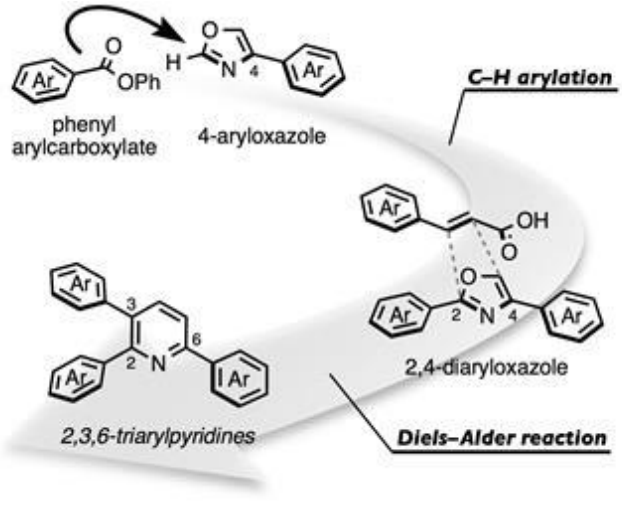
Rapid Access to Triarylpyridines and Synthesis of GE2270s

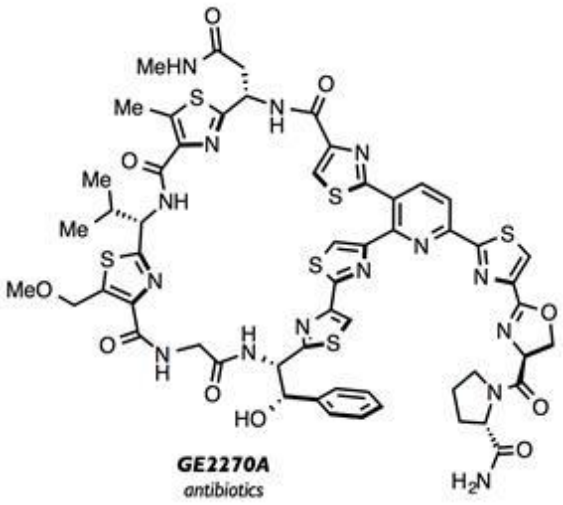
Kazuma Amaike[1], Junichiro Yamaguchi[1], Kenichiro Itami[1,2,3]

[1]Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Furo-Cho, Japan, [2]JST-ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Nagoya, Furo-Cho, Japan, [3]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Nagoya, Furo-Cho, Japan

Poster Session 2

Many of recently emerging thiopeptide antibiotics are composed of a 2,3,6-triarylpyridine moiety and a macrocyclic oligopeptide. Biological assays of these compounds have shown that they are protein synthesis inhibitor candidates against gram-positive bacteria. Owing to their interesting structures and remarkable biological activities, these compounds have attracted considerable attention as synthetic targets. Herein, we describe a novel method for the synthesis of triarylpyridines. Key steps include a nickel-catalyzed C–H coupling reaction1 of 4-aryloxazoles with phenyl arylcarboxylates to afford 2,4-diaryl oxazoles, followed by a decarboxylative Diels–Alder reaction of oxazoles with aryl acrylic acids to generate triarylpyridines. We have also accomplished a formal synthesis of GE2270s, a thiopeptide antibiotic.





P-419

Nitrenium Ions: A Novel Lewis Base and Lewis Acid

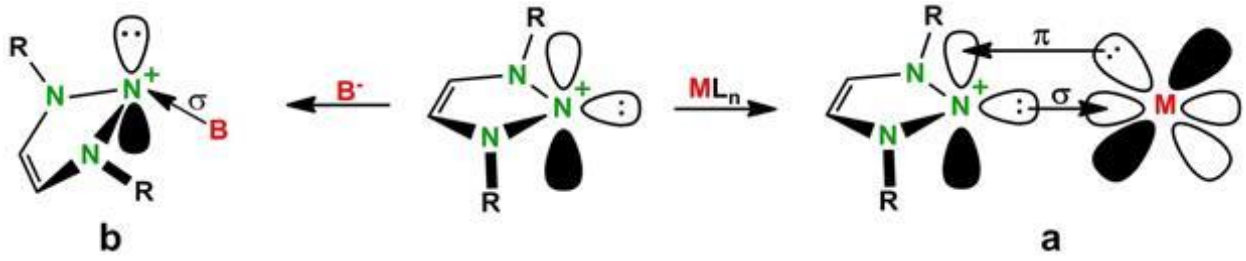
Miss Alla Pogoreltsev[1], Dr. Yuri Tulchinsky[1], Prof. Mark Gandelman[1]
[1]*Technion – Israel Institute of Technology, Haifa, Israel*

Poster Session 2

N-heterocyclic nitrenium ions are the nitrogen-derived cationic analogues of N-heterocyclic carbenes. Like N-heterocyclic carbenes and their analogues, these species possess a Lewis amphoteric character, due to a lone pair of electrons in sp^2-orbital and an empty p_π-orbital. However, these species have been known as stable compounds and completely inert towards transition metals and Lewis bases for a long time.
Here we present the chemistry of nitrenium species as ligands (Lewis bases) for transition metals (Scheme 1a).[sup][1][/sup] Under proper conditions, these cationic ligands readily coordinate to transition metals in various oxidation states, thus affording mono- , di- and even tri-cationic nitrenium-based complexes. The formation of di- and tri-cationic complexes is particularly interesting, since the coordination of a cationic ligand to a cationic metal is extremely rare. Moreover, such unexplored complexes can lead to a novel unusual reactivity, since this cation-cation (L+-M+) system enhances the electrophilicity of the metal center.
We also present the function of nitrenium species as Lewis acid (Scheme 1b).[sup][2][/sup] Nitrenium ions react with various basic species affording new type of Lewis acid-base pairs. In light of chemistry of frustrated Lewis pairs and Lewis acid-base pairs based on carbenes and their analogues, we hope that these new pairs will expand the field of metal-free activation of small molecules.

References

[1] (a) Tulchinsky, Y.; Iron, M. A.; Botoshansky, M.; Gandelman, M. Nature Chem., 2011, 3, 525. (b) Tulchinsky, Y.; Kozuch, S.; Saha, P.; Botoshansky, M.; Shimon, L.; Gandelman, M. Chem. Sci., 2014, 5, 1305. (c) Y. Tulchinsky, S. Kozuch, P. Saha, A. Mauda, G. Nisnevich, M. Botoshansky, L. J.W. Shimon, M. Gandelman, Chem. Eur. J., 2015, 21, 1-13.
[2] A. Pogoreltsev, Y. Tulchinsky, N. Fridman, M. Botoshansky, M. Gandelman, Manuscript in preparation.



Scheme 1 Schematic representation of reactivity of nitrenium species as Lewis base (a) and acid (b).

P-420

gem-DIHALO ALKANES AND THEIR APPLICATIONS

Miss Kseniya Kulbitski[1], Dr. Xiaojian Jiang[1], Dr. Gennady Nisnevich[1], Prof. Mark Gandelman[1]
[1]*Technion – Israel Institute of Technology, Haifa, Israel*

Poster Session 2

Organic iodides are extremely useful compounds, and novel methodologies for their efficient synthesis are an important goal in organic chemistry. Recently, we developed a novel, general and robust method for the conversion of carboxylic acids to organic iodides without the use of heavy metals or strong oxidizing agents. N-Iodoamides were used for both initiation and halogen donation under irradiative conditions. Isolation of the product is extremely simple and the major co-product is removed as a water-soluble biodegradable material. This new methodology was further applied to the successful synthesis of geminal diiodo- and iodo(halo)-compounds (halo = Br, Cl, F) (Scheme 1, A). [1]
We demonstrate that dihaloalkanes, prepared by our methodology, can be used in direct synthesis of valuable organic products. For example, geminal halo(fluoro)-alkanes are utilized in enantioselective metal mediated cross-coupling reactions to efficiently result in chiral secondary organic fluorides (Scheme 1, B). [2],[3] This approach allows for site-selective fluorination of non-activated alkyl chains, and synthesis of tailor-made secondary organic fluorides. Geminal iodo(chloro)-alkanes are utilized in successive cross-coupling reactions to obtain tertiary sterioselective carbon centers in one-pot manner (Scheme 1, C). [4]

References
[1]. K. Kulbitski; G. Nisnevich; M. Gandelman Adv. Synth. Catal. 2011, 353, 1438.
[2]. X. Jiang, S. Sakthivel, K. Kulbitski, G. Nisnevich, M. Gandelman J. Am. Chem. Soc., 2014, 136, 9548
[3]. X. Jiang, M. Gandelman J. Am. Chem. Soc., 2015, 137, 2542
[4]. X. Jiang, K. Kulbitski, G. Nisnevich, M. Gandelman Submitted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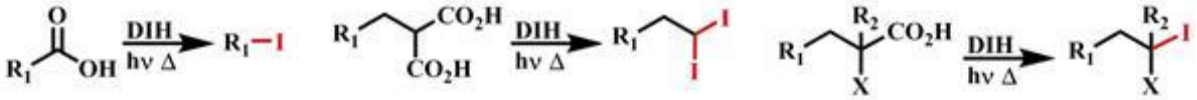
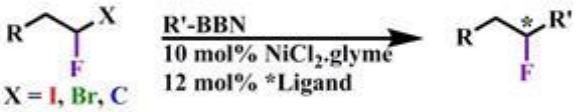
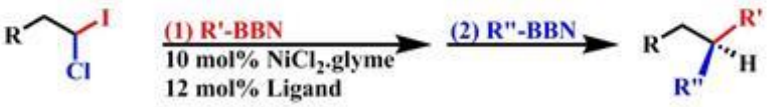
(A)


DIH
hν Δ
R1 = Alkyl, Aryl
R1 = Alkyl, Aryl
DIH = 1,3-diiodo-5,5-dimethylhydantoin
R1 = Alkyl, Aryl
R2 = H; X = I, Br, Cl, F
R2 = CO2Et; X = F

(B)


X = I, Br, C
R'-BBN
10 mol% NiCl2.glyme
12 mol% *Ligand

(C)


(1) R'-BBN
10 mol% NiCl2.glyme
12 mol% Ligand
(2) R"-BBN

Scheme 1

P-421

Thiazole in organic photovoltaics: chemistry and features.

Dr Patricia Chavez[1], Master Ibrahim Bulut[1], Dr Patrick Lévêque[2], Dr Stéphane Mery[3], Prof Dr Thomas Heiser[2], Dr Raymond Ziessel[1], Dr Nicolas Leclerc[1]

[1]ICPEES : Institut de Chimie et Procédeés pour l'Energie, l'Environnement et la Santé, Strasbourg, France, [2]ICube - Equipe Composants Organiques, Strasbourg, France, [3]IPCMS : Institut de Physique et de Chimie de Strasbourg, Strasbourg, France

Poster Session 2

Over the last few decades, significant progress has been made in the design, synthesis and application of organic semi-conducting materials containing electron-rich (donor D) and electron-deficient (acceptor A) alternating units. However, there is still a need for the elaboration of new and innovative building blocks in order to enlarge the field of applications of conjugated materials.

In the present work, the incorporation of thiazole as an original π-conjugated fragment is addressed. In particular, we describe an intensive and complete study about its chemical reactivity, using dedicated direct arylation cross-coupling catalysis. It is noteworthy that despite its unsymmetrical nature, successful control of the orientation of thiazole along the conjugated backbone was attained without requiring any protection step. Furthermore, we present an investigation on how the orientation of thiazole impacts the optical properties of thiazole containing semiconducting materials.[1] Finally, it has been found that the thiazole moiety allows to lower both HOMO and LUMO levels, relative to the thiophene-based counterpart, while keeping the energy band gap almost unchanged.[2] For the first time, these features are used to increase photovoltaic performances of small molecules based bulk heterojunction compared to thiophene counterparts, leading to a higher power conversion efficiency for soluble small molecules-based devices.

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[2] Zaborova, E.; Chávez, P.; Bechara, R.; Lévêque, P.; Heiser, T.; Méry, S.; Leclerc, N. Chem. Commun. 2013, 49, 9938-9940.


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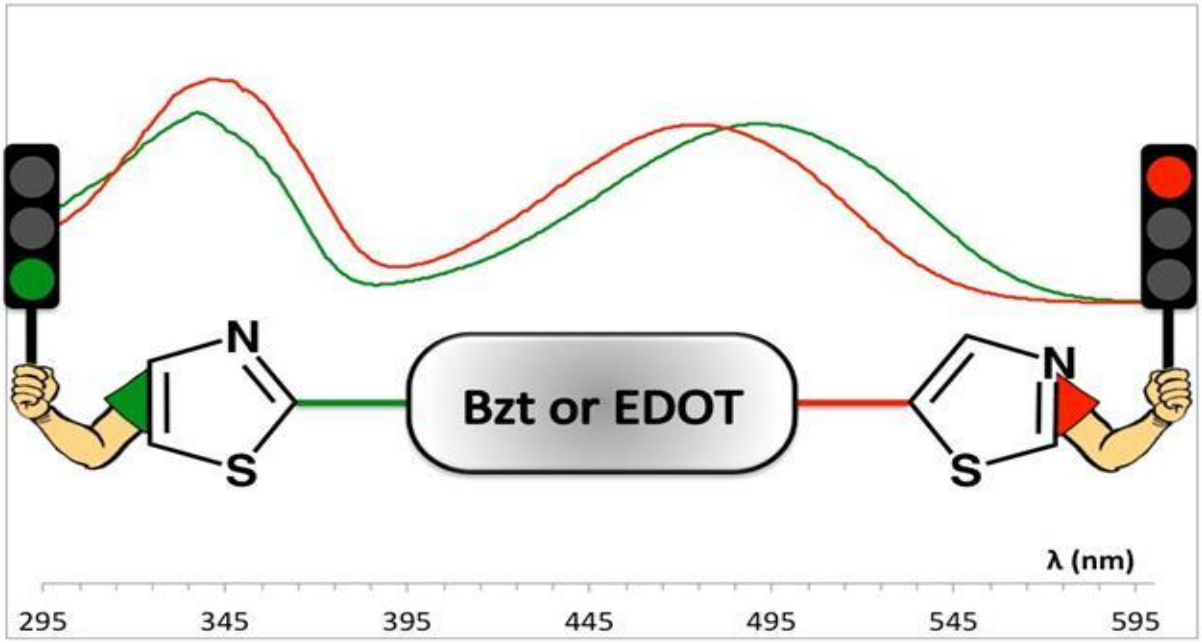

N
S
Bzt or EDOT
N
S
λ (nm)
295
345
395
445
495
545
595

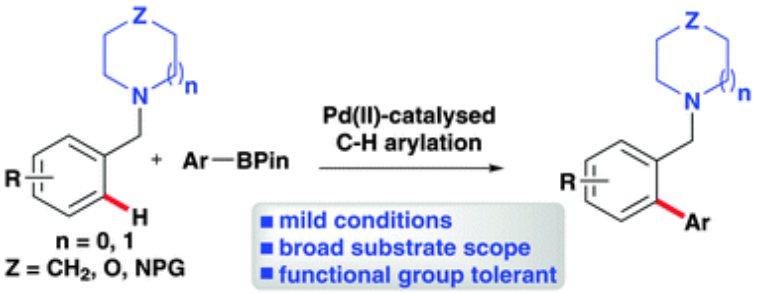
P-422

Palladium(II)-catalysed ortho-arylation of N-benzylpiperidines

Mr Peng Wen Tan[1]
[1]*University of Oxford, Oxfordshire, UK*

Poster Session 2

Pd(II)-catalysed ortho-arylation of benzylic heterocycles with arylboronic acid pinacol esters (Ar-BPin) via directed C–H bond activation to generate the desired biaryl products is reported. This methodology is efficient and applicable to a wide range of functionalised Ar-BPin and benzylic heterocycles, allowing the direct synthesis of important biaryl motifs in modest to good yield.



P-423

Rhodium-catalysed MTM-directed hydroacylation of alkynes with α-amino aldehydes

Dr. Sangwon Seo[1], Dr. Joel Hooper[1], Dr. Fiona Truscott[1], Mr. James Neuhaus[1], Prof. Michael Willis[1]
[1]*The University of Oxford, Oxford, UK*

Poster Session 2

In recent years, the intermolecular hydroacylation of alkynes has been developed as a powerful method for the construction of enones from simple aldehydes.[1] This process involves the addition of an acyl unit and a hydrogen atom across a C-C multiple bond, which is generally achieved through chelation-controlled transition metal-catalysed activation of an aldehyde C–H bond. The use of a chelating heteroatom in the substrate offers the most effective method that suppresses undesired side reactions and subsequent catalyst decomposition. This work describes the use of the methylthiomethyl (MTM) protecting group[2] as an easily removable directing group for the rhodium-catalysed hydroacylation of alkynes with α-amino aldehydes.[3] The mild reaction conditions using our rhodium catalyst allowed the enantiomerically enriched aldehydes that are configurationally unstable under forcing conditions to react with complete retention of enantiopurity. A wide range of enones could be prepared in excellent yields, showing the high functional-group tolerance and versatility of this reaction. To further demonstrate its utility, this MTM-directed hydroacylation reaction was employed in a short enantioselective synthesis of sphingosine. In conclusion, we have developed the rhodium-catalysed hydroacylation of alkynes with α-amino aldehydes using the MTM directing group. Given the wealth of the aldehydes that can be accessed from readily available α-amino acids, this process should provide a useful method for the synthesis of enantiomerically enriched α'-amino enones.

References
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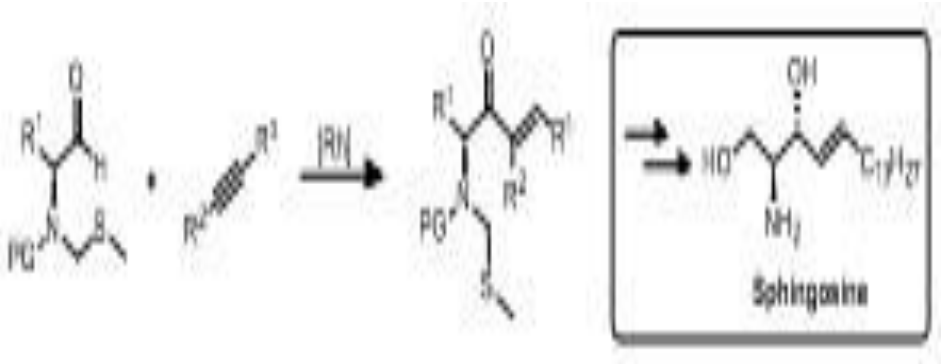
2. S. R. Parsons, J. F. Hooper and M. C. Willis, Org. Lett., 2011, 13, 998-1000.
3. S. Seo, J. F. Hooper, F. R. Truscott, J. Neuhaus and M. C. Willis, manuscript in preparation.



P-424

Effective Rh(II)-Catalyzed Synthesis of Polyether Macrocycles and Subsequent Isomerization

Mr Alexandre Homberg[1], Mr Daniele Poggiali[1], Mr Mahesh Vishe[1], Dr. Radim Hrdina[1], Dr. Céline Besnard[2], Dr. Laure Guénée[2], Prof. Jérôme Lacour[1]

[1]Department of Organic Chemistry, University of Geneva, Quai Ernest Ansermet 30, CH-1211 Genève 4, Geneva, Switzerland, [2]Laboratory of Crystallography, University of Geneva, Quai Ernest Ansermet 30, CH-1211 Genève 4, Geneva, Switzerland

Poster Session 2

Recently, several one-step syntheses of medium-sized ring and functionalized 15- to 18-membered macrocycles have been shown to proceed under high concentration only (> 0.6 M).[sup]1-4[/sup] These [3+N+3+N] (N = 5 to 7) multi-condensation of cyclic ethers and α-diazo-β-ketoesters (1) were developed using simple Rh2(OAc)4 or Rh2(Oct)4 as catalysts (1 mol%). Herein, based on mechanistic studies, it is shown that Ikegami-Hashimoto complexes of type 3 improve greatly the applicability; the reactions being now scalable up to 20 g of products 2 with only 0.001 mol% of catalyst. (AttachedFile1)

A straightforward access to chiral crown ethers of type 4 and 5 is then possible through a sequence of amidation and isomerisation reactions. With anilines, the two steps can be performed in one-pot[5] while, with aliphatic amines, a preformation of conjugated bisamide intermediates is necessary.[6] Interestingly in both case, only the chiral (racemic) diastereoisomer is obtained with moderate to good yields. (AttachedFile2)

References:

(1) Zeghida, W.; Besnard, C.; Lacour, J. Angew. Chem. Int. Ed. 2010, 49, 7253.
(2) Rix, D.; Ballesteros-Garrido, R.; Zeghida, W.; Besnard, C.; Lacour, J. Angew. Chem. Int. Ed. 2011, 50, 7308.
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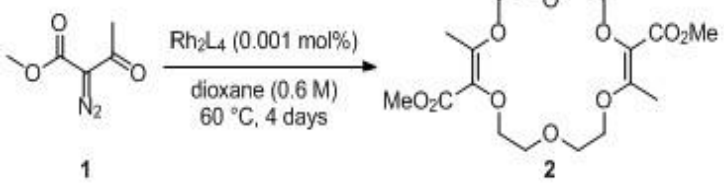
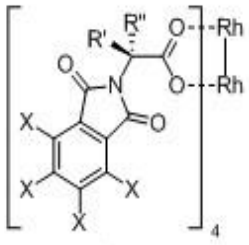


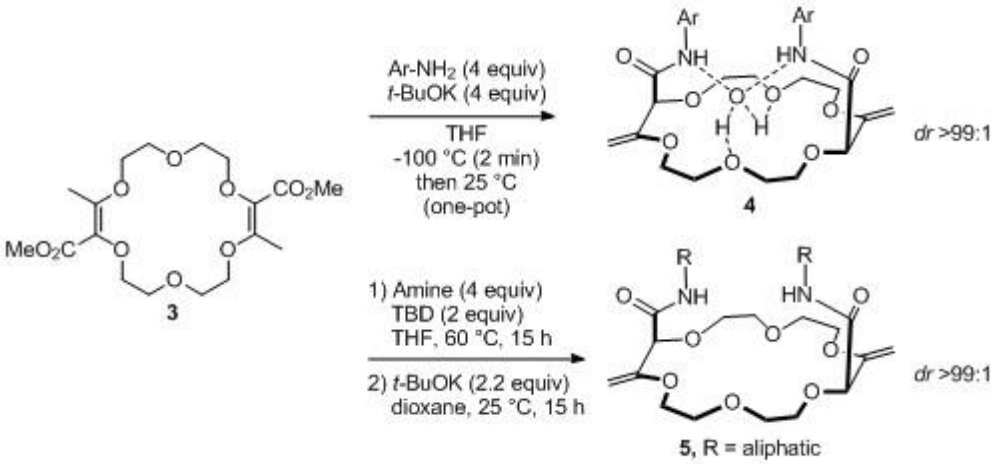
1
20 g

2
20 g (71%)



3

X = H, R' = *t*-Bu, R'' = H : Rh_2((*S*)-PTTL)$_4$
X = Cl, R' = *t*-Bu, R'' = H : Rh_2((*S*)-TCPTTL)$_4$
X = Cl, R', R'' = -$(CH_2)_5$- : Rh_2(TCPTCC)$_4$



3

4

5, R = aliphatic

P-425

Asymmetric Conjugate Addition of Alkylzirconocenes to Cyclopentene-3,5-dione Monoacetals.

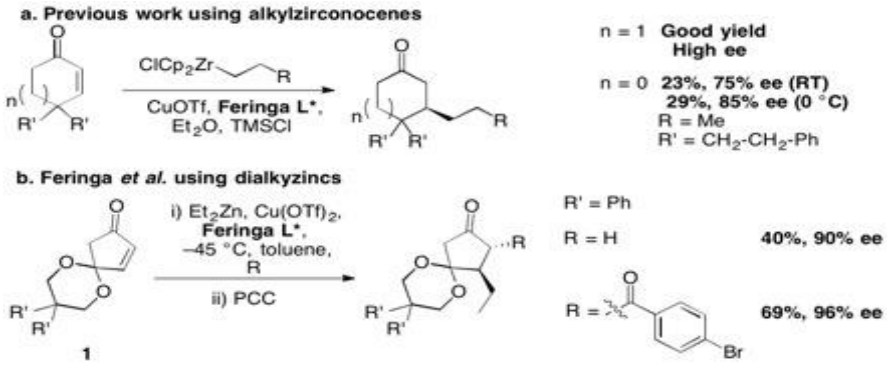
Emeline Rideau[1], Florian Masing[1], Stephen Fletcher[1]
[1]*University of Oxford, Oxford, UK*

Poster Session 2

The asymmetric conjugate addition of organometallics to cyclopentenones is highly desirable.[1] Many methodologies have been developed in recent years but fail to address the challenges of cyclopentenones.[2] Our group demonstrated that the conjugate addition of alkylzirconocenes to cyclohexenone derivatives is advantageous (Figure 1a).[3] However, when applying the methodology conditions to cyclopentenones, the yield was poor (23%) and the ee dropped (to 75%). Feringa et al. reported[4] the derivatisation of cyclopentene-3,5-dione monoacetal 1 with diakylzinc reagents (Figure 1b) in moderate yield (40%) and high ee (90%). The yield was significantly improved (to 69%) when trapping an aldehyde.

We decided to examine the hydrozirconation/asymmetric conjugate addition of alkenes to cyclopentene-3,5-dione monoacetal 1 (Figure 2). After extensive screening, we have demonstrated that functionalized, enantioenriched cyclopentanone derivatives can be successfully prepared by asymmetric conjugate addition with alkylzirconocene species. Further studies are currently undergoing to apply this methodology to the synthesis of prostaglandins.

References:
(1) (a) Brown, M. K.; Hoveyda, A. H. J. Am. Chem. Soc. 2008, 130, 12904 (b) Jansen, D. J.; Shenvi, R. A. J. Am. Chem. Soc. 2013, 135, 1209. (2) (a) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. Chem. Rev. 2008, 108, 2824 (b) Alexakis, A.; Backvall, J. E.; Krause, N.; Pamies, O.; Dieguez, M. Chem. Rev. 2008, 108, 2796. (3) Maksymowicz, R. M.; Roth, P. M. C.; Fletcher, S. P. Nat. Chem. 2012, 4, 649. (4) (a) Arnold, L. A.; Naasz, R.; Minnaard, A. J.; Feringa, B. L. J. Am. Chem. Soc. 2001, 123, 5841 (b) Arnold, L. A.; Naasz, R.; Minnaard, A. J.; Feringa, B. L. J. Org. Chem. 2002, 67, 7244.

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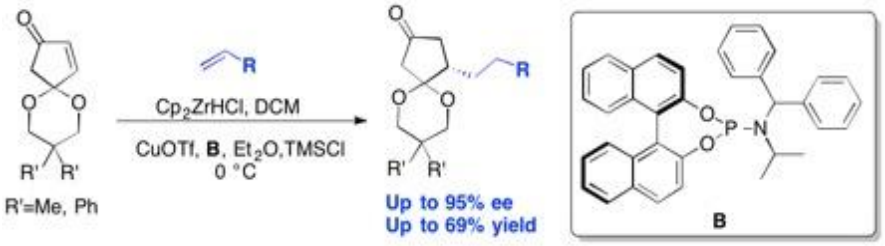

R
Cp2ZrHCl, DCM
CuOTf, B, Et2O,TMSCl
0 °C
R'=Me, Ph
Up to 95% ee
Up to 69% yield
B

P-426

Programmed Synthesis of Multiply Arylated Arenes

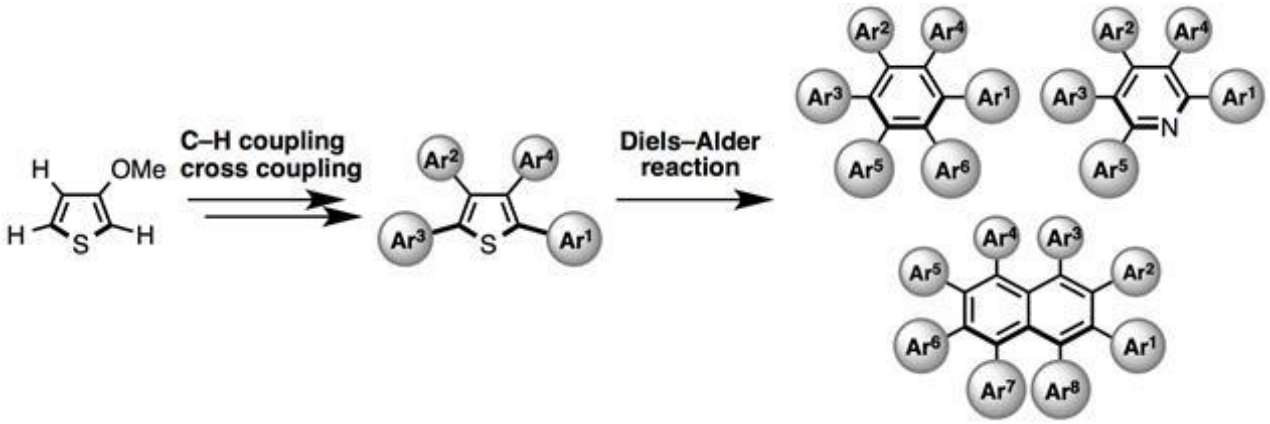
Shin Suzuki[1], Yasutomo Segawa[1,2], Junichiro Yamaguchi[1], Kenichiro Itami[1,2,3]

[1]Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Furo-Cho, Japan, [2]JST-ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Nagoya, Furo-Cho, Japan, [3]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Nagoya, Furo-Cho, Japan

Poster Session 2

Multiply arylated arenes are privileged structures with many interesting functions and fascinating optoelectronic or biological properties. The development of a general synthetic method towards these molecules with controlled regioselectivity, namely “programmed synthesis,” has been in high demand because it is crucial to understand structure-property relationships and to discover hitherto unknown functional molecules. We and others have developed general methods to access multiply arylated olefins and heteroaromatics by installing aryl substituents at the desired positions of core structures in a predictable and programmed manner. However, programmed syntheses of multiply arylated arenes such as benzenes, pyridines, and naphthalenes, which have highly symmetrical structures, have not been accomplished.

Herein, we achieved the programmed synthesis of multiply arylated arenes using sequential C–H couplings, cross couplings, and Diels–Alder reaction of thiophenes. This synthetic method can provide hexaarylbenzenes, pentaarylpyridines, and multiply arylated naphthalenes bearing different aryl groups.



P-427

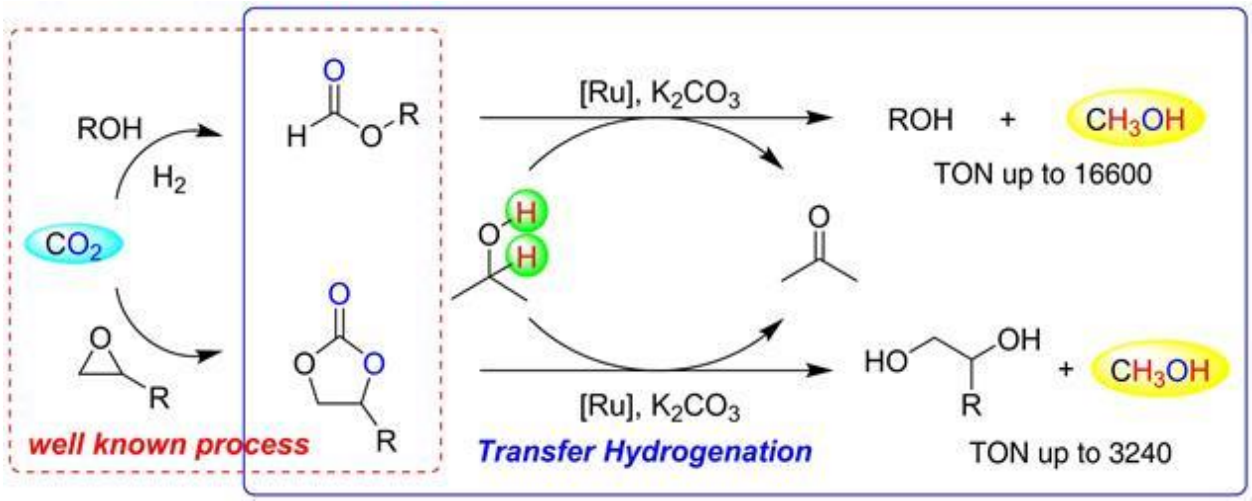
Transfer Hydrogenation of Organic Formates and Cyclic Carbonates: An Alternative Route to Methanol from Carbon Dioxide

Mr Seung Hyo KIM[1], Prof. Dr. Soon Hyeok Hong[1,2]

[1]Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul, South Korea, [2]Center for Nanoparticle ResearchInstitute for Basic Science (IBS), Seoul, South Korea

Poster Session 2

Methanol is used as an important fuel and C1 building block for C-C bond construction to prepare value added chemicals such as acetic acid and olefins in industrial scale. Production of methanol from renewable resource is a big challenge in both industry and academia. Carbon capture and use (CCU) strategy was applied to prepare methanol from carbon dioxide derivatives. The direct conversion to methanol from CO_2 require a harsh reaction condition and showed low efficiency. The reduction of cyclic carbonates obtained from CO_2 and epoxide is an alternative promising route to convert CO_2 to methanol. Therefore, the syntheses of carbonates using CO_2 gas from combustion sources are an attractive strategy for carbon recycling. We devised our strategy as follows: 1) selective capturing of CO_2 from fossil fuel combustion using an alkanolamine solution, 2) generation of cyclic carbonates from epoxide and CO_2 released from the captured material, and 3) transfer hydrogenation (TH) of cyclic carbonates to generate methanol and diol. Although significant progress has been achieved in the TH of aldehydes, ketones, imines, and nitriles, TH of carbonates has not yet been reported due to resonance stabilization of alkoxy group. Our group disclosed the TH of cyclic carbonates for the first time using a commercially available ruthenium catalyst. Non-toxic and inexpensive 2-propanol was used as both solvent and hydrogen source instead of using flammable H_2 gas under high pressure. This operationally simple strategy is an attractive way to produce methanol using CO_2 from exhaust gas indirectly.



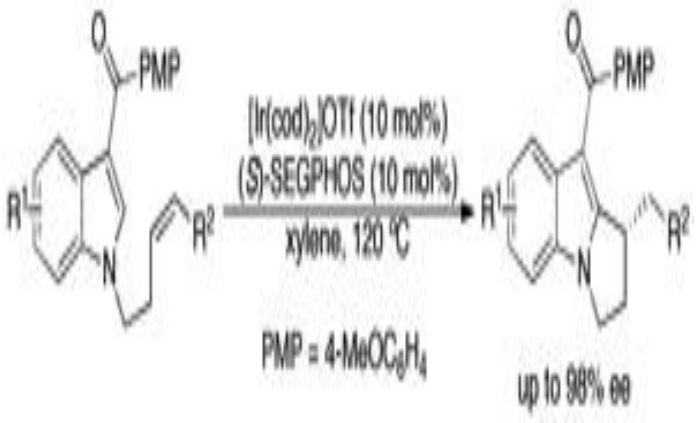
P-429

Enantioselective Intramolecular C-H Alkylation at the C-2 Position of Indole by a Chiral Cationic Iridium(I) Catalyst

Hideaki Takano[1], Naoto Ryu[1], Takanori Shibata[1,2]
[1]*Waseda University, Shinjuku, Japan,* [2]*JST ACT-C, Kawaguchi, Japan*

Poster Session 2

We have reported intermolecular C2-potision selective C-H alkylation of indole with alkenes, where the choice of directing group and ligand could control the liner/branch selectivity. However, the enentioselective induction in the branched product was moderate (42% ee). We next examined intramolecular enantioselective C-H alkylation of N-alkenylindole at the C2-position in the presence of a cationic iridium catalyst with a chiral diphosphine ligand. In this reaction, aroyl groups at the C3-position operated as directing groups, and chiral 1-substituted-2,3-dihydro-1H-prrolo[1,2-a]indoles were obtained in high yield with excellent ee.



P-431

Catalytic Oxidative Halogenation by Vanadium(V) Catalyst under Molecular Oxygen

Dr Toshiyuki Moriuchi[1], Dr Kotaro Kikushima[1], Yasuhiro Fukui[1], Tomomi Kajikawa[1], Satoshi Kato[1], Dr Toshikazu Hirao[1,2]

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Poster Session 2

Halogenation reaction is one of the most fundamental reactions in organic synthesis, providing important precursors and substrates in various coupling reactions. We herein report the vanadium(V)-catalyzed oxidative halogenation reaction of arenes, alkenes, alkynes, and ketones under molecular oxygen, providing an environmentally-favorable halogenation system.[1]

The catalytic oxidative bromination reaction was achieved by using 5 mol% of NH_4VO_3, 300 mol% of Bu_4NBr, and trifluoroacetic acid under molecular oxygen to give the bromination product. The utilization of 50 mol% of $AlBr_3$ instead of trifluoroacetic acid under molecular oxygen was found to afford the bromination product selectively in a high yield. $AlBr_3$ serves as both a bromide source and a Lewis acid to induce the smooth bromination. The catalytic oxidative chlorination was also demonstrated by using a vanadium catalyst in the presence of Bu_4NI and $AlCl_3$ under molecular oxygen.

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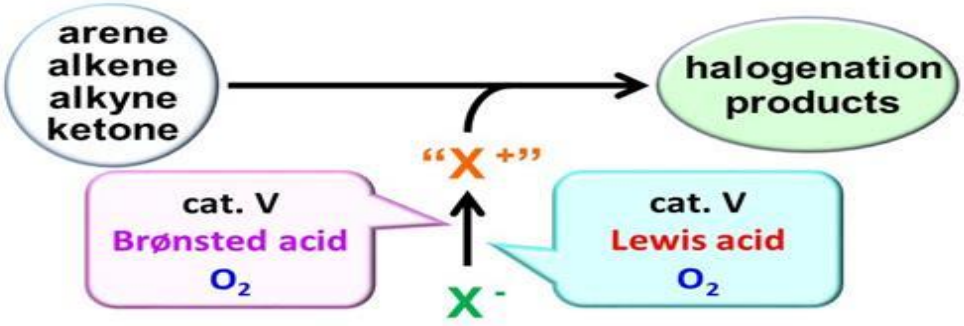
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Lewis acid
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P-432

Construction of Quaternary Stereogenic Carbon Centers through Copper-Catalyzed Enantioselective Allylic Coupling with Alkylboranes

Kentaro Hojoh[1], Yoshinori Shido[2], Dr. Hirohisa Ohmiya[3], Dr. Masaya Sawamura[4]
[1]Hokkaido University, Sapporo 060-0810, Japan, [2]Hokkaido University, Sapporo 060-0810, Japan, [3]Hokkaido University, Sapporo 060-0810, Japan, [4]Hokkaido University, Sapporo 060-0810, Japan

Poster Session 2

Catalytic enantioselective construction of all-carbon quaternary stereogenic centers in acyclic systems is one of the biggest challenges in organic synthesis. This paper reports the first demonstration of the construction of a quaternary stereogenic carbon center through transition metal-catalyzed enantioselective allylic substitution with non-allylic alkylboron compounds. The S_n2'-type enantioselective allylic cross-coupling between alkyl-9-BBN reagents and γ,γ-disubstituted primary allyl chlorides under catalysis of a Cu(I)-DTBM-MeO-BIPHEP system generates all-carbon quaternary stereogenic centers branched with three sp^3-alkyl groups and a vinyl group.[1] This protocol allowed the use of terminal alkenes as nucleophile precursors, thus representing a formal reductive allylic cross-coupling of terminal alkenes. A reaction pathway involving addition-elimination of a neutral alkylcopper(I) species with the allyl chloride substrate is proposed.

Reference
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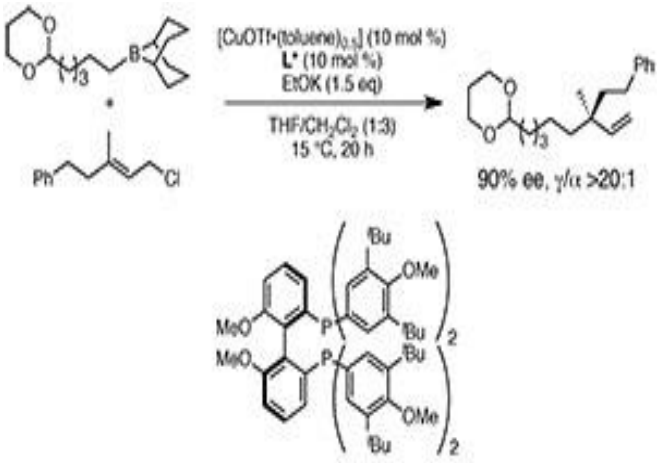


P-433

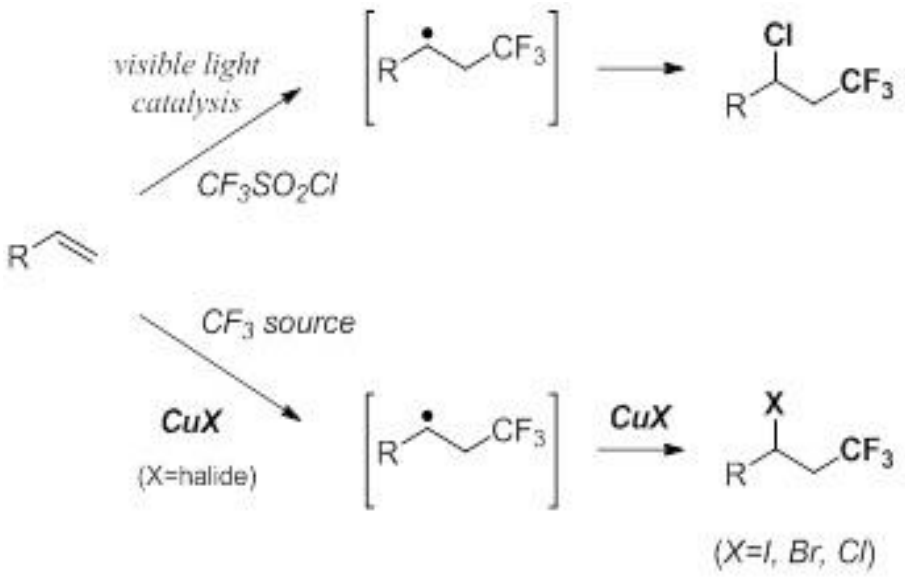
Vicinal Halotrifluoromethylation of Unactivated Alkenes

Dr. Soo Bong Han[1], Dr. Young-Sik Jung[1], Mr. Se Hwan Oh[1], Dr. Yashwardhan Malpani[1], Mr. Neul Ha[1], Ms Won An[1]

[1]*Korea Research Institute of Chemical Technology, Daejeon, South Korea*

Poster Session 2

We developed a vicinal halotrifluoromethylation of unactivated alkenes. In the presence of Ru(Phen)3Cl2, CF3SO2Cl was used as a source for the CF3 radical and chloride ion under visible light irradiation. In addition, the same intermediate can be generated with Umemoto's reagent with various copper salts that can be a source for other halogens. Various terminal and internal alkenes were transformed to their vicinal halotrifluoromethylated derivatives. Biologically active compounds were applied under the condition to obtain desired products, suggesting that the method could be feasible for late-stage modification in drug discovery



P-434

Synthesis of Cyclopentenones by an Asymmetric Nickel-Catalyzed [3+2] Reductive Cycloaddition of Enoates with Alkynes

Mr. Joachim Sven Ernst Ahlin[1], Prof. Dr. Nicolai Cramer[1]
[1]*Laboratory of Asymmetric Catalysis and Synthesis, EPF Lausanne EPFL SB ISIC LCSA, Lausanne, Switzerland*

Poster Session 2

Amongst the members of the family of five membered carbocyclic rings, cyclopentenones are of utmost importance in chemistry. They are found in numerous natural and synthetic products and are also versatile building blocks in several routes towards the synthesis of complex molecules.[1] Thus, the generation of cyclopentenones in a straightforward manner from readily available substrates remains an important target.

Several transition metal-catalyzed reactions for accessing cyclopentenones have been reported over the past years,[1] including an intermolecular nickel-catalyzed [3+2]-cycloaddition of enoates with alkynes.[2] We report an asymmetric nickel-catalyzed [3+2] reductive cycloaddition of enoates with alkynes using a chiral bulky C_1-symmetric N-heterocyclic carbene ligand to provide an efficient highly yielding and enantioselective route to chiral cyclopentenones from simple, stable, and readily available acyclic π-systems.[3]

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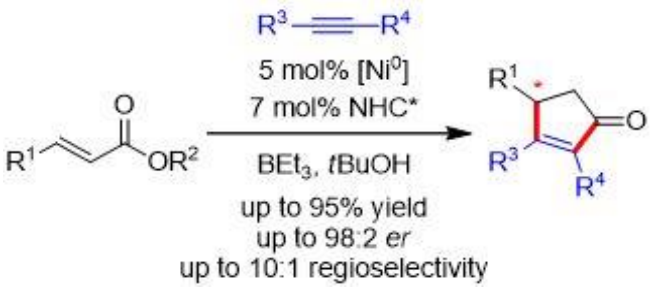
3. J. S. E. Ahlin, P. A. Donets, N. Cramer, Angew. Chem. Int. Ed. 2014, 53, 13229–13233.



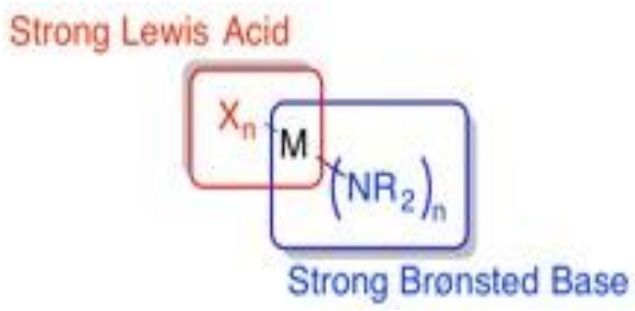
P-435

Lewis Acid/Metal Amide Hybrids as Efficient Catalysts for Carbon-Carbon Bond Forming Reactions

Mr. Yuki Saito[1], Yakuhiro Yamashita[1], Shu Kobayashi[1]
[1]*Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan*

Poster Session 2

Lewis acids have been playing key roles in synthetic organic chemistry in both stoichiometric and catalytic use. On the other hand, metal amides have also been used as strong Brønsted bases. Although these two species are one of the most frequently used metal species, they are believed to be incompatible when combined, as they are intrinsically acid and base. When the structure of the Lewis acid is focused on, the electron-withdrawing counter anions such as halides and triflate decreases the energy of LUMO of the metal complex, which makes the complex more Lewis acidic. On the other hand, in metal amides chemistry, anionic nitrogen atom is the key to achieve strong Brønsted basicity.
Combining these two structural features, we designed the Lewis acid/metal amide hybrids as metal complexes bearing both electron-withdrawing couteranion and amide moiety (Fig. 1). These hybrid catalysts are expected to possess both strong Lewis acidity and Brønsted basicity. Furthermore the balance of acidity and basicity can be easily tuned by simply changing the counter anions of the metal. First, $In(HMDS)_2Cl$ was synthesized as a representative Lewis acid/metal amide hybrid, and it demonstrated the excellent and unique catalyst activity in the alkynylation of nitrones. It should be mentioned that neither conventional metal amide ($In(HMDS)_3$) nor simple Lewis acid ($In(OTf)_3$) could catalyze the reaction at all. These results strongly indicate the potential of hybrid catalysts as novel and efficient acid/base cooperative catalysts. It was also found that the concept of the Lewis acid/metal amide hybrid could be expanded to other complexes. The detail of this catalyst system will be discussed in the presentation.



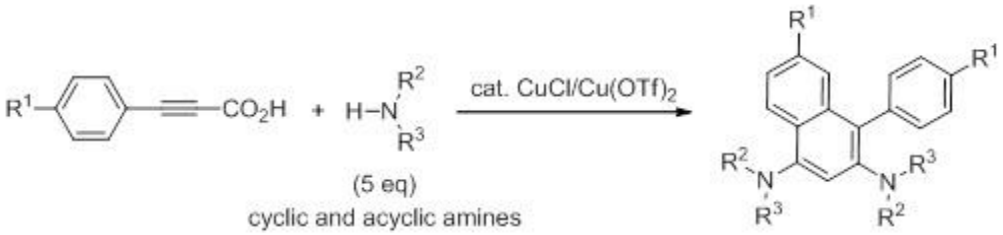
P-436

Synthesis of Amino-substituted Naphthalene Derivatives from Propiolic Acids and Amines

Mr. Jinseop Choi[1], Prof. Sunwoo Lee[1]
[1]*Chonnam National University, Gwangju, South Korea*

Poster Session 2

One-pot sequential synthetic method is one of the most powerful tools in the organic synthesis fields because it saved reaction time and process steps. A number of decarboxylative coupling reactions with propiolic acid derivatives have been developed since we first reported the palladium catalyzed decarboxylative coupling of aryl halides and propiolic acid. In the continuous interesting to develop the decarboxylative coupling reaction, we discovered that amino-substituted naphthalene was formed when phenyl propiolic acid was reacted with amine in the presence of copper catalyst. Here, we report the copper-catalyzed one pot synthesis of amino-substituted naphthalene derivatives from alkynyl carboxylic acid and amine.



P-437

Nickel-catalyzed Direct Amination of Allylic Alcohols in the presence of Ammonium Salts

Dr Yusuke Kita[1], Mr Daisuke Nakauchi[1], Mr Hironobu Sakaguchi[2], Dr Yasuhito Nakahara[1], Dr Yoichi Hoshimoto[2], Dr Sensuke Ogoshi[2], Dr Jean-Francois Carpentier[3], Dr Kazushi Mashima[1]

[1]Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Japan, [2]Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Japan, [3]Organometallics; Materials and Catalysis Dept. Universite de Rennes 1, Rennes, France

Poster Session 2

Allyl amines are ubiquitous compounds of biologically active compounds and are versatile substrates used for different types of reactions, including asymmetric isomerization and ring-closing metathesis. Thus, as a reliable synthetic methodology to obtain a wide variety of allyl amines and their derivatives, metal-catalyzed reaction of allylic substrates with amines have been widely utilized. These standard synthetic protocols usually require activated allylic compounds, such as allylic halides, which are usually derived from the corresponding allylic alcohols; however, the use of the activated substrates lead to the formation of more than stoichiometric amounts of waste both in the pre-activation and amination steps. Thus, direct amination of allylic alcohols, which forms water as the sole coproduct, is highly desirable.[1]
During the course of our continuing interest in functionalization of allylic alcohols,[2] we found the remarkable additive effects of nBu_4NOAc to efficiently improve performance for the direct amination of allylic alcohols using a Ni catalyst supported by diphosphine ligands: a low catalyst loading, wide substrate scope, and high mono-allylation selectivity were achieved. Such remarkable additive effects of nBu_4NOAc were elucidated by isolating and characterizing some intermediates, including a η^2-π-allyl alcohol complex and a charge neutral pentacoordinated η^3-π-allyl acetate complex.

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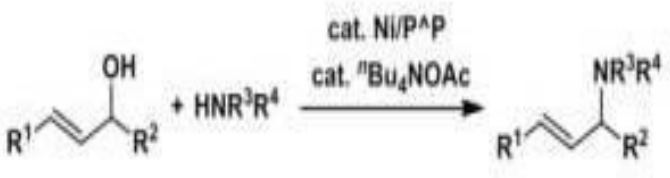

P-438

Rh(III)-Catalyzed One-Carbon Oxidative Cycloaddition of Guanidines with Alkynes: A Novel Entry to C4-Disubstituted 1,4-Dihydroquinazolin-2-amines

Ms Ana Cajaraville[1], Dr. Jaime Suárez[1], Dr. Susana López[1], Dr. Jesús A. Varela[1], Dr. Carlos Saá[1]
[1]*Departamento de Química Orgánica, Centro Singular de Investigación en Química Biológica y Materiales Moleculares (CIQUS), Universidad de Santiago de Compostela, Santiago De Compostela, Spain*

Poster Session 2

Guanidine units are found in a wide range of products with remarkable physiological and biological activities. Guanidines have also been broadly investigated as coordination groups with different metals in cyclometallated complexes.[1] In fact, guanidines have been studied as directing groups in C-H bond functionalization by Pd-catalyzed ortho C-H bond arylation and olefination of aryl guanidines.[2] However, to the best of our knowledge, metal-catalyzed oxidative cycloadditions have not been explored with this type of substrates.

Herein we report a novel Rh(III)-catalyzed one-carbon oxidative cycloaddition[3] of aryl guanidines 1 with alkynes 2 to give the medicinally interesting C-4 disubstituted 1,4-dihydroquinazolin-2-amines 3. The proposed mechanism would involve the formation of an eight-membered rhodacycle (characterized by X-Ray analysis) in which the imino group of the guanidine is coordinated to the Rh center.(Figure)

Acknowledgements: This work was supported by MICINN [projects CTQ2011-28258 and Xunta de Galicia and European Regional Development Fund (projects GRC2014/032 and EM 2012/051). A.C. and J. S. thank Spanish MINECO and Xunta de Galicia for a predoctoral FPI fellowship and postdoctoral contract, respectively.

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[Cp*RhCl2]2 (2.5 mol%)
AgOAc (2.1 equiv.)
iPrOH, Air, 60 °C
1
2
3
Hypoglycaemic Activity
α2-Adrenoceptor Antagonist

P-439

Base-Free Hiyama Coupling Reaction via Group 10 Metal Fluoride Key Intermediates Gerenated by C-F Bond Activation

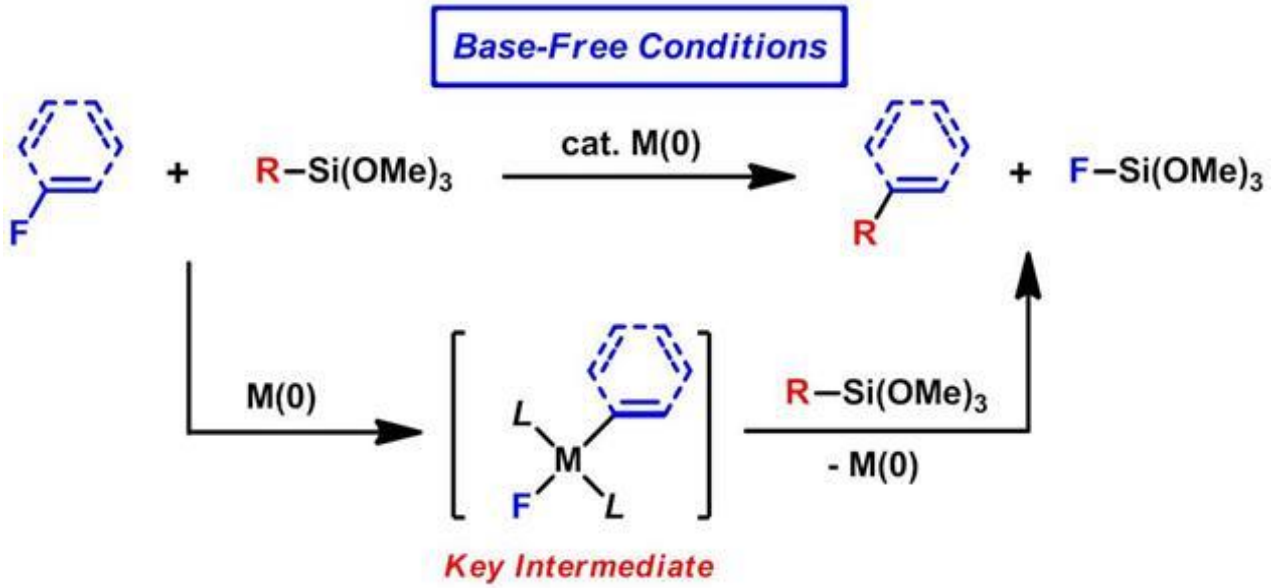
Hironobu Sakaguchi[1], Hiroki Saijo[1], Masato Ohashi[1], Sensuke Ogoshi[1]
[1]*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Japan*

Poster Session 2

Tetrafluoroethylene (TFE) is industrially an economical bulk organofluorine feedstock for the production of polytetrafluoroetylene and copolymers with other alkenes. We have already reported Pd(0)-catalyzed coupling reaction of TFE with aryl zinc compounds (Negishi Coupling) or organoborane compounds (Suzuki-Miyaura Coupling) to yield trifluorostyrene derivatives. In this study, we demonstrated a novel base-free Hiyama type cross-coupling reaction of TFE with organosilanes via C-F bond activation.

In the presence of 2.5 mol% $Pd_2(dba)_3(C_6H_6)$ and 5 mol% $PCyp_3$, the reaction of TFE with trimethoxyphenylsilane gave trifluorostyrene in 76% yield. This coupling reaction proceeded smoothly without the use of any base which is usually essential to enhance the reactivity of organosilanes. On the basis of mechanistic studies, we estimated that a metal fluoride complex generated in situ by the oxidative addition of a C-F bond played an important role in this base-free reaction.

Futhermore, we expanded this base-free strategy to the coupling reaction of fluoroarenes. In the presence of 5 mol% $[Ni_2(iPr_2Im)_4(COD)]$, the reaction of octafluorotoluene with trimethoxyphenylsilane proceeded in the absence of any base, to afford 4-phenyl-heptafluorotoluene in excellent yield. On the other hand, the Pd(0)/$PCyp_3$ catalyst did not work at all in the reaction.



P-440

Nickel-Catalyzed Selective Cross-Trimerization Reaction of Tetrafluoroethylene, Ethylene and Aldehydes

Hiroshi Shirataki[1], Nickel-Catalyzed Selective Cross-Trimerization Reaction of Tetrafluoroethylene, Ethylene and Aldehydes Kotaro Kikushima[1], Nickel-Catalyzed Selective Cross-Trimerization Reaction of Tetrafluoroethylene, Ethylene and Aldehydes Masato Ohashi[1], Nickel-Catalyzed Selective Cross-Trimerization Reaction of Tetrafluoroethylene, Ethylene and Aldehydes Sensuke Ogoshi[1,2]

[1]*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Japan,* [2]*JST, ACT-C, Suita, Japan*

Poster Session 2

Organofluorine compounds have attracted much attention due to their outstanding application in pharmaceutical and materials science. Tetrafluoroethylene (TFE) is an ideal starting material in fluorine chemistry because of the industrial usage. It has been known that oxidative cyclization of TFE and unsaturated compounds with transition metal proceeded to gain metalacycle. [1] To our best knowledge, only one catalytic reaction involving oxidative cyclization of TFE as a C-C bond formation step has been reported. [2]

We found that a Ni(0)/N-heterocyclic carbene (NHC) system catalyzed the cross-trimerization of TFE, ethylene and aldehydes effectively. In the presence of catalytic amount of Ni(cod)2 and IPr, the reaction of TFE, ethylene and benzaldehyde in toluene at 150 °C for 30 min afforded 4,4,5,5-tetrafluoro-1-phenylpentan-1-one in 98% yield (Scheme 1). Stoichiometric reaction revealed that the present reaction might proceed via a five-membered nickelacycle of TFE and ethylene.

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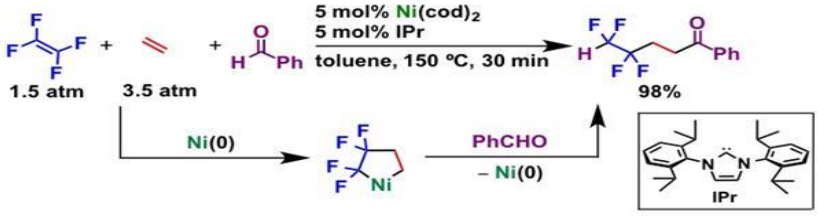


P-441

Zinc and magnesium alkylperoxides supported by N,N-bifunctional ligands: New and efficient catalysts for epoxidation of enoens

Tomasz Pietrzak[1], Karolina Zelga[1], Marcin Kubisiak[1], Zbigniew Ochal[1], Iwona Justyniak[2], Peter Roesky[3], Janusz Lewiński[1,2]

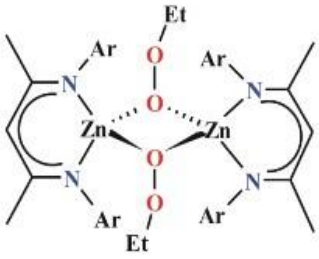
[1]Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland, [2]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland, [3]Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

Poster Session 2

Stereoselective epoxidation of α,β-unsaturated ketones is continually a challenging task for modern organic synthesis and the ongoing research on the system allowing efficient synthesis of electron deficient epoxides can be observed. A number of catalytic systems for effective epoxidation of enones have been discovered over the last two decades, but none of them has gained a widespread attention amongst synthetic chemists.

Our studies provide compelling evidence that the alkylperoxozinc compounds are highly active in catalytic epoxidation of enones. In the mother research group various supporting ligands have been developed allowing efficient and reproducible synthesis of zinc alkylperoxides. Preliminary studies show that N,N-bifunctional compounds are very potent supporting ligands. Oxygenation of RZn(N,N) stabilized by a β-diketiminate ligand leads to a dimeric zinc ethylperoxide, the first alkylperoxide to be structurally authenticated (Scheme 1). Following this result we continued studies concerning alkylzinc peroxides, their structure, properties and potential applications in epoxidation of enoens and also expanded the research to test the activity of magnesium alkylperoxides in the studied reaction.

In the current work will be presented synthesis and structure of new alkyperoxozinc and alkylperoxomagnesium complexes stabilized by N,N-monoanionic ligands, such as a α-diimines, β-diketiminate and aminotroponiminates (Scheme 2). Their application as catalysts in epoxidation of enones and a proposed mechanism of the catalytic reactions will be also discussed.



Ar = 2,6-diisopropylphenyl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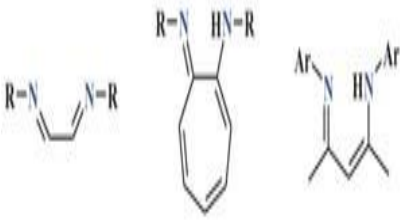

R-N
N-R
R-N
HN-R
Ar
N
HN
Ar

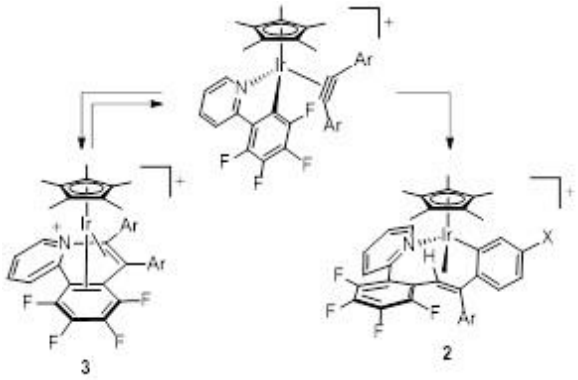
P-442

Competition between Vinylidene Rearrangement and 1,2-Insertion of Internal Alkynes at an Ir(III) Complex

Dr. Shintaro Kodama[1], Dr. Yousuke Ikeda[1], Dr. Noriko Tsuchida[2], Dr. Youichi Ishii[1]
[1]Chuo University, Kasuga, Bunkyo-Ku, Tokyo, Japan, [2]Saitama Medical University, Morohongo, Moroyama-machi, Iruma-gun, Saitama, Japan

Poster Session 2

Although the vinylidene rearrangement of terminal alkynes has been studied extensively from viewpoints of both reaction mechanism and application, that of internal alkynes is still recognized as an uncommon process. This may be ascribed to the fact that the vinylidene rearrangement of internal alkynes is slower than that of terminal alkynes, and therefore it rarely competes favorably with other metal mediated reactions, e.g. 1,2-insertion of the alkynes into the metal−carbon bond of an alkyl- or aryl-metal complex. To broaden the synthetic applicability of vinylidene rearrangement, it is important to develop a method to control the preference between these processes. As a model system, we have adopted [Cp*IrCl(ppy-F_4)] (1) (ppy-F_4 = 2,3,4,5-tetrafluoro-6-pyridylphenyl), where the C_6F_4 group is considered to bind strongly to the metal center and hence to slow down the 1,2-insertion. As expected, the iridacycle complexes 2 derived from the vinylidene rearrangement of diarylacetylenes were obtained as the thermodynamic product in preference to complex 3 derived from the 1,2-insertion of the alkyne.
The reaction of 1 with PhC≡CPh in the presence of NaBAr[sup]F[/sup]$_4$ at 50 ˚C affords (o-vinyl)aryl complex 2a in 87% isolated yield by way of the vinylidene rearrangement of the alkyne followed by the 1,1-insertion of the vinylidene ligand into the Ir−Ar bond and the 1,4-Ir migration to the ortho position of a Ph group. Similarly, the reaction with para-substituted diphenylacetylene derivatives p-$XC_6H_4C{\equiv}CC_6H_4X$-p (X = Me, Cl) gave the corresponding cyclometallated complexes (2b, 2c) in good yield. Interestingly, detailed analysis of these reactions revealed that 2 and Ir(I) pyridoisoquinolinium complex 3, the latter of which is a normal 1,2-insertion–reductive elimination product, are competitively generated in the early stage of the reaction, while 3 is gradually isomerized to 2 at 50 ˚C.



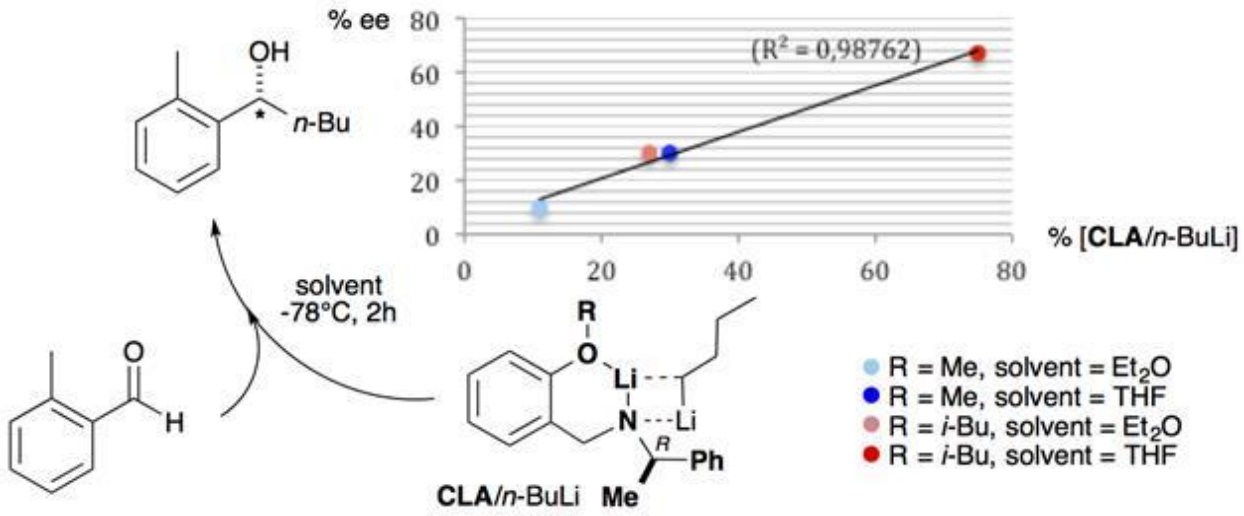
P-443

A structure / reactivity relationship study involving polar organo(bi)metallic reactants

Gabriella Barozzino-Consiglio[1], Anne Harrison-Marchand[1], Jacques Maddaluno[1], Hassan Oulyadi[1]
[1]*UMR CNRS 6014 - University of Rouen, MONT SAINT AIGNAN Cédex, France*

Poster Session 2

To date, polar organo(bi)metallic reactants are the object of particular interest because of the many solutions they can provide with respect to problems encountered when using their parent-reagents alone. Now, when it comes to approach the related reactions on a mechanism understanding point of view, either to improved the yield or the stereoselectivity, much less is known due to the complexity of the reaction media. Being able to refine the structure of reaction intermediates, tackling the reactions through a structure / reactivity relationship thanks to a complementary synthesis / analysis work, is essential to develop an innovative methodology.
In this communication is reported an NMR study made on a 1:1 mixture of a chiral lithium amide (CLA) and n-BuLi. Depending on the solvent employed (Et_2O or THF), a mixed aggregate is formed in propositions that are directly related to the ee's measured during the enantioselective alkylation of o-tolualdehyde by these same species.



P-444

Copper-Catalyzed Intermolecular C(sp^3)-H Bond Functionalization Towards the Synthesis of Tertiary Carbamates

Dr. Prasanna Kumara Chikkade[1], Prof. Dr. Yoichiro Kuninobu[1,2], Prof. Dr. Motomu Kanai[1,2]

[1]*Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo, Japan,* [2]*ERATO, Japan Science and Technology Agency (JST), Kanai Life Science Catalysis Project, Tokyo, Japan*

Poster Session 2

Carbamates are ubiquitous in nature as key functional and structural motifs in many important compounds, such as agrochemicals, pharmaceuticals, and functional materials. The development of catalytic transformations of hydrocarbon feedstocks is a challenging theme. Many amidation and amination of hydrocarbons have been reported in nitrene chemistry, but such transformations produce stoichiometric amounts of wastes and have limited substrate scope. Despite the remarkable progress of C-H amidation and amination reactions, the direct formation of tertiary carbamates from inert hydrocarbons is underdeveloped. Here we developed a copper-catalyzed C(sp^3)-H carbamation of unactivated alkanes with isocyanates. This efficient and greener approach allowed us to obtain tertiary carbamates directly from hydrocarbon feedstocks in good to excellent yields.[1]

Reference:

[1]. P. K. Chikkade, Y. Kuninobu, M. Kanai, Chem. Sci. 2015, DOI: 10.1039/C5SC00238A.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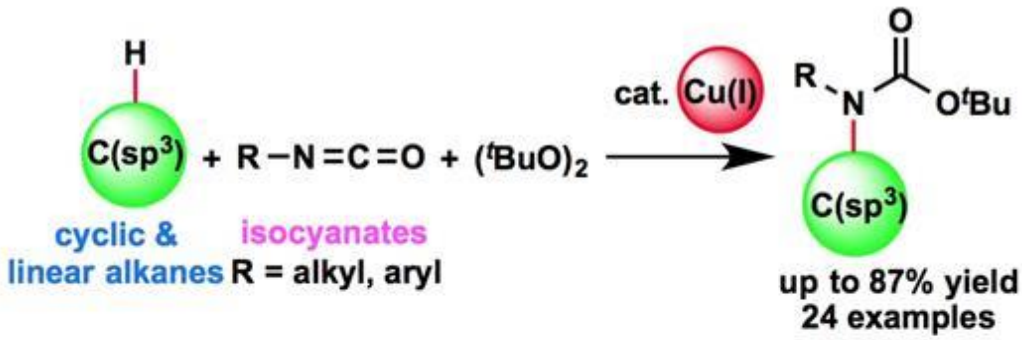
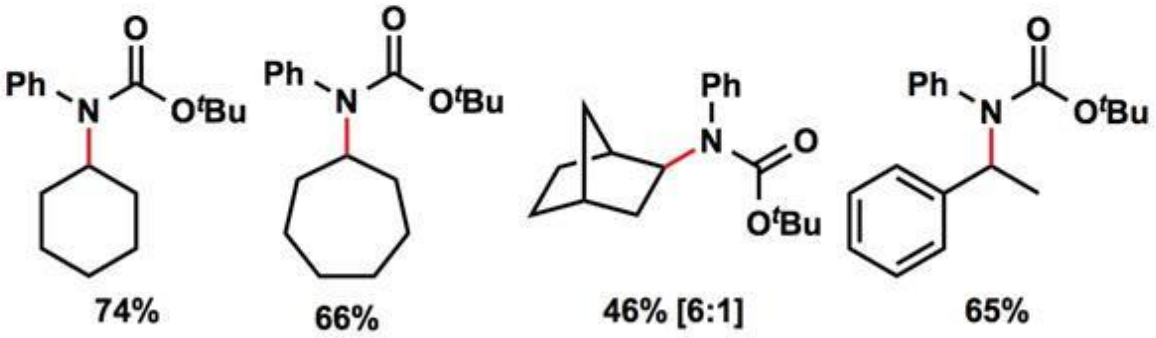

H
C(sp3)
+ R–N=C=O + (tBuO)2
cat. Cu(I)
R
N
O
OtBu
C(sp3)
cyclic & linear alkanes
isocyanates
R = alkyl, aryl
up to 87% yield
24 examples


Ph
N
O
OtBu
74%
66%
46% [6:1]
65%

P-488

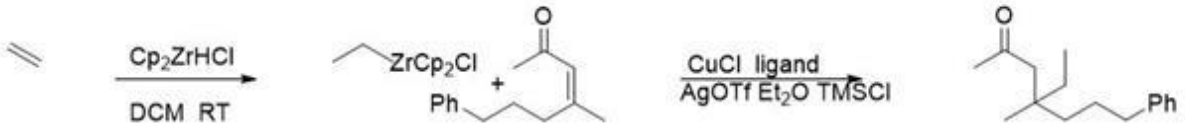
Formation of Non-cyclic Quaternary Centres by Copper Catalyzed Asymmetric Conjugate Addition of Alkylzirconium Reagents

Mr Zhenbo Gao[1], Prof Stephen Fletcher[1]
[1]*Oxford University, Oxford, UK*

Poster Session 2

Our group recently reported that alkylzirconium species undergo asymmetric conjugate addition reactions to a variety of cyclic Michael acceptors, including enones, to give tertiary and quaternary carbon centre products.1 The used of acyclic enones in asymmetric conjugate addition reactions are more difficult, presumably because of ready to cis/trans conformational interconversion. We recently reported addition to acyclic disubstituted enones to provide tertiary carbon centres,2 and here we will discuss our recent effort to use alkyl zirconium species in ACA to enantioselectively build non-cyclic quaternary centres.

Reference:
1. Maksymowicz, R. M., Roth, P. M. C. & Fletcher, S. P. Catalytic asymmetric carbon–carbon bond formation using alkenes as alkylmetal equivalents. Nat. Chem. 4, 649–654 (2012).
2. Roth, P. M. C. & Fletcher, S. P. Enantioselective Copper(I)-Phosphoramidite Catalyzed Addition of Alkylzirconium Species to Acyclic Enones. Org. Lett. 150129154356007 (2015). doi:10.1021/acs.orglett.5b00021



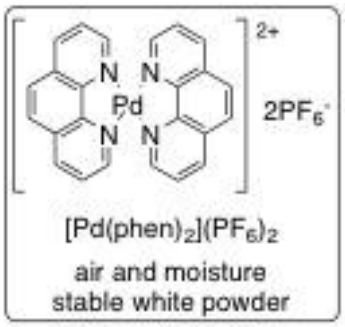
P-445

C-H Bond Functionalization of Thiocarbonylated Heteroarenes Catalyzed by Pd-Phenanthroline Complexes

Takayuki Yamauchi[1], Fumitoshi Shibahara[1], Toshiaki Murai[1]
[1]*Gifu Univ., Gifu city, Japan*

Poster Session 2

Previously, carbonylated π-conjugated systems have been frequently found in main structures of organic functional materials. It has been revealed that reduction of HOMO-LUMO energy gap and stronger π-π interaction are realized by substitution of carbonyl oxygen to sulfur, by theoretical and experimental studies so far. In addition, thiocarbonylated π-conjugated systems often lead to appropriate HOMO and LUMO energy levels for semiconducting materials. On the other hand, transition metal-catalyzed cross-coupling reactions have attracted significant attention in synthesis of π-conjugated systems since various derivatives are easily obtained by changing readily available substrates for coupling. However, it is troublesome to apply such transition metal-catalyzed reaction to thiocarbonyl compounds due to reactivities of thiocarbonyl groups. One of the reasons is that thiocarbonyl groups often deactivate catalyst, namely those groups might directly react with transition metals and/or phosphine ligands. Meanwhile, we previously reported that palladium complexes bearing nitrogen-based ligands, in particular [Pd(phen)2](PF6)2 (phen: 1,10-phenanthroline), show excellent catalytic activities for direct C-H arylation of heteroarenes. In addition, we have found that reactivity of those complexes are different from that of Pd/phophine ligand systems. We have developed several reactions that are hardly achieved by using Pd/phophine ligand systems. Then, we have focused on structure of Pd/phenanthroline complexes which do not have phosphine ligands, and has stable chelate coordination. We envisioned that the catalytic systems would be applied to reaction with thiocarbonyl substrates since those catalysts are not easily deactivated by thiocarbonyl group. In this presentation, direct C-H bond arylation of thiocarbonylated arenes catalyzed by Pd-phenanthroline complexes and mechanistic studies of the reaction will be shown.



P-446

Application of Bifunctional Iridium Complexes to Catalytic Hydrogen Production from Formic Acid

Application of Bifunctional Iridium Complexes to Catalytic Hydrogen Production From Formic Acid Asuka Matsunami[1], Application of Bifunctional Iridium Complexes to Catalytic Hydrogen Production From Formic Acid Yoshihito Kayaki[1], Application of Bifunctional Iridium Complexes to Catalytic Hydrogen Production From Formic Acid Takao Ikariya[1]

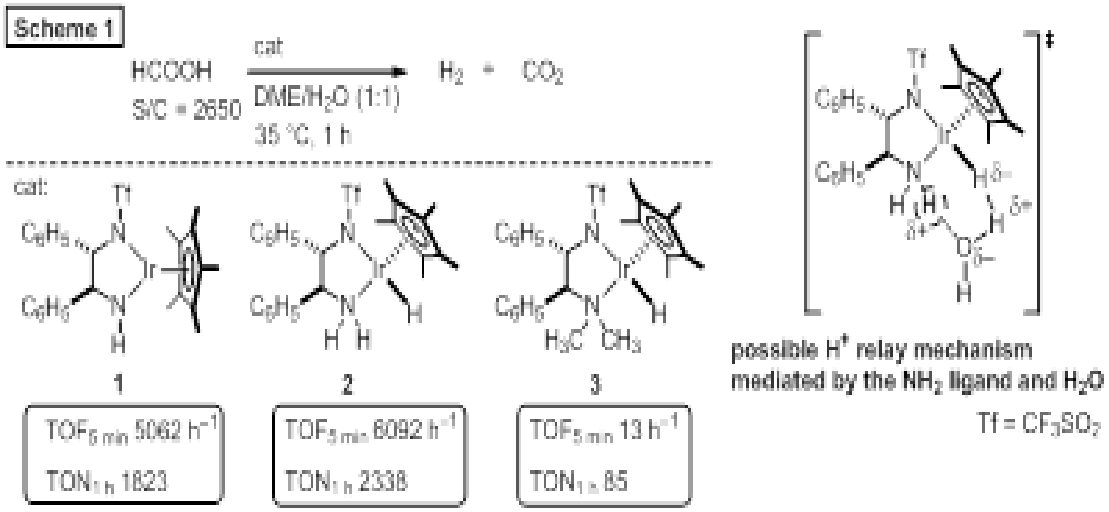
[1]*Tokyo Institute of Technology, Tokyo, Japan*

Poster Session 2

We have developed a series of bifunctional catalysts bearing a chelating amine ligand, which efficiently catalyses asymmetric transfer hydrogenation of aromatic ketones using formic acid/triethylamine azeotrope as a hydrogen source.[1] We report herein an extensive studies of the bifunctional complexes toward hydrogen generation catalysts.

In the absence of the hydrogen acceptor like ketone substrates, formic acid was catalytically transformed into H_2 and CO_2 gas with bifunctional iridium complexes. Cp*Ir complexes having TfDPEN (N-triflyl-1,2-diphenylethylenediamine) ligand showed excellent catalytic activity in 1,2-dimethoxyethane (DME) even in the absence of base additives. Notably, the catalytic performance of the complexes 1 and 2 was markedly enhanced by addition of water as a co-solvent, leading to turnover numbers around 2,000 and initial turnover frequency up to 6,000 at ambient temperature of 35˚C, as shown in Scheme 1. In contrast, the reaction was mostly hampered by using a related hydrido complex 3 without NH moiety. Based on the above results, we assumed a proton-relay mechanism facilitated by the protic amine ligand and H_2O, depicted below.

References:
1. T. Ikariya, Bull. Chem. Soc. Jpn. 2011, 84, 1.



P-447

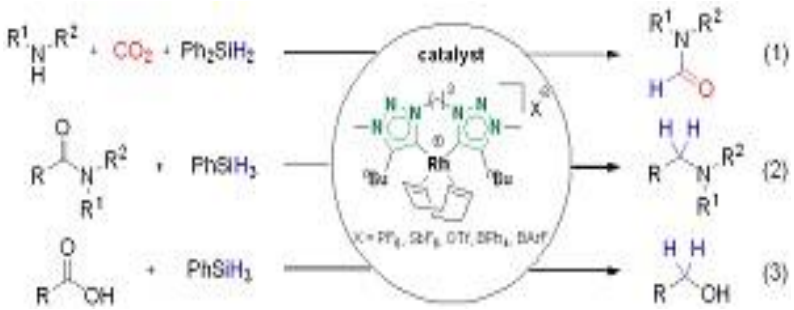
Chelating bis(tzNHC) Rhodium Complexes: Versatile Catalysts for Hydrosilylation Processes

Mr. Nguyen Thanh V. Q.[1], Dr. Woo-Jin Yoo[1], Dr. Shu Kobayashi[1]
[1]*Department of Chemistry, School of Science, the University of Tokyo, Tokyo, Japan*

Poster Session 2

Despite the rapid development of tzNHCs (tz = 1,2,3-triazol-5-ylidene, NHC = N-heterocyclic carbene) as ligands in transition metal catalysis, the preparation and catalytic activity of metal complexes bearing bidentate bis(tzNHC) remained almost unexplored. Based on a previous report that bis(NHC) rhodium complexes effectively catalyzed the hydrosilylation of ketones, we envisioned that replacing the "normal" NHC backbones to tzNHCs may result in more active catalysts and the scope of hydrosilylation reactions could be extended to more challenging substrates. Herein, we reported a modular synthesis of a series of alkyl bridge chelating bis(tzNHC) rhodium complexes and their applications for various reduction processes using hydrosilanes as the reductants. Highly efficient formylation of amines with CO_2 with broad substrate scope and excellent functional group tolerance was achieved using low catalyst loadings of the newly prepared complexes under ambient temperature. Notably, in this reductive transformation, rhodium complexes with tzNHC backbones outperformed their imidazolylidene analogs. The catalytic ability of these complexes was further expanded to the hydrosilylation of challenging carbonyl compounds, such as amides and carboxylic acids to generate the corresponding amines and alcohols in excellent yields.

References:



P-449

Copper-catalyzed enantioselective desymetrization of cyclopropenes: Synthesis of cyclopropylboronates.

Dr. Manuel Guisan Ceinos[1], Dr. Alejandro Parra[1], Graduate Laura Amenós[1], Graduate Aurora López[1], Dr. José Luis García Ruano[1], Dr. Mariola Tortosa[1]
[1]*Universidad Autónoma De Madrid, Cantoblanco, Spain*

Poster Session 2

The high versatility of boron compounds along with the abundance of biologically active compounds containing the cyclopropane motif, make the synthesis of cyclopropylboronates an interesting target in organic chemistry.[1] The classical approach for the synthesis of enantiomerically enriched cyclopropylboronates requires the use of stoichiometric amounts of a chiral auxiliary, and there are only two examples using asymmetric catalysis.[2]

Recently, our group has been involved in the development of different copper-catalyzed borylation reactions using unsaturated compounds.[3] In this context, we decided to extend our study to the challenging desymetrizacion of cyclopropenes using chiral boryl-copper complexes.[4]

In this work, we report the first diastereo- and enantioselective copper-catalyzed hydroboration of cyclopropenes. We have synthesized a series of cyclopropyl boronic esters with good yield and high diastero- and enantioselective ratios. Additionally, trapping the cyclopropylcopper intermediate with an electrophilic source of nitrogen allows for the preparation of interesting cyclopropylaminoboronates.

References:
[1] (a) C. W. Liskey, J. F. Hartwig, J. Am. Chem. Soc. 2013, 135, 3375-3378; (b) W. A. Donaldson, Tetrahedron 2001, 57, 8589–8627.

[2] (a) C. Zhong, S. Kunii, Y. Kosaka, M. Sawamura, H. Ito, J. Am. Chem. Soc. 2010, 132, 11440-11442. (b) M. Rubina, M. Rubin, V. Gevorgyan, J. Am. Chem. Soc. 2003, 125, 7198-7199.

[3] (a) A. Parra, A. López, S. Díaz-Tendero, L. Amenós, J. L. García-Ruano, M. Tortosa*, Synlett 2015, 26, 494-500; (b) R. Alfaro, A. Parra, J. Aleman, J. L. Garcia-Ruano, M. Tortosa*, J. Am. Chem. Soc. 2012, 134, 15165-15168. (c) M. Tortosa*, Angew. Chem. Int. Ed. 2011, 50, 3950-3953.

[4] A. Parra, L. Amenós, M. Guisán-Ceinos, A. López, J. L. García Ruano, M. Tortosa*, J. Am. Chem. Soc. 2014, 136, 15833-15836.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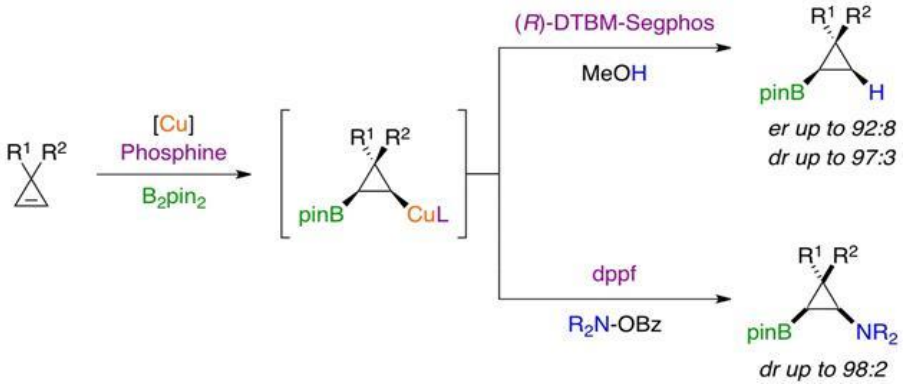
R1 R2
[Cu]
Phosphine
B2pin2
pinB
CuL
(R)-DTBM-Segphos
MeOH
pinB
H
er up to 92:8
dr up to 97:3
dppf
R2N-OBz
pinB
NR2
dr up to 98:2

P-450

Pd(II)-Catalyzed the direct intramolecular arylation of unactivated aryl benzyl ethers for the synthesis of 6H-benzo[c]chromenes using essential oils as precursors

Marlyn Catalina Ortiz Villamizar[1], Chemist, MSc Carlos Eduardo Puerto Galvis[1], Chemist, MSc, PhD Leonor Yamile Vargas Méndez[2], Chemist, MSc, PhD Vladimir V. Kouznetsov[1]

[1]*Universidad Industrial de Santander, Guatiguará/Piedecuesta, Colombia,* [2]*Universidad Santo Tomás de Aquino, Bucaramanga, Colombia*

Poster Session 2

Introduction. Phenylpropanoids present in the essential oil (EO) of Eugenia caryophyllus and Plectranthus amboinicus, like eugenol (71.8%) and carvacrol (67.1%) respectively, are of great interest for the organic and medicinal chemistry due to their use as synthetic building blocks in the formation of more complex structures and for their antioxidant activities.[1] Our laboratory has been working on the use of raw materials as synthetic precursors and here we report the synthesis of novel 6H-benzo[c]chromenes through the direct intramolecular arylation catalyzed by palladium (II) from phenolic cores found in EOs.

Results and discussion. The EOs, rich in eugenol, isoeugenol, carvacrol and thymol (1a-d), were obtained through hydrodistillation from the dried vegetal material and were subjected to the o-alkylation with the respective benzyl bromides (2a-b). After an extensive screening, we found that $PdCl_2(MeCN)_2$, $P(p\text{-}FPh)_3$, PivOH, K_2CO_3 in DMA promote the intramolecular C-C coupling of the aryl benzyl ethers (3a-i). The scope of this C-H coupling was examined and a new library of novel 6H-benzo[c]chromenes (4a-i) were obtained in good yields and characterized by IR, GC-MS and NMR (1D and 2D). (Scheme 1).[2]

Conclusion. A new strategy, robust enough to be used with plant extracts, was developed for the synthesis of products (4a-i) via Pd(II)-catalyzed cross-coupling. In comparison to the metal-free approach, $PdCl_2(MeCN)_2$ resulted to be an efficient catalyst to obtain structures with relevant medical applications.

Acknowledgments. This work was financially supported by Bio-Red-Co-CENIVAM (No. RC-0572-2012). MCOV thanks to VIE-UIS for its financial support.

References

1. T. Vog, Mol. Plant. 2010, 3, 2-20.
2. M. Lafrance, D. Lapointe, K. Fagnou, Tetrahedron. 2008, 64, 6015-6020

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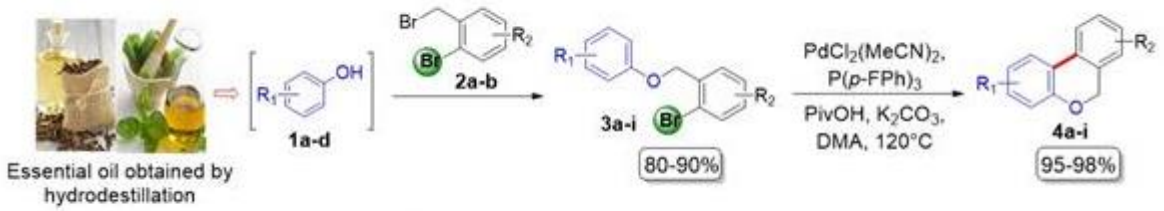


Scheme 1. Strategy for the synthesis of 6*H*-benzo[*c*]chromenes from Essential Oils (EOs)

P-451

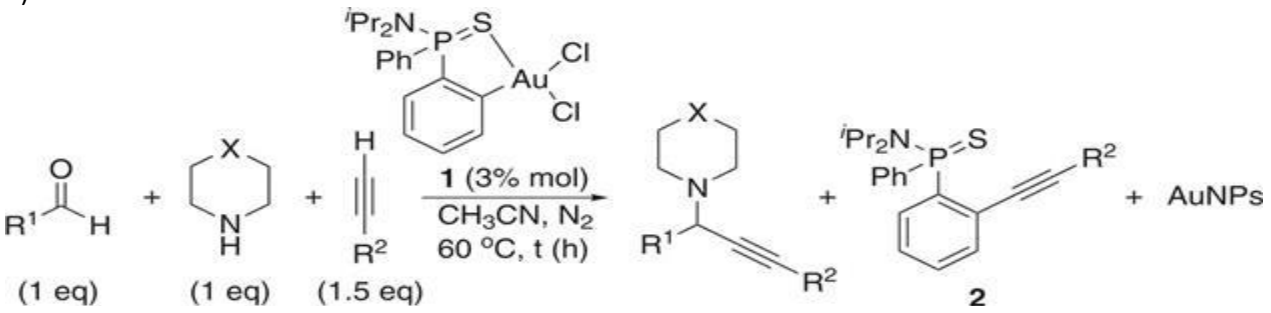
Structural and theoretical study of alkyne insertion into phosphinothioic gold(III) precatalyst in the synthesis of propargylamines via gold nanoparticles

Ms. Eva Belmonte Sánchez[1], Mr. Fernando López Ortiz[1], Mr. Jesús García López[1], Mrs. María José Iglesias Valdés-Solís[1]

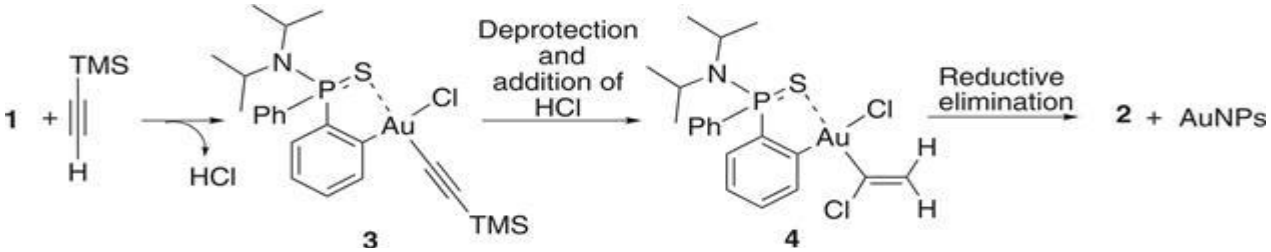
[1]*Universidad De Almería, La Cañada De San Urbano, Spain*

Poster Session 2

Over the last twenty years, gold(I) and gold(III) complexes have received a lot of interest as a very important class of organometallic catalysts in organic synthesis, due to their high regio- and chemo-selectivities.[1] More recently, gold nanoparticles (AuNPs) are emerging as powerful heterogeneous catalysts, showing higher chemical reactivity and "green" character.[2] We have previously demonstrated the in situ formation of catalytically active gold nanoparticles (AuNPs) when the gold(III) metallacycle 1 is used as precatalyst in the three-component coupling (A^3) reaction (Scheme 1 -A^3 coupling in presence of 1)



Isolation and characterization of intermediate 4 (Scheme 2) allowed us to propose a pathway for the decomposition of 1, that includes the displacement of the chlorine atom anti to the sulfur by the alkyne, followed by a reductive elimination that gives rise to the ortho alkynylphosphinothioic amide 2 with release of the metal ion as Au(I). (Scheme 2. Proposed mechanism for the decomposition of 1)



We have also found experimental evidences that the presence of the amine promotes the transformations of the gold(III) complex in the A^3 coupling. Theoretical calculations at the M06(SMD,Acetonitrile)/SDD-6-311+G(d,p)//B3LYP/LANL2DZ-6-31G(d) level showed that the amine participates in a ternary transition state with the alkyne and 1, and that the reductive elimination with insertion of the alkyne in the ortho position is clearly exotermic, with a free energy difference of -38.7 kcal/mol.

References:
[1] Jia, M.; Bandini, M. ACS Catal. 2015, 5, 1638.
[2] Takale, B. S.; Bao, M.; Yamamoto, Y. Org. Biomol. Chem. 2014, 12, 2005.

P-452

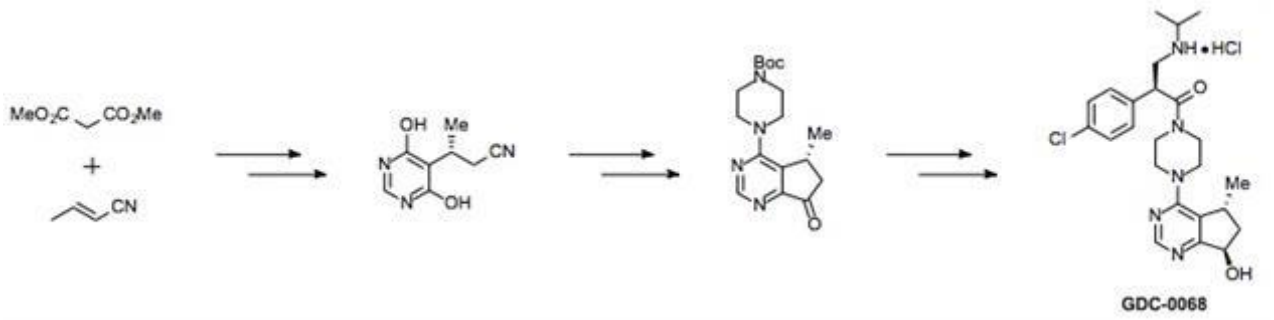
Efficient, Streamlined Synthesis of Functionalized Cyclopentapyrimidine Ketone: An Intermediate of the Akt Inhibitor GDC-0068

Scott Savage[1], Francis Gosselin[1], Chong Han[1], Mohammad Al-Sayah[1], Meenakshi Goel[1], Beat Wirz[2], Patrick Stocker[2], Hans Iding[2], Reinhard Reents[2]

[1]Genentech, Inc., South San Francisco, USA, [2]F. Hoffmann-La Roche Ltd., Basel, Switzerland

Poster Session 2

An efficient, seven step process was developed to construct the functionalized cyclopentapyrimdine core of GDC-0068, an oral Akt inhibitor. Malonate addition to crotonitrile, followed by enzymatic resolution generates the highly enantioenriched nitrile. Treatment with formamidine acetate affords the dihydroxypyrimidine. A streamlined, three-step, through-process of chlorination, bromine exchange and aromatic substitution affords the penultimate bromonitrile pyrimidine. Halogen-metal exchange and anionic cyclization was then used to generate the cyclopentapyrimidine ketone product in high yield and purity. This process was identified, optimized and executed to metric ton scale in less than one year.



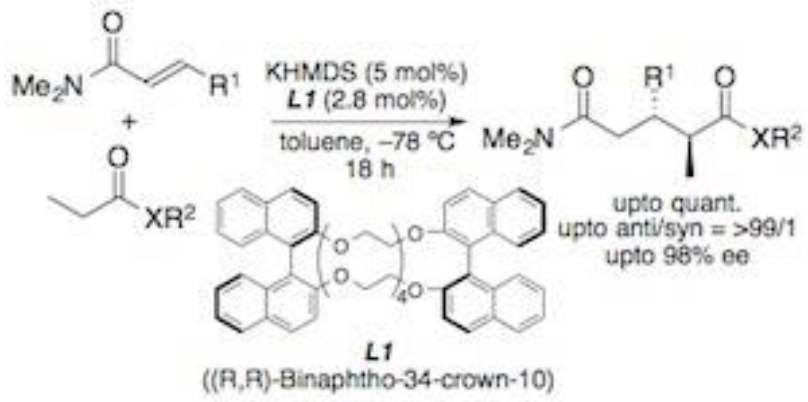
P-453

Development of Catalytic Asymmetric Direct-type 1,4-Addition Reactions of Simple Amides and Esters

Mr Hirotsugu Suzuki[1], Mr Io Sato[1], Dr Yasuhiro Yamashita[1], Prof Shu Kobayashi[1]
[1]*The University of Tokyo, Tokyo, Japan*

Poster Session 2

Carbon-carbon bond formations are one of the most fundamental and important reactions in organic synthesis. Especially, reactions using base species are atom-economical and have been developed intensively including catalytic direct-type reactions. However, methodologies for catalytic reactions using carbanion precursors with less acidic hydrogens, such as simple amides and esters, have not been established. In general, deprotonation of less acidic carbonyl compounds requires more than a stoichiometric amount of strong base species, because the catalyst regeneration step via the deprotonation of the conjugate acid of Brønsted bases does not proceed smoothly. Therefore, strong base species have not often been employed as effective catalysts. To overcome the catalyst regeneration problem, we focused on the basicity of reaction intermediates. If the intermediates possessed strong basicity, deprotonation of the conjugated acids or nucleophiles would occur smoothly. Recently, we have developed catalytic direct-type Mannich-type reactions and 1,4-addition reactions using less acidic compounds with this concept. Next, we focused on the asymmetric variant of 1,4-addition reactions. In our hypothesis, these asymmetric reactions could be accomplished with an appropriate chiral ligand because an asymmetric induction step (a nucleophilic addition step) would be the same as well-investigated mild base catalyzed reactions. Surprisingly, a unique chiral macro crown ether, binaphtho-34-crown-10, was found to be the optimal chiral ligand for the asymmetric 1,4-addition reactions of amides to afford the desired products in excellent yields with excellent diastereo- and enantioselectivities. In addition, the catalyst was found to be suitable for simple esters. We also showed transformation of the products obtained, selective conversion of the amide moiety and formal synthesis of natural products. Finally, we identified the chiral potassium complex as the catalytically active species through X-ray crystallography, dynamic ^{1}H NMR and MALDI-TOF MS analyses. We have demonstrated significant progress in catalytic 1,4-addition reaction using simple amides and esters.



P-454

Carboxylation of Halocarbons with CO_2 Using a Structurally strained Disilane

Mr. Kenta Suga[1], Dr. Tsuyoshi Mita[1], Ms. Kaori Sato[1], Dr. Yoshihiro Sato[1]
[1]*Faculty of Pharmaceutical Science, Hokkaido University, Sapporo, Japan*

Poster Session 2

Carbon dioxide (CO_2) is an ideal C1 source in the field of organic chemistry due to its abundance, low cost, and low toxicity. Therefore, considerable efforts have recently been made for the development of effective CO_2 incorporation reactions.

Organometallic reagents such as alkyllithium and Grignard reagents can react with CO_2 to give benzoic acid derivatives. However, low temperature and strictly anhydrous conditions are indispensable for these classical methods, which results in low functional group tolerance. Transition-metal-catalyzed carboxylation reactions of aryl halides using Pd[1], Ni[2], and Cu[3] thus have been developed to avoid these problems.

We report herein a mild carboxylation reaction with very high functional group tolerance using a structurally strained disilane and CsF. The Si-Si bond of this strained disilane could be cleaved by CsF to generate silyl anion, and the resulting reactive silyl anion would then attack to a halide to form a carbanion-like species, which could be trapped by CO_2 to afford the desired carboxylic acid. Carboxylation of aryl halides tolerated various substituents such as the phenolic hydroxy group, an ester, a ketone, and the nitro group. In addition, carboxylations of heteroaryl, alkenyl, and alkynyl halides proceeded to afford the corresponding carboxylic acid derivatives in high yields. Furthermore, allyl and alkyl halides were also applicable for this reaction.

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2) Tsuji, Y. et al. J. Am. Chem. Soc. 2012, 134, 9106.
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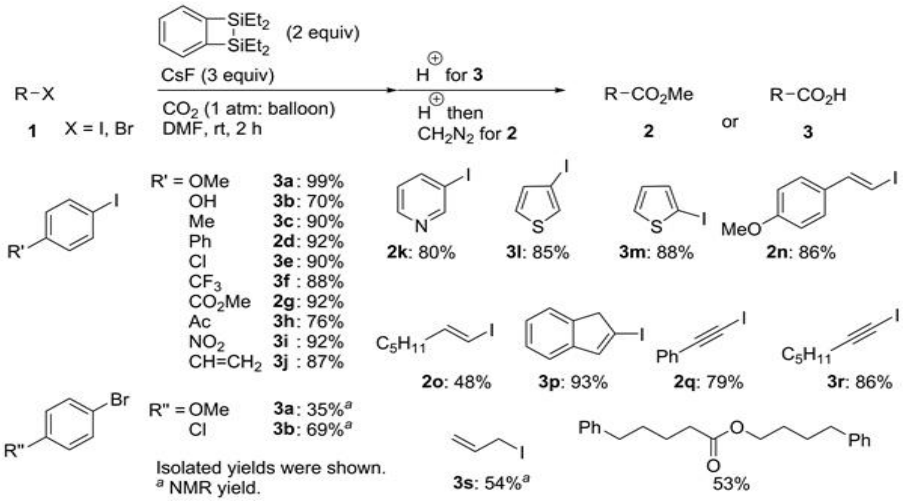

P-455

Dihydrogen Activation using Frustrated Lewis Pair

Dr Pablo Mauléon, Dr Paolo Tosatti, Dr Alex Marti, Dr Jaroslav Padevet, Prof. Andreas Pfaltz
[1]*Department of Chemistry, University Basel, Basel, Switzerland*

Poster Session 2

Avoiding the use of transition metals for the activation of molecular hydrogen is an attractive area of research that has led to intriguing results over the last decade. In particular, the discovery of so-called Frustrated LEWIS Pairs (FLPs) that catalyze dihydrogen activation and hydrogenation of organic substrates by the group of Stephan has triggered the interest of the scientific community.[1]
During the last few years a wide range of FLP catalysts has been developed for hydrogen activation and transition metal-free hydrogenation. Most of these systems rely on the use of highly LEWIS acidic boranes like B(C6F5)3 in conjunction with hindered LEWIS bases such as phosphines or amines.[2,3]
In our group we have studied the use of less active LEWIS acids for FLP systems such as Ph3B using electronically tunable phenolates as LEWIS bases. This FLP system was able to split molecular hydrogen and to reduce imines. Moreover, it was found that this borane prone to decomposition, resulting in formation of the inactive species (Ph4)B-K+ (scheme 1).

scheme 1: Dihydrogen activation using BPh3 and phenolate as FLP for the reduction of imine.

In an attempt to broaden the FLP scope and to avoid this undesired process, we prepared several boranes bearing various substituents differing in their electronic and steric properties.

References:
1 : G. C. Welch, D.W. Stephan, Science 2006, 314, 1124-1126.
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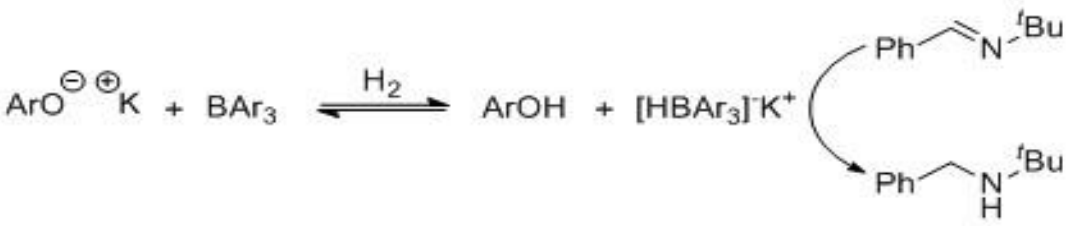

P-457

Pd-catalysed Urea Synthesis in Ionic Liquid

Nanette Zahrtmann[1], Dr. Cyril Godard[1], Prof. Carmen Claver[1], Dr. Eduardo José García Suárez[2], Associate Prof. Anders Riisager[2]

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Poster Session 2

Work hypothesis and objective:
Ureas are indispensable compounds commonly found in the structures of a large number of biologically active compounds, and are widely used as agrochemicals, dyes, antioxidants and HIV inhibitors, furthermore ureas are key intermediates in organic synthesis.[1] Palladium catalysts are commonly used for carbonylation reactions and have previously been applied for the carbonylation of amines, but the best results have been obtained at high pressure, high temperature and under an explosive gas mixture,[2] making the system unsafe. It is thus desirable to develop a system which is active under milder conditions. Ionic liquids are reported to have a beneficial effect in many reactions[3] and it is our hypothesis that the combination of ionic liquid and a new palladium catalysts can lead to an efficient, robust, versatile catalytic system for the carbonylation of both aliphatic and aromatic amines, at low pressures and temperatures. The objective is, to find a new palladium/IL based catalytic systems that will afford the carbonylation of a range of aromatic amines under mild reaction conditions.

Results:
We have developed a system which operates under mild conditions, is fully recyclable, fully selective and have a TOF of 325, which is 2 orders of magnitude higher than published results obtained at comparable pressure.[4]

Conclusion:
We have shown that several oxidants can facilitate the formation of ureas, that ionic liquid is a effective promoter and as such reduces the pressure required for the reaction.

References:
[1] D. J. Díaz, A. K. Darko, L. McElwee-White, Eur. J. Org. Chem., 2007, 27, 4453
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[3] Supported Ionic Liquids: Fundamentals and Applications, R. Fehrmann, A. Riisager, M. Haumann, ISBN: 978-3-527-32429-3, 496 pages, January 2014
[4] B. Chen, S. S. C. Chuang, Green Chem., 2003, 5, 484.


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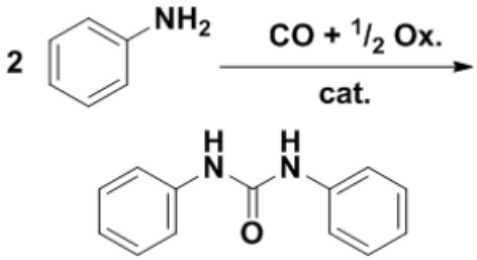
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CO + 1/2 Ox.
cat.
H
N
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P-458

Arylallylation of Alkenes by Cooperative Palladium/Copper Catalysis

Mr Naoki Ohta[1], Prof. Kazuhiko Semba[1], Prof. Yoshiaki Nakao[1,2]

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Poster Session 2

Transition metal-catalyzed cross-coupling reaction is one of the most reliable methods for C–C bond formation. Organometallic reagents generally need to be prepared before the transformation, leading to multistep operations. On the other hand, cross-coupling reaction employing catalytically prepared organometallic reagents is more step-economical. In particular, functionalized alkyl- and alkenyl metal species can be generated through the addition of organotransition-metal species across alkenes and alkynes.[1,2,3]

Our group and Brown have recently reported the arylboration of alkenes by cooperative palladium/copper catalysis.[4,5] Herein, we report the arylallylation of alkenes by cooperative palladium/copper catalysis. In this reaction, organocopper species are generated through the addition of an arylcopper species across alkenes.

References:
1. S. Ma, Z. Shi, J. Org. Chem. 1998, 63, 6387–6389.
2. Y. Shi, E. Roth, S. D. Ramgren, S. A. Blum, J. Am. Chem. Soc. 2009, 131, 18022–18023.
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4. K. Semba, Y. Nakao, J. Am. Chem. Soc. 2014, 136, 3732–3735.
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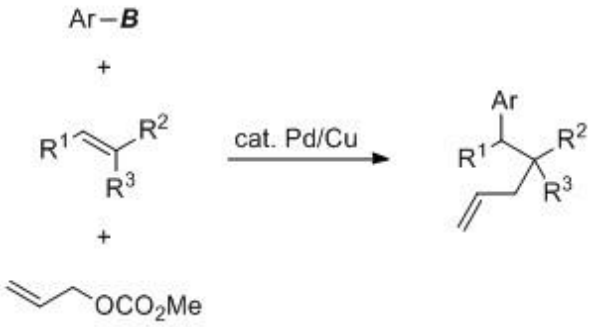
Scheme 1



P-459

Palladium-catalyzed annulation of aryl silylethynyl ethers with allyl pivalates through double C–H activation

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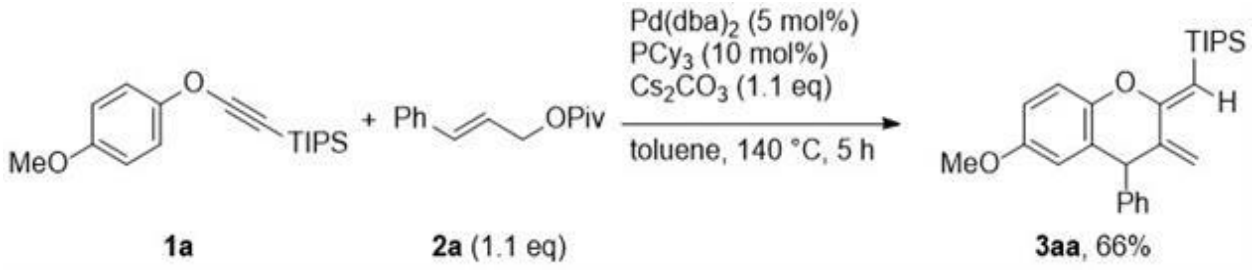
Poster Session 2

Catalytic C–H activation is a promising approach in view of environmentally-benign organic synthesis. Annulation reactions via double C–H bond cleavage are a valuable method for rapid synthesis of an annulated polycycles with atom economy and step economy. Our group has disclosed that the silylethynyloxy group in the title substrate is the key for ortho C–H bond activation in the aryl group. Herein we report that palladium-catalyzed annulation of alkynyl aryl ethers 1 with allyl pivalates 2 proceeds via double cleavage of ortho-C–H bond in 1 and β-C–H bond in 2 to give chromane derivatives 3 containing methylidene moieties at both C2 and C3 positions. For example, 4-$MeOC_6H_4OC{\equiv}CSi(i\text{-}Pr)_3$ (1a) reacted with cinnamyl pivalate (2a) in the presence of $Pd(dba)_2$, PCy_3, and Cs_2CO_3 to give bis-methylenechromane 3aa in 66% yield. With α-phenylallyl pivalate (2b), the same product (3aa) was produced in 70% yield, showing that the reaction apparently proceeds via cross-coupling of π-allyl palladium intermediate with 1a followed by ring-closure by C–H bond activation at ortho-aryl and olefinic carbons.



P-460

A new synthesis of functionalized imidazo[1,2-a]benzoimidazole derivatives by palladium-catalyzed oxidative aminocarbonylation-cyclization of (1-prop-2-ynyl-1H-benzimidazol-2-yl)amines

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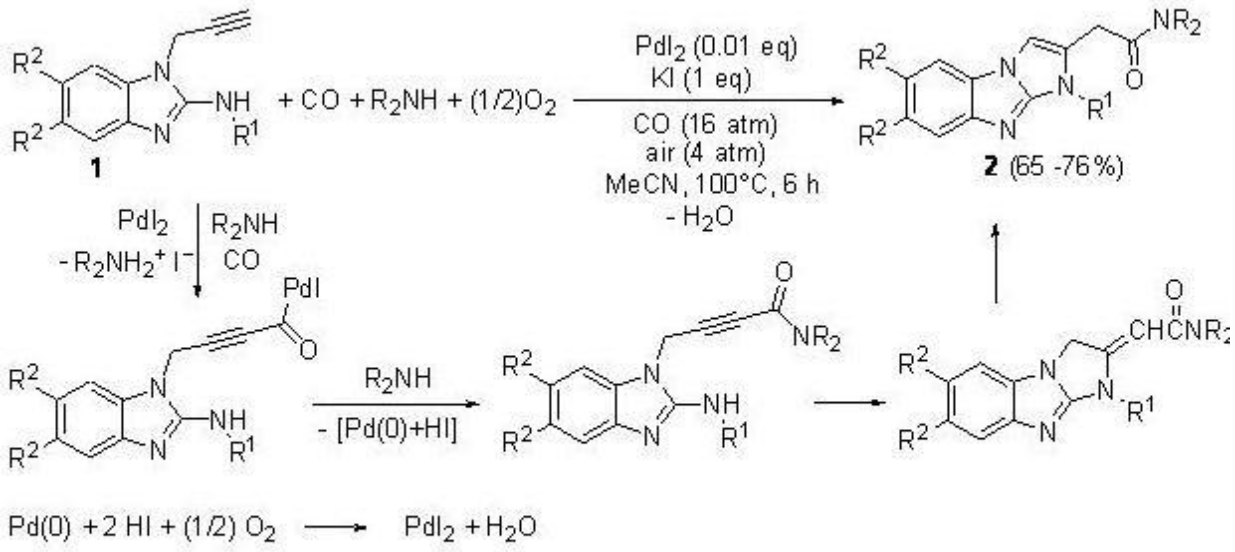
Poster Session 2

Imidazo[1,2-a]benzimidazole derivatives exhibit a wide spectrum of biological activities. In particular, their structural scaffold is present in drugs displaying analgesic, antinfiammatory, hypotensive, antiaggregant, hypoglicemic, and anti-cancer activities.

In this Communication, we report a novel carbonylative approach to functionalized imidazo[1,2-a]benzoimidazoles 2, starting from readily available (1-prop-2-ynyl-1H-benzoimidazol-2-yl)amines 1. Our method consists in the PdI_2/KI catalyzed oxidative monoaminocarbonylation of the terminal triple bond of 1, followed by in situ intramolecular conjugate addition and double bond isomerization.

Reactions were carried out in MeCN at 100 °C for 6 h, under 20 atm of a 4:1 mixture of carbon monoxide and air and in presence of catalytic amounts of PdI_2 (0.01 eq) in conjunction with KI (1 eq), using a secondary amine as nucleophile, to give N,N-disubstituted 2-(1-alkyl-1H-imidazo[1,2-a]benzoimidazol-2-yl)-acetamides 2 in satisfacory yields (65-76%).



P-461

Copper-catalyzed intermolecular hydroamination of tifluoromethyl group substituted internal alkynes with anilines

Mr. Taro Sonehara[1], Mr. Tomoki Ishikawa[1], Ms. Maki Minakawa[1], Mr. Motoi Kawatsura[1]
[1]*Nihon University, Setagaya-ku, Japan*

Poster Session 2

We developed the intermolecular hydroamination of trifluoromethyl group substituted internal alkynes with anilines. The copper (II) trifluoromethanesulfonate catalyzed reaction of aryl and trifluoromethyl group substituted unsymmetrical internal alkynes with anilines proceeded smoothly to give desired hydroaminated product in high yield with high regioselectivity.

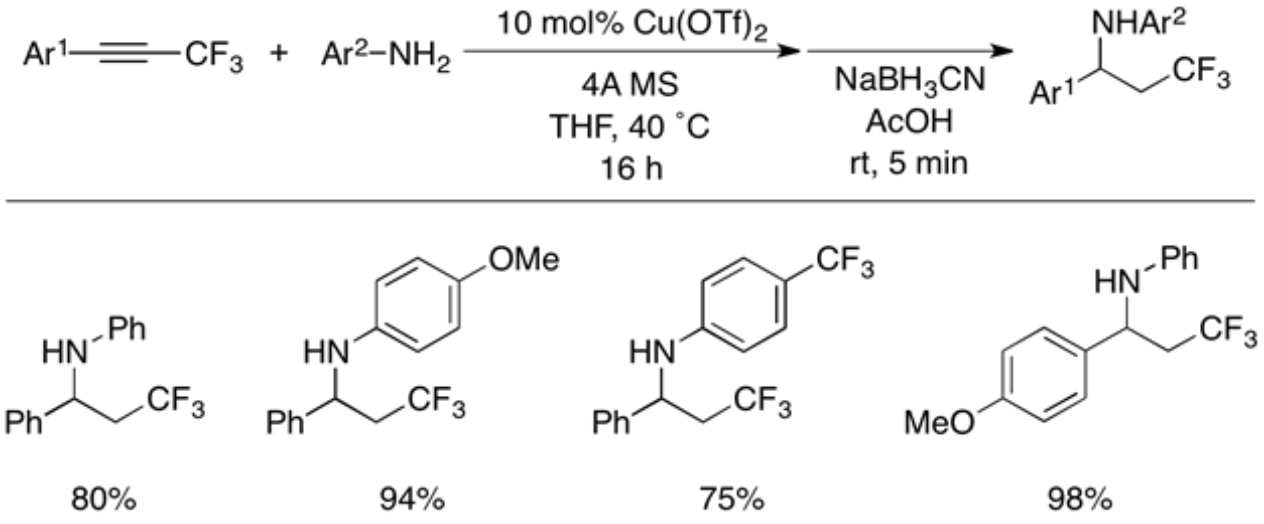


Figure. Copper-catalyzed hydroamination of internal alkynes.

P-462

Studies on the Synthesis of Prenylated Quinoline-2-one Alkaloids, Aspoquinolones

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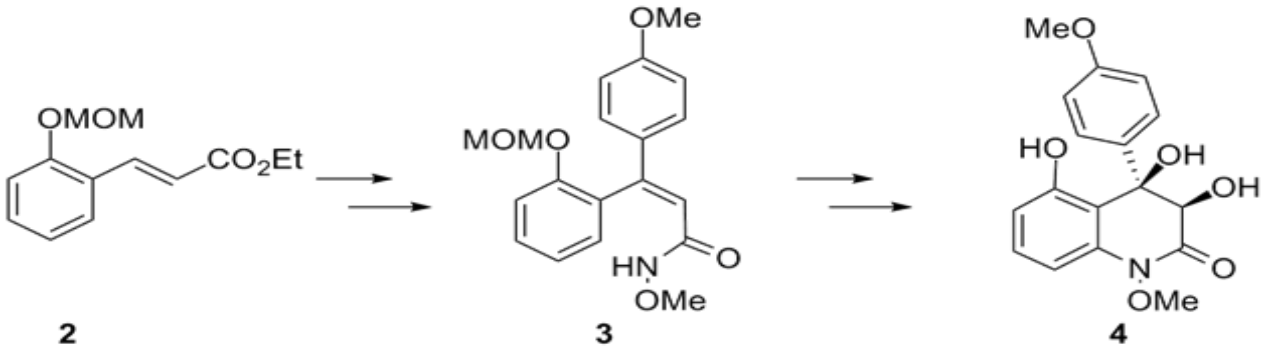
[1]Hoshi University, Shinagawa, Japan, [2]Rikkyo University, Toshima, Japan

Poster Session 2

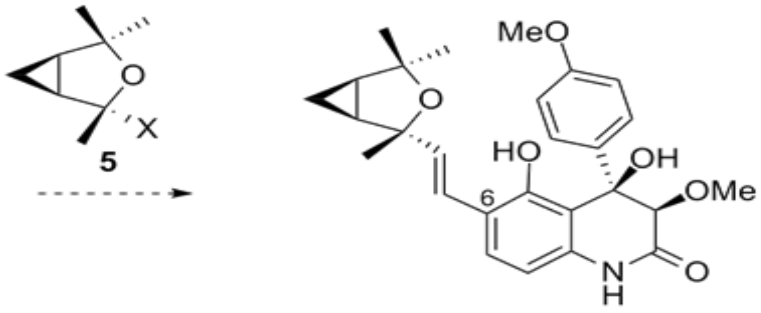
Aspoquinolone A (1), a quinolinone alkaloid isolated from Aspergillus nidulans (HKI 0410) by Hertweck et al., exhibits high cytotoxity against L-929 mouse fibroblast cell lines (GI50 10.6 µg ml-1) and good antiproliferative effects on human leukemia cell line K-562 (GI50 17.8 µg ml-1). The structural features of aspoquinolone A are highly oxygenated quinolone skeleton and unprecedented terpene part at the C-6 position. The structural complexity and its biological activity have attracted us to study the aspoquinolone A synthesis. Here, we report the synthesis of dihydroxyquinolinone part and construction of terpene part, 2,4,4-trimethyl-3-oxa[3.1.0]hexane framework, in aspoquinolone A.

Dihydroquinolinone part 4 was prepared in 6 steps via Heck reaction between cinnamate 2 and p-iodoanisole, hydrolysis of acrylate followed by amidation, Pd-catalyzed lactam formation of hydroxamate 3, and dihydoroxylation with OsO4.

Terpene part 5 was synthesized by methanolysis of known cyclopropanedicarboxylic anhydride followed by amidation, treatment of Weinreb's amide with MeLi, cyanation of hemiacetal with TMSCN, reduction of nitrile, and conversion of aldehyde to vinyl boronate. Efforts to complete the synthesis of aspoquinolone A are in progress.



2 **3** **4**



aspoquinolone A (**1**)

P-463

Truncated polycyclizations and unexpected stereoselectivities in Ti(III)-catalyzed cyclizations of ketoepoxypolyprenes

Sandra Resa[1], Sara Patricia Morcillo[1], Delia Miguel[1], Alba Millán[1], José Justicia[1], Juan Manuel Cuerva[1]
[1]*University of Granada, Granada, Spain*

Poster Session 2

In recent years, the radical cyclisation of epoxypolyprenes catalyzed by titanocene(III) complex Cp_2TiCl has emerged as a powerful tool for the synthesis of terpenic structures. This bioinspired protocol has been used for the cyclization, under smooth reaction conditions, of different polyprenes with high diastereoselectivity.[1] However, the preparation of compounds from incomplete cyclizations was not possible using this method.

In the present communication, we describe a new strategy to control the number of cyclization steps in bioinspired radical (poly)-cyclizations involving epoxypolyenes containing keto units positioned along the polyene chain. This approach provides an unprecedentedly straightforward access to natural terpenoids with pendant unsaturated side chains. Additionally, in the case of bi- and tricyclizations, decalins with cis stereochemistry have been obtained as a consequence of the presence of the ketone. The preferential formation of cis-fused adducts was rationalized using DFT calculations. This result is completely unprecedented in biomimetic cyclizations and permits the access to natural terpenoids with this stereochemistry, as well as to non-natural analogues.

Figure 1

This strategy has been used in the synthesis of several natural terpenoids, as monocycles 1 and 2, isolated from Atermisia chamaemelifolia and Celistopholis glauca, respectively, in a few steps and complete selectivity. [2]

Figure 2

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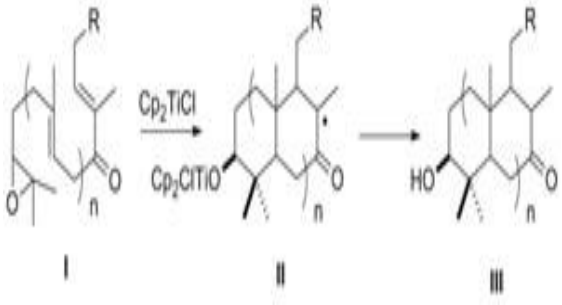
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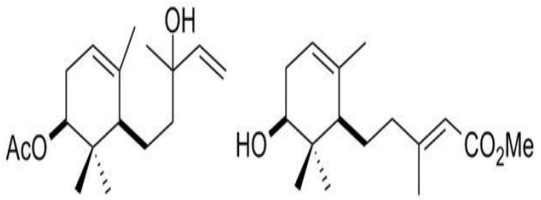
OH
AcO
HO
CO2Me

1 2

P-464

Iron-Catalyzed Enantioselective Cross-Coupling Reactions of α-Chloroesters with Grignard Reagents

Masayoshi Jin[1], Dr. Laksmikanta Adak[2], Prof. Masaharu Nakamura[2]

[1]*Daiichisankyo Co., Ltd., Hiratsuka, Japan,* [2]*International Research Center for Elements Science, Institute for Chemical Research, Kyoto University and Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Uji, Japan*

Poster Session 2

Transition-metal-catalyzed enantioconvergent cross-coupling reaction has been emerging as a powerful tool in the synthesis of chiral compounds. During the past decade, remarkable progress in this field has led the development of a new class of coupling reactions by using nickel[1] and cobalt[2] catalysts. On the other hand, despite its less toxic and cost-effective nature, iron catalyst has never been used in the enantioconvergent nor any enantioselective coupling reactions of organometallic reagents. We herein present the first iron-catalyzed enantioconvergent cross-coupling reaction between an organometallic compound and an organic electrophile. Synthetically versatile racemic α-chloroalkanoates are coupled with aryl Grignard reagents in the presence of catalytic amounts of $Fe(acac)_3$ and (R,R)-BenzP*, giving the products in high yields with good enantioselectivities (er up to 91:9). The coupling products, α-arylalkanoates, are readily converted to α-arylalkanoic acids with high optical enrichment (er up to >99:1). Radical probe experiments suggest that an alkyl radical is formed as an intermediate, then coupled with an aryl group in enantioselective manner. The developed asymmetric coupling offers facile and practical access to various chiral α-arylalkanoic acid derivatives, which are of significant pharmaceutical importance.

References

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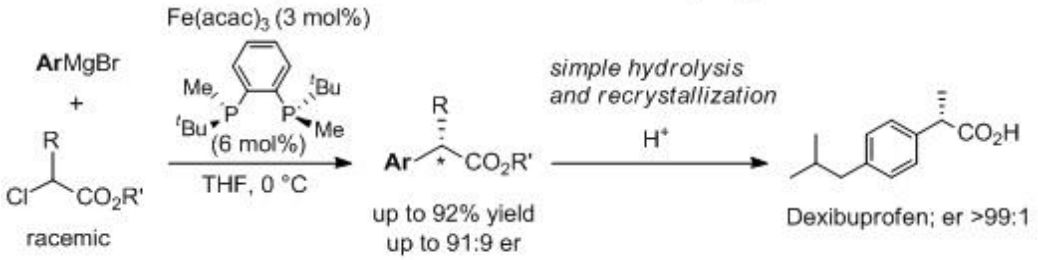
2. Mao, J.; Liu, F.; Wang, M.; Wu, L.; Zheng, B.; Liu, S.; Zhong, J.; Bian, Q.; Walsh, P. J. J. Am. Chem. Soc. 2014, 136, 17662.

Scheme 1. Iron-Catalyzed Enantioselecitve Cross-Coupling Reaction



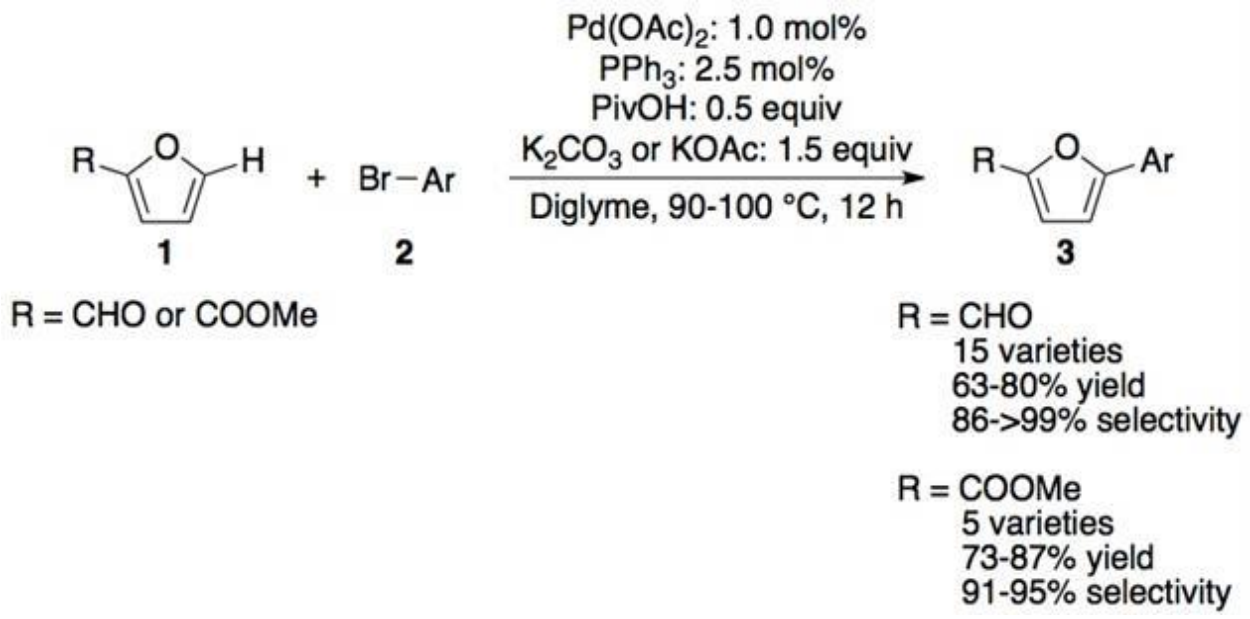
P-465

Palladium-catalyzed Direct Arylation of Furan Derivatives with Aryl Bromides via C-H Activation

Shun Satoh[1], Maki Minakawa[1], Motoi Kawatsura[1]
[1]*Nihon University, Sakurajosui, Japan*

Poster Session 2

The direct use of furan derivarives derived from biomass in organic synthesis is an important challenge for green chemistry. Aryfuran derivatives are significant building blocks which are omnipresent in synthetic bioactive compounds, natural products, and innovative organic materials. Palladium-catalyzed Suzuki, Negishi and Stille cross-coupling reactions are among the most useful procedures to prepare such arylfuran derivatives. However, these reactions require the preliminary preparation of organometallic furan derivatives. Recently, direct arylation of 2-furaldehyde with aryl halides has been performed using palladium catalyst. The direct arylation provides a cost-effective and environmentally friendly method for the preparation of the arylfuran derivatives. Here we report the development of palladium-catalyzed direct arylation of 2-furaldehyde with aryl bromides. The direct arylation method applied a variety of aryl bromides by use of Pd(OAc)2 (1.0 mol%) with PPh3 (2.5 mmol) and PivOH (0.5 mol equiv) to give the corresponding 5-aryl furan derivatives in 63-80% isolated yield with 86->99% selectivity (15 varieties). Furthermore, the reaction of methyl furan-2-carboxylate with aryl bromides was also performed in the similar conditions to afford the corresponding 5-aryl furan derivatives in 73-87% yield with 91-95% selectivity (5 varieties).



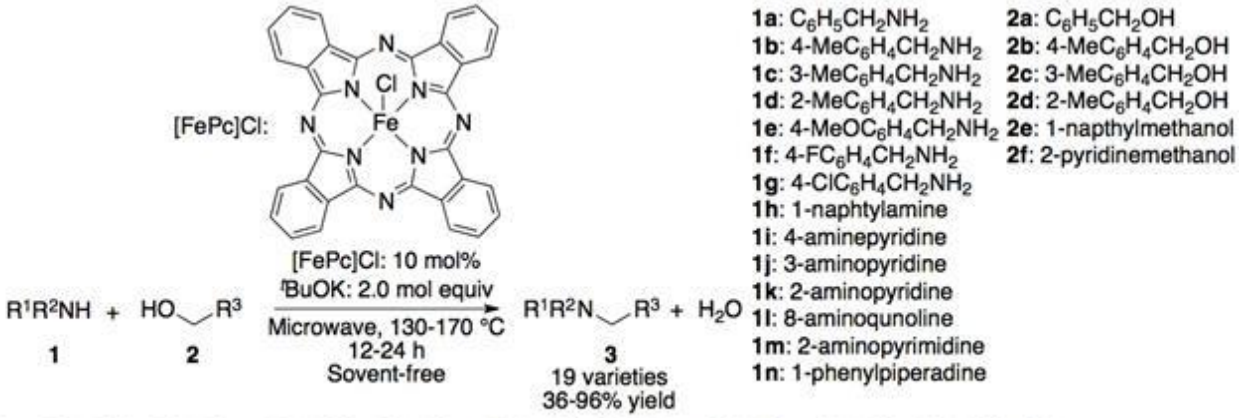
P-466

Selective Direct N-Alkylation of Amines with Alcohols using Iron Phthalocyanine Chloride under Solvent-free Conditions

Masataka Okubo[1], Maki Minakawa[1], Motoi Kawatsura[1]
[1]*Nihon University, Sakurajosui, Japan*

Poster Session 2

N-Alkylated amines are important building blocks for synthesis of pharmaceuticals, agrochemicals, dyes, and bioactive molecules. The N-alkylation of amines with alcohols is an attractive and environmentally friendly alternative to conventional method that is typically achieved by reaction with an alkyl halide. The conventional procedure is problematic due to overalkylation and the toxic nature of alkyl halides and related alkylating reagents. On the other hand, the N-alkylation with alcohols is less hazardous and more atom economical process because of theoretically produces only water as a byproduct. Most common metals used for the catalytic N-alkylation of amines with alcohols based on Ru and Ir. Recently, catalysts derived from other metals, such as Au, Ag, Cu, Ni, Rh, Pd, Pt, and Fe have also been explored. However, Fe-catalyzed N-alkylation of amines with alcohols has remained a challenging topic. We developed the selective and efficient N-alkylation of amines with alcohols using iron catalysis under microwave irradiation in solvent-free conditions. The reaction employed [Fe(III)Pc]Cl (Pc = phthalocyaninato), an inexpensive commercial compound that is typically used as an industrial additive for ink and rubber manufacturing. The [Fe(III)Pc]Cl catalyst showed good activity with excellent selectivity for the N-alkylation of amines with alcohols.



3aa: 91%, **3ba**: 80%, **3ca**: 84%, **3da**: 59%, **3ea**: 64%, **3fa**: 69%, **3ga**: 36%, **3ha**: 97%, **3ia**: 86%, **3ja**: 86%, **3ka**: 64%, **3la**: 94%, **3ma**: 59%, **3na**: 82%, **3ab**: 65%, **3ac**: 85%, **3ad**: 96%, **3ae**: 89%, **3af**: 92%

P-467

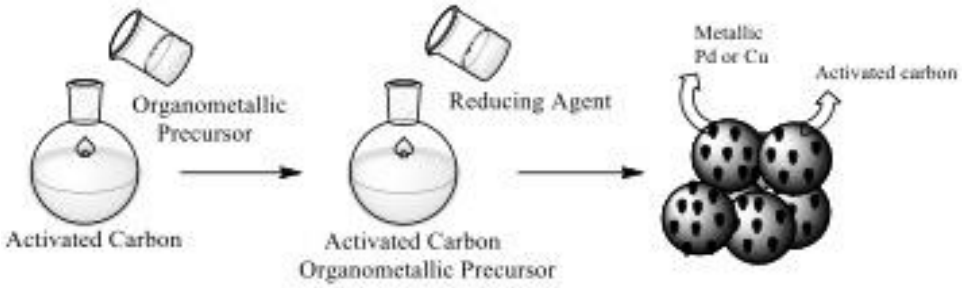
Synthesis Of Novel vic-Dioxime Metal Complexes and Using As Precursors For Metallic Deposition Methods

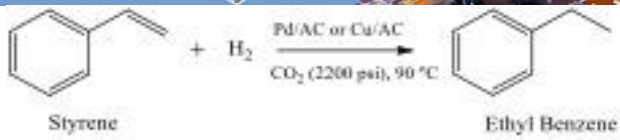
PhD Burcu Darendeli[1], Prof. Dr. Bilgehan Güzel[1]
[1]*Çukurova University, Adana, Turkey*

Poster Session 2

Nowadays, metal nanoparticles supported on high surface area substrates are used as catalysts in many organic reactions owing to their advantages. Solid substrate supported nanocatalysts are classified as heterogeneous catalysts and like their group; they can be easily removed from a solution after the reaction. For the preparation of supported nanocatalysts; various techniques have been developed. These methods are classified as micro emulsion, sol-gel, impregnation, sonochemical, deposition-precipitation, chemical vapor deposition and supercritical fluids deposition technique[1]. Deposition-precipitation and impregnation methods are more favorable and preferred ones cause of their simplicity techniques (Fig 1).
In this work, vic-dioxime derivative ligands and their Pd(II) and Cu(II) metal complexes were synthesized use as precursors in the deposition of metal nanoparticles. All ligands and their metal complexes were characterized via various analyses including FT-IR, ^{1}H NMR, elemental analysis and magnetic susceptibility. The synthesized metal complexes were used as precursors in two different deposition methods; impregnation and deposition-precipitation, to prepare activated carbon supported metallic nanoparticles. The size and distribution of the synthesized nanocatalysts was analyzed by SEM/EDX and XRD. According to analysis results, the smaller and well dispersed nanoparticles were obtained by deposition-precipitation method. The Pd particles ranged from 2-20 nm and the Cu nanoparticles ranged from 20-30 nm. The catalytic activity of activated carbon supported nanocatalysts were performed in a hydrogenation reaction of styrene (Fig 2). Styrene/ethyl benzene ratio was determined with gas chromotography (GC).

Reference:
[1] P. M. Arvela, D. Y. Murzin, Effect of catalyst synthesis parameters on the metal particle size applied catalysis, review A: General, 451 (2013) 251-281





Styrene Ethyl Benzene

P-469

Synthesis and Characterization of 4-amino-3-hydroxynaphthalene-1-sulphonic acid Schiff Base and Metal Complexes

Mr Selahattin Serin[1], Msc Gizem Gümüşgöz[1], PhD Seda Kozay[1]
[1]*Çukurova University, Adana, Turkey*

Poster Session 2

Schiff bases and metal complexes have an extensive area of use and they increasingly become more and more important. Existence of functional groups bonded to these ligands is one of the factors in contributing various properties to these structures. Presence of sulphonic acid group in these structures provides Schiff base ligands and metal complexes synthesized with solubility in water, high stability in varying pH mediums as wells as adding thermal stability to these structures.

In the scope of this study, 3 new Schiff bases and Ni(II), Cu(II) complexes of these bases have been synthesized and characterized by enabling reaction of 4-amino-3-hydroxy-naphthalene-1-sulfonic acid with salicylaldehyde, 5-chloro salicylaldehyde, and 5-bromo salicylaldehyde respectively, under suitable conditions (Fig 1). Whether or not R groups within these structure have any effect on thermal stability has also been discussed.

Structures of synthesized Schiff bases and Ni(II), Cu(II) complexes have been characterized by using spectroscopic techniques, elemental analysis and magnetic susceptibility methods such as FT-IR, UV-Vis, ^{1}H-NMR and ^{13}C-NMR. Thermal stability of the structures has been determined by using TG/DTA device. On the basis of analysis results and literature search, certain structural formulas are suggested for Schiff bases and metal complexes. What's more, catalytic activities of metal complexes have been examined thoroughly.

Acknowledgment: This study is sponsored by Scientific And Technological Research Council Of Turkey (TUBITAK) (No: 113Z280)

Reference:
SKOROKHOD, L.S., SEIFULLINA, I.I., MININ, V. V., VLASENKO, V.G., PIROG, I.V., 2007. Synthesis and Structure of Co(II), Ni(II), and Cu(II) Complexes with Schiff Bases, Condensation Products of 2-Amino-4,8-naphthalenedisulfonic Acid and Aromatic Carbinols. Russian Journal of Inorganic Chemistry, Vol.52, No.7, pp 1006-1012.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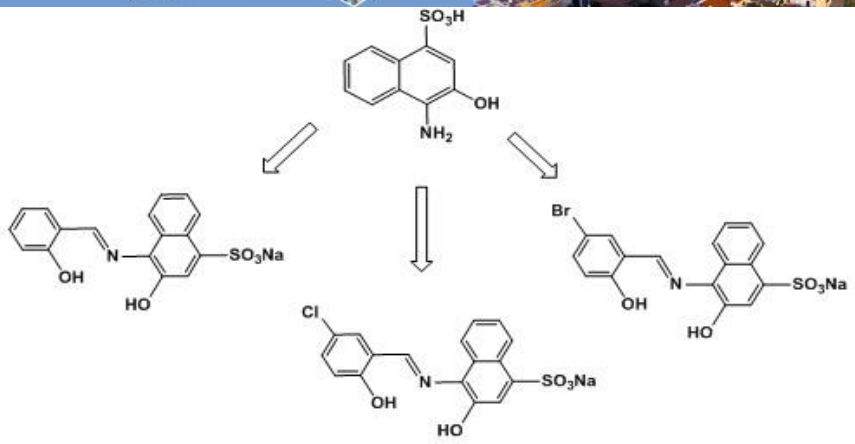
SO3H
OH
NH2
N
SO3Na
OH
HO
Br
Cl

P-470

Synthesis and surface study of Rh nanoparticles stabilized by NHC ligands and their application in selective catalysis

Francisco Martinez Espinar[1], Prof. Carmen Claver[1], Prof. Sergio Castillón[1], Prof. Bruno Chaudret[2], Dr. Cyril Godard[1]

[1]*URV, Tarragona, Spain,* [2]*LPCNO, Toulouse, France*

Poster Session 2

Over the last decades, transition-metal nanoparticles (MNPs) have received a great deal of attention in various areas of research such as optoelectronics, sensing, medicine and catalysis. In catalysis, metal NPs display the advantages of both homogeneous and heterogeneous catalysts, considering that they are extremely active, their reactivity can be modulated and they can be recovered and reused.[1] The stabilization of MNPs can be achieved in the presence of polymers, surfactants or ligands, which allow the control of their size, shape and dispersion as well as their surface state. The choice of an appropriate stabilizer for the MNPs is thus of critical importance to tailor their catalytic performance.[2] Among the reported stabilizing ligands, N-Heterocyclic Carbenes exhibit a strong coordination to the surface of metal NPs and as such provide control of the selectivity of these catalysts.[3,4] Recently, Ru and RhNPs were shown to efficiently catalyze several processes with high selectivity such as hydrogenation of aromatic ketones [5] and the H/D exchange in molecules such as pyridine-containing compounds.[6] In this work, we describe the synthesis of Rh NPs stabilized by N-Heterocyclic carbene ligands. These NPs have been characterized by TEM, IR, TGA, XRD, XPS and also spectroscopic techniques such as liquid and solid state NMR using isotopically labelled ligands to facilitate the location of these stabilizers. The present work also describes their application in selective catalytic processes.

References:

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[6]G.Pieters, C.Taglang, E.Bonnefille, T.Gutmann, C.Puente, J.C.Berthet, C.Dugave, B.Chaudret, B.Rousseau, Angew. Chem. Int. Ed. 2014, 53, 230-234.


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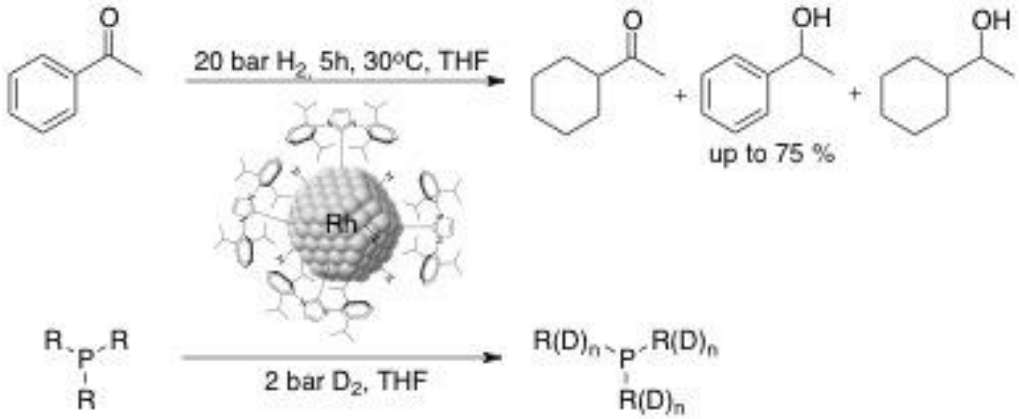
O
20 bar H2, 5h, 30ºC, THF
O
OH
OH
up to 75 %
Rh
R
P
R
R
2 bar D2, THF
R(D)n
P
R(D)n
R(D)n

P-471

Palladium Catalyzed Synthesis of Benzo-fused Carbo- and Heterocycles Through Cascade Processes based on N-Tosylhydrazones.

Miguel Paraja Ramos[1], María del Carmen Pérez-Aguilar[1], Prof. Carlos Valdés[1]
[1]*Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Oviedo, Spain*

Poster Session 2

The cross-coupling reaction between sulfonylhydrazones and organic halides, first described in our research group in 2007,[1] has become since then a very useful transformation in organic synthesis, with applications in the preparation of polysubstituted alkenes, carbocycles and heterocycles.[2]
In the context of our current interest on Pd-catalyzed cascade reactions with sulfonylhydrazones,[3] we turned our attention on processes that combine the migratory insertion typical of the reactions based on tosylhydrazones with an intramolecular Heck reaction. We have found that o-haloallylbenzenes 1 are suitable substrates for this class of cascade reaction under proper catalytic conditions. Thus, after the migratory insertion of the carbene derived from the N-tosylhydrazone on intermediate I, the alkyl palladium complex generated II is intercepted through an intramolecular 5-exo-trig carbopalladation. After the final β-hydride elimination on complex III, indanes with an exocyclic bond 3, and substituted benzofurans 4, can be obtained in a process in which two C-C bonds are formed on the same carbon atom.

References:
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[2] For some reviews see: (a) Barluenga, J.; Valdés, C. Angew. Chem. Int. Ed. (2011), 50, 7486. (b) Xiao, Q.; Zhang, Y.; Wang, J. Acc. Chem. Res. (2013), 46, 236. (c) Liu, Z.; Wang, J. J. Org. Chem. (2013), 78, 10024.
[3] (a) Barluenga, J.; Quiñones, N.; Cabal, M. P.; Aznar, F.; Valdés, C. Angew. Chem. Int. Ed. (2011), 50, 2350. (b) Florentino, L.; Aznar, F.; Valdés, C. Chem. Eur. J. (2013), 19, 10506. (c) Barroso, R.; Valencia, R. A.; Cabal, M. P.; Valdés, C. Org. Lett. (2014), 16, 2264.


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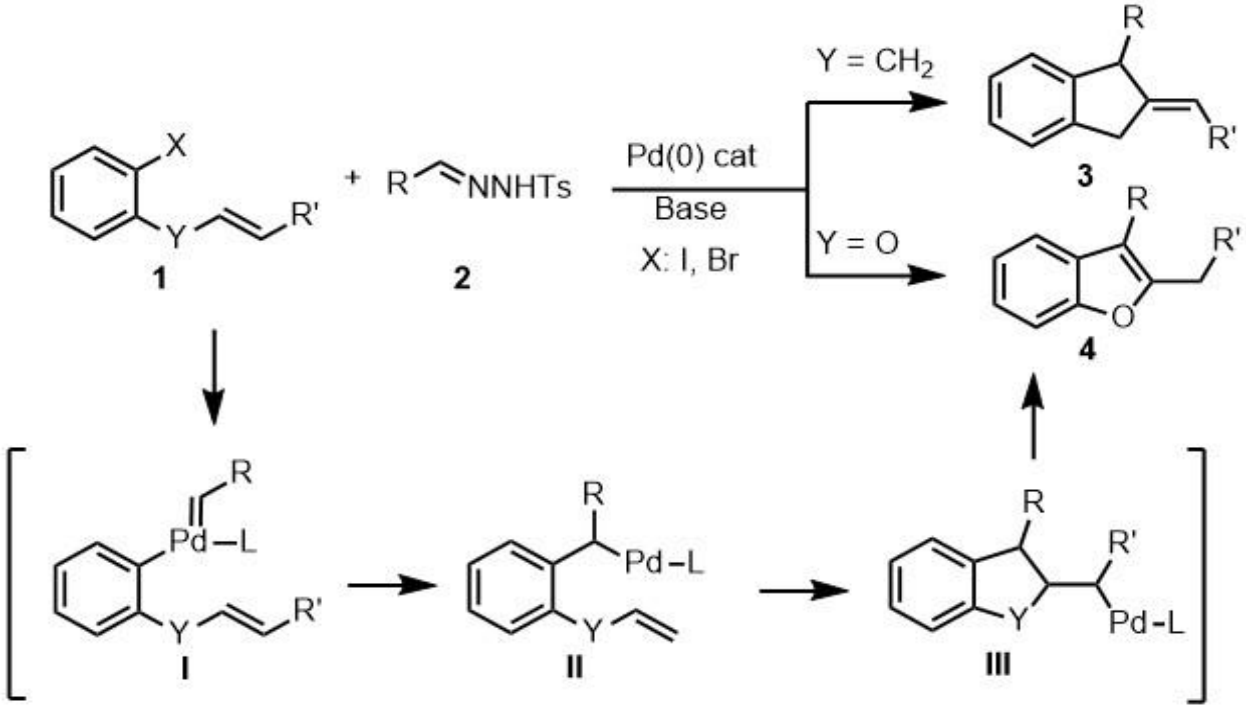
X
Y
R'
1
+
R
NNHTs
2
Pd(0) cat
Base
X: I, Br
Y = CH2
Y = O
R
R'
3
R
R'
O
4
R
Pd–L
Y
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I
R
Pd–L
Y
II
R
R'
Y
Pd-L
III

P-472

A highly improved Heck-Matsuda desymmetrization of cyclopenten-3-ol: towards the exclusive synthesis of 4-arylcyclopentenols scaffolds as Heck products

Dr. Juliana Silva[1], Ricardo A. Angnes[1], Vitor H. M. da Silva[2], Bruno M. Servilha[2], Prof. Ataualpa A. C. Braga[2], Prof. Carlos R. D. Correia[1]

[1]State University of Campinas (Unicamp), Campinas, Brazil, [2]São Paulo University (USP), São Paulo, Brazil

Poster Session 2

The first examples of the enantioselective Heck-Matsuda reaction were reported by Correia et al. in 2012.[1] Recently, we have further demonstrated the synthetic potential of the Heck-Matsuda desymmetrization strategy for the construction of important arylated five-membered carbocyclic scaffolds in a straightforward and efficient manner.[2] In spite of its synthetic potential, the reactions provided mixture of two Heck products identified as the allylic 4-aryl cyclopentenols (3) and the 3-aryl cyclopentanones (4) byproducts.

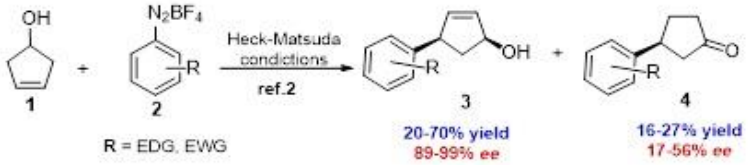
In an attempt to improve the reaction selectivity we investigated the reaction conditions with the support of computational tools. Thus, transition state computational calculations were performed to the migratory insertion step in two different solvents: methanol and toluene. Gratifyingly, calculations have shown us that the hydroxyl group of (1) has a strong stabilizing effect when at the endo position, closer to the cationic palladium. This stabilizing effect was predicted to be even more pronounced in toluene. These results gave us the insight that toluene could provide the aryl cyclopentenols (3) with higher enantioselectivity, while minimizing the formation of the 3-aryl cyclopentanones byproducts. By performing the reaction in toluene, 4-aryl cyclopentenols (3) were obtained as exclusive products, albeit in low yields. However, when we used a binary mixture of toluene and methanol the 4-arylcyclopentenols (3) were obtained exclusively in better yields and higher enantiomeric excess.

References:

[1] Correia, C. R. D.; Oliveira, C. C.; Salles Jr., A. G.; Santos, E. A. F. Tetrahedron Lett. 2012, 53, 3325.

[2] Angnes, R. A.; Oliveira, J. M.; Oliveira, C. C.; Martins, N. C.; Correia, C. R. D. Chem. Eur. J. 2014, 20, 13117.

Previous results



Recent improvements

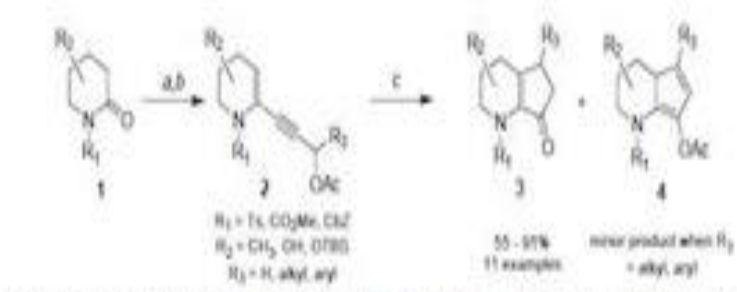
P-473

Synthesis of Cyclopenta-fused Aza-derivatives by Tandem Gold(I)-catalyzed 3,3-Rearrangement/Nazarov Reaction of Propargylic Ester Derivatives

Martina Petrović-Hunjadi[1], Dina Scarpi[1], Ernesto G. Occhiato[1], Béla Fiser[2], Enrique Gómez-Bengoa[2]
[1]*Dipartimento di Chimica "U. Schiff", Università degli Studi di Firenze, Florence, Italy* [2]*Departamento de Química Orgánica I, Universidad del País Vasco (UPV-EHU), Donostia-San Sebastian, Spain*

Poster Session 2

The gold(I)-catalyzed 3,3-rearrangmet of acyl group followed by Nazarov cyclization of N-protected enynyl acetates 2, prepared by Sonogashira coupling of lactam derived enol phosphates or triflates, provides target cyclopentanones 3 in good to excellent yield using hexafluoroantimonate as counter ion while using triflate the acetate 4 was isolated as major product. The whole process has been studied experimentally and computationally, and the influence of the reaction conditions and the structure of the substrates on the reaction rate, regio- and stereoselectivity have been evaluated.
Compared to the tandem process of carbacyclic enynyl acetates, the presence of the N atom influences the regioselectivity of the reaction. Futher, moderate to high torquoselectivity was observed in the ring closure of 4 or 6-methyl substituted piperidines when the propargyl moiety bears a substituent at C3'. Besides tosyl, Cbz and CO2Me as N-protecting groups are also compatible with the reaction conditions while Boc is not. In the end, the scope of the reaction vas extended to azepane and indole.
Combination of easily accessible propargyl alcohols and readily available lactams in the assemblage of the substrates required for the tandem process makes the methodology suitable for the preparation of natural and biologically active cyclopenta-fused N-heterocyclic compounds.



Scheme 1. (a) KHMDS, $(PhO)_2POCl$, -78 °C, THF; (b) alkynol, CuI, $(Ph_3P)_2PdCl_2$, $CHCl_3$, Et_3N, 1-2, 55 °C; (c) Ac_2O, Et_3N, DMAP, DCM, 0 °C to r.t.; (d) 3-5% $Ph_3PAuCl/AgSbF_6$, DCM, RT/reflux

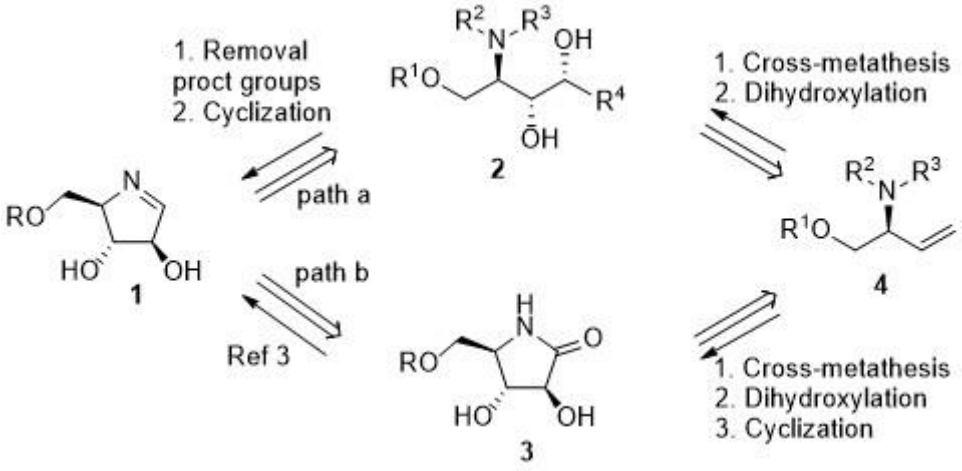
P-474

Enantioselective Formal Synthesis of Nectrisine

Ph.D Student Sebastien Soriano Istat[1], Maribel Matheu[1], Yolanda Díaz[1], Sergio Castillón[1]
[1]*Universitat Rovira i virgili, Tarragona, Spain*

Poster Session 2

Nectrisine 1 is an azasugar isolated from a strain of the fungus Nectricine lucida as immunomodulator FR-900483 and found to exhibit inhibitory activity on α–glycosidases. Moreover, nectrisine is involved in the prevention of different diseases such as Newcastle disease virus.
We recently described that Trost's DYKAT process based on Pd-catalyzed asymmetric allylic amination in combination with cross-metathesis and dihydroxylation reactions is an efficient strategy for accessing important natural products such as sphingosine, phytosphingosine and Jaspine. Here we describe a short, enantioselective formal synthesis of nectrisine based on these reactions as key steps. Two different pathways were explored (paths a,b, Scheme). In path a cyclization to form the imine takes place in the last step, while in path b cyclization to form lactame 3 is first proposed. Allylamine 4 is obtained in high enantiomeric purity by a DYKAT process from racemic butadiene monoepoxide using Pd/DACH as a catalytic system.



P-475

Asymmetric Lactam Synthesis via Pd(0)-Catalysed C(sp3)-H Alkylation

Julia Pedroni[1], Prof. Nicolai Cramer[1]
[1]*Laboratory of Asymmetric Catalysis and Synthesis, EPF Lausanne, Lausanne, Switzerland*

Poster Session 2

Chemical transformations that allow for a build-up of molecular complexity by means of transition metal catalysed C-H bond functionalisation are becoming attractive alternatives to classical synthetic routes. While Pd(0)-catalysed arylations of C(sp3)-H bonds are well precedented, the corresponding alkylation reactions remain challenging.[1]

Herein, we report enantioselective lactam synthesis using a Pd(0)-catalysed C(sp3)-H alkylation protocol.[2] Lactams are commonly found as structural motif in many natural and unnatural biologically active compounds.[3] Concerning lactams with a stereogenic center at the β-position, classical cyclisation strategies require enantiomerically enriched acyclic precursors. Our enantioselective C-C bond forming approach allows for their synthesis from achiral, readily accessible α-chloroamides in good yields and selectivities.

References:
[1] Baudoin, O., Chem. Soc. Rev. 2011, 40, 4902; Li, H.; Li, B-J.; Shi, Z-J., Catal. Sci. Technol. 2011, 1, 191.
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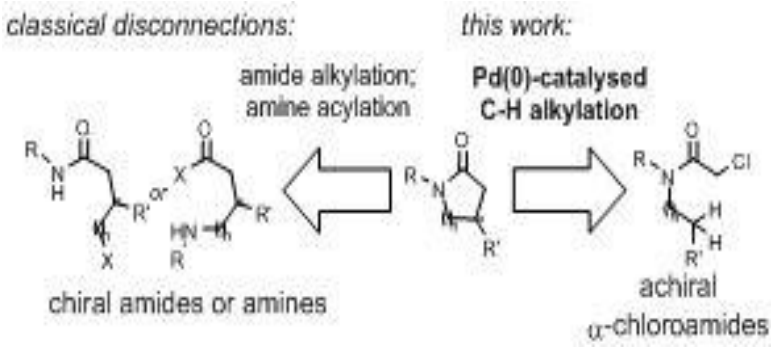
[3] Ye, L.-W.; Shu, C.; Gagosz, F., Org. Biomol. Chem. 2014, 12, 1833; Pitts, C. R.; Lectka, T., Chem. Rev. 2014, 114, 7930; Escolano, C.; Amat, M.; Bosch, J., Chem. Eur. J. 2006, 12, 8198.



P-476

Selective Hydrogenation of Quinolines with Co-containing MOF catalyst

Dr. Feng Chen[1], Dr. Annette-Enrika Surkus[1], Dr. Lin He[1], Dr. Marga-Martina Pohl[1], Dr. Christoph Topf[1], Dr. Kathrin Junge[1], Prof. Dr. Matthias Beller[1]

[1]*Leibniz Institute for Catalysis (LIKAT Rostock), Rostock, Germany*

Poster Session 2

We developed a novel Co_3O_4/NGr@α-Al_2O_3 NPs catalyst featuring a core-shell structure and a graphitic layer around the cobalt particles upon pyrolysis. This Co-containing metal-organic framework (MOF) catalyst has been successfully applied in the hydrogenation of quinolines. The peculiar structure of the catalyst enables both high activity and selectivity in this hydrogenation process. The Co_3O_4/NGr@α-Al_2O_3 NPs catalyst is stable under air atmosphere and it could be recycled up to six times with a little loss of activity. This is crucial for its application in industry because the recycle possibility is an important issue for the development of heterogeneous catalyst. Furthermore, 5 gram scale catalyst also was synthesized and shows high activity for the model reaction with 94% yield. Notably, this Co_3O_4/NGr@α-Al_2O_3 NPs catalyzed system could facilitate the 10 mmol scale hydrogenation of quinoline under standard conditions in 90% yield.The results of the scaled up reactions and the recycling experiments indicate that supported Co NPs have a bright future in the hydrogenation of heteroaromatic nitrogen compounds to corresponding saturated N-heterocycles which represent important building blocks in the pharmaceutical industry as well as in medicinal chemistry.[234]

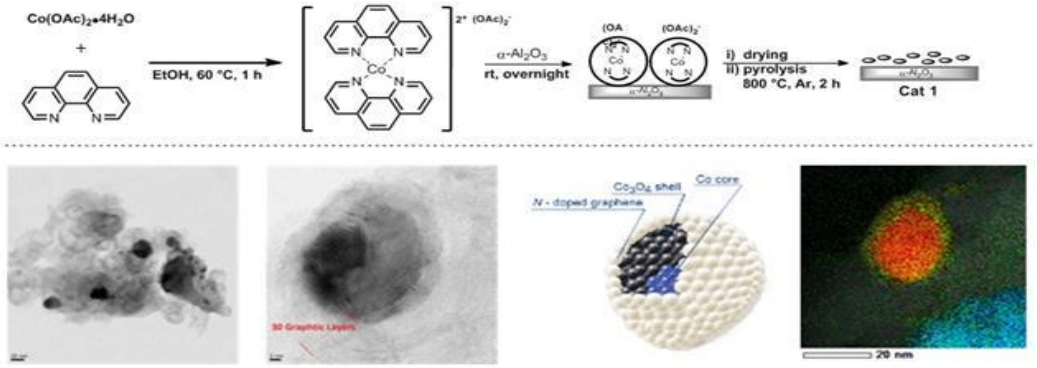
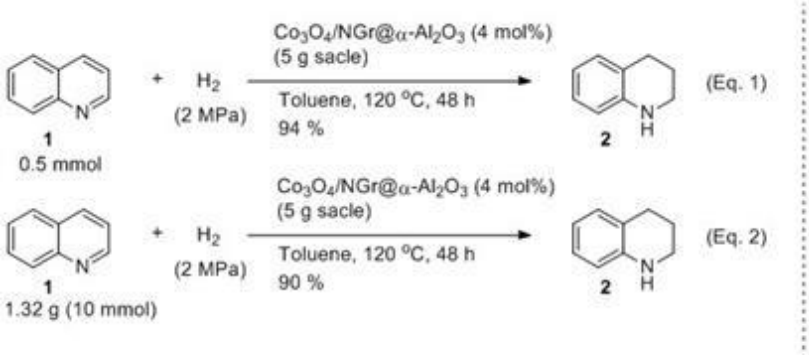


Figure 1. Preparation and Characterization of Co_3O_4/NGr@α-Al_2O_3 NPs Catalyst



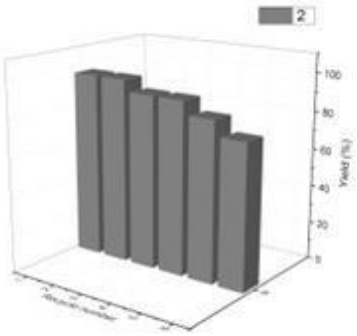


Figure 2. Scaled Up Reactions and Recycling Experiments

P-477

Functionalization of imidazo[1,2-a]pyridines mediated by LiHMDS

Simone Cavalcante Silva[1], Ph.D. Shirley M.M. Rodrigues[1], MsC Evelyn M. L. Pina Diniz[1], Ph.D. Samuel R. A. Ferreira[1], MsC João Henrique Carvalho Batista[1], Ph.D. Giuliano Cesar Clososki[1]
[1]*Universidade De São Paulo, Ribeirão Preto, Brazil*

Poster Session 2

Imidazopyridines structures are present in a large quantity of biological relevant molecules displaying a variety of pharmaceutical properties. In addition, imidazo[1,2-a]pyridines ring show interesting biological activities such as antiinflammatory, antiparasitic, antiviral, antiulcer, antibacterial and antifungal. [1,2] In this work, the metalation of some imidazo[1,2-a]piridines has been investigated using lithium and mixed lithium/magnesium organometallic reagents.[3] LiHMDS was found to be the best base promoting the deprotonation in mild conditions. In addition, the reaction of the corresponding organolithium intermediates with different electrophiles has allowed the synthesis of the desired products in good yields (Figure 1).
Aiming to evaluate the influence of an electron withdrawing substituent at the imidazopyridine, the 7-chloro-3-phenylimidazo[1,2-a]pyridine (2a) was also studied. Interestingly, the metalation with LiHDMS occurred with high selectivity at the position C-2 leading to the expected derivatives in yields varying from 65 to 90% after reaction with electrophiles. Application of this methodology and its applicability towards the shynthesis of biologically active molecules are being investigated in our laboratories.

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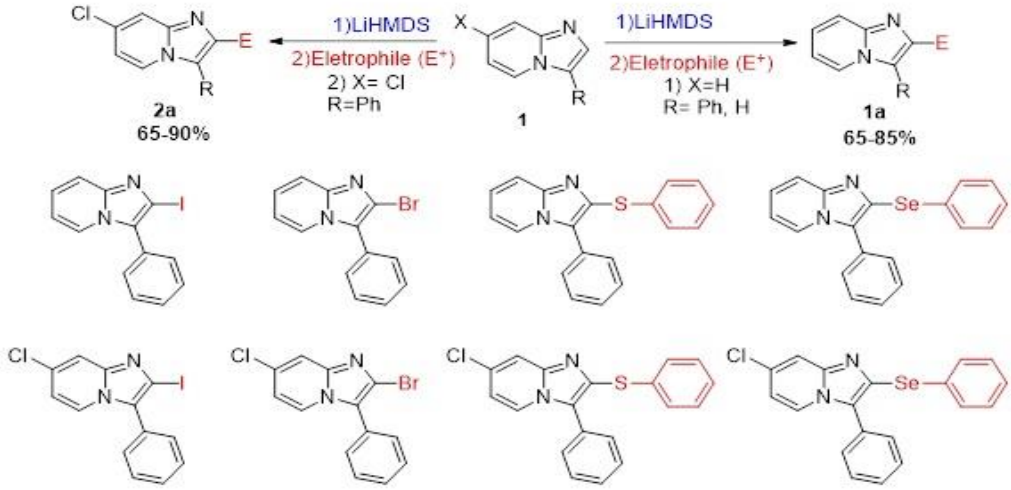

Figure 1. Some examples synthesized

P-479

Heteroatom-directed C–H Borylation of Functionalized Alkanes Catalyzed by Silica-supported Monophosphine–Ir Systems

Ryo Murakami[1], Kiyoshi Tsunoda[1], Dr. Tomohiro Iwai[1], Dr. Masaya Sawamura[1]
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Poster Session 2

Transition metal catalyzed borylation of C–H bonds in alkyl groups of organic molecules offers a powerful tool for the synthesis of alkylboronates, improving the overall efficiency[1] [2]. Recently, we reported heteroatom-directed borylation of primary and secondary C–H bonds of 2-alkylpyridines catalyzed by an Ir complex with a silica-supported monophosphine ligand Silica-SMAP[3]. In addition, C–H borylations of N-alkylated amides, ureas and aminopyridines at the position α to the N atom were achieved with a heterogeneous Rh catalyst system using a triptycene-type immobilized phosphine ligand Silica-TRIP[4]. Herein, we report that combination of Silica-SMAP as a ligand and $[Ir(OMe)(cod)]_2$ as a metal precursor produced a heterogeneous catalyst system which was effective for heteroatom-directed C–H borylation of alkanes functionalized with various N-containing heterocyclic compounds. This reaction occurs under relatively mild conditions with excellent site-selectivity at the position γ to the N atom of the heterocycles, affording the corresponding alkylboronates. C–H borylations of cyclopropane and cyclobutane derivatives proceeded at exceptional cis stereochemistry relative to the directing group[5]. The site- and stereoselectivities of these reactions suggest that the C–H bond cleavage occurred with the assistance of a proximity effect due to N-to-Ir coordination.

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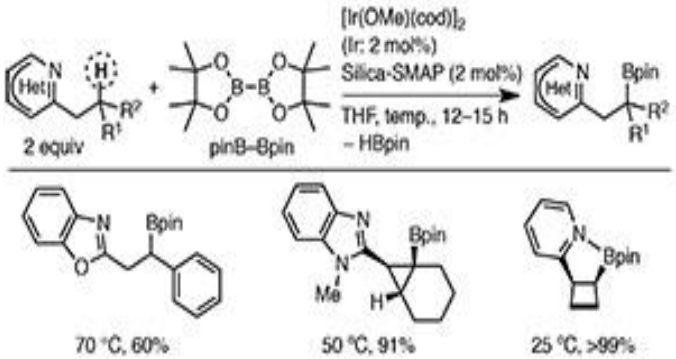

P-480

Progress in the Enantioselective Total Synthesis of Rumphellaone A

Phd Beatrice Ranieri[1], Dr. Carla Obradors[1], Dr. Javier Carreras[1], Dr. Laura López[1], Dr. Antonio Maria Echavarren[1]

[1] *Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

In the last decade gold catalysis has been employed successfully in the synthesis of natural products, allowing the construction of complex structures under mild conditions and according to atom economy.[1] Because of our interest in total synthesis, [2] we wish to report our efforts toward the asymmetric total synthesis of rumphellaone A, which belongs to the family of caryophyllene-related sesquiterpenes and was isolated from the gorgonian coral Rumphella antipathies.[3] According to the retrosynthetic strategy, the main cyclobutane ring could be formed by an asymmetric gold-catalysed [2+2] cycloaddition between commercially available phenylacetylene and 6-methylhept-5-en-2-one, followed by hydrogenation. Oxidation of the phenyl ring to carboxylic acid, stereoselective allylation and reverse Wacker oxidation are other pivotal reactions of our synthetic plan.

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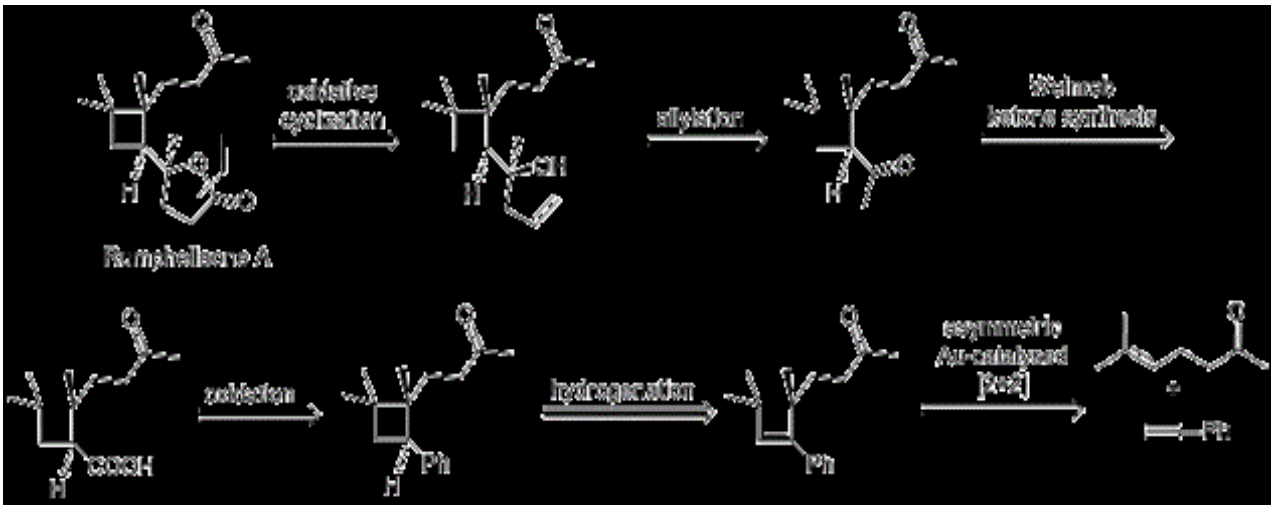

P-481

Synthesis of benzofuran derivatives by the palladium-catalyzed reaction of 2-haloallyl esters and phenols

Mr. Takumi Udagawa[1], Mr. Eito Nomada[1], Mr. Hirotaka Watanabe[1], Mr. Mitsuaki Yamamoto[1], Ms. Maki Minakawa[1], Mr. Motoi Kawatsura[1]

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Poster Session 2

Generally, the palladium-catalyzed reaction of allylic substrates with nucleophiles proceeds through the π-allylpalladium and provides allylic substituted products or cyclopropane derivatives. However, there is an alternative reaction process for the palladium-catalyzed reaction of 2-haloallyl compounds with nucleophiles, and the reaction mainly affords doubly substituted products. Recently, our group also reported double substitution reaction of 2-fuluoroallyl substrates with carbon or oxygen nucleophiles. In line with our palladium-catalyzed reaction of 2-fluoroallyl compounds, we succeeded in obtaining benzofuran derivatives by the palladium-catalyzed reaction of 2-haloallyl esters with phenols. The reaction of 1a, 1b and 1c with phenol (2a) by [Pd(C3H5)Cl]2/DPPP produced 2-benxylbenzofuran (3a) in 89%, 83% and 90% yield, respectively (Figure). Reactions of 1a with several phenols also proceeded in moderate to good yield.

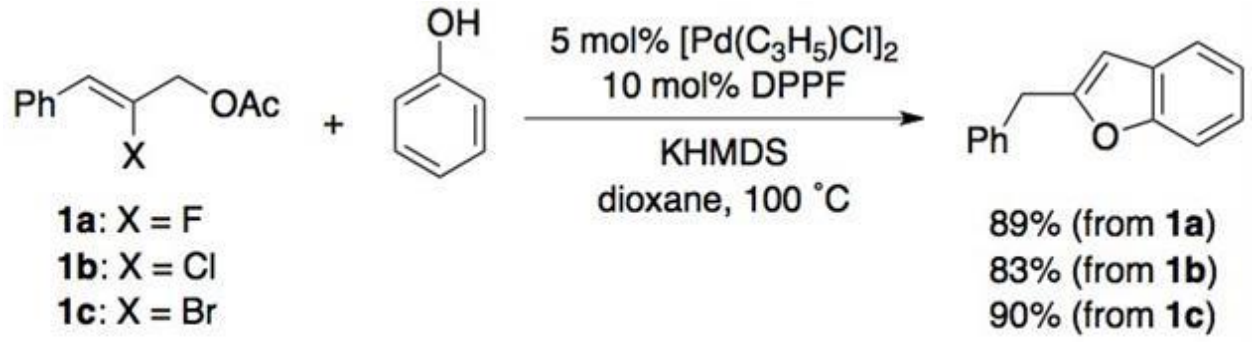

Figure. Palladium-catalyzed reaction of 2-haloallyl acetates with phenol.

P-482

Ru-Catalyzed Synthesis of N-Unsubstituted α-Silylimines: Formimine Analogues for Diverse Access toward Homoallylic Amines

Mr. Wook Jeong[1], Dr. Jaiwook Park*[1], Dr. Young Ho Rhee*[1]
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Poster Session 2

Homoallylic amines are versatile synthetic intermediates for the numerous bioactive natural products. Thus, the development of efficient synthetic methods for homoallylic amines is an important goal in synthetic organic chemistry. Recently, Ru-catalyzed synthesis and characterization of N-unsubstituted imines from alkyl azides under photolytic condition had been developed.[sup]1)[/sup] Next, we investigated the formation of N-unsubstituted α-silylimines, which could be potent formimine analogues due to the ease of the removal of silyl group by protodesilylation. We envisioned this formimine analogue could allow for the stereoinduction at allylic position of homoallylic amines.
This presentation will describe Ru-catalyzed synthesis of N-unsubstitued α-silylimine from silylmethyl azide and its synthetic usage for diverse access to homoallylic amines. Highly substituted homoallylic α-silylamines possessing multiple stereocenters with high enantioselectivity and diastereoselectivity were generated by allylations of N-unsubstituted α-silylimines.[sup]2)[/sup] After protodesilylation, γ-selective adduct was afforded. We also discovered desilylative formal [1,3]-sigmatropic rearrangement of homoallylic α-silylamine to give α-selective adduct.[sup]3)[/sup] High diastereoselectivity and chirality transfer between substrate and product was noted.

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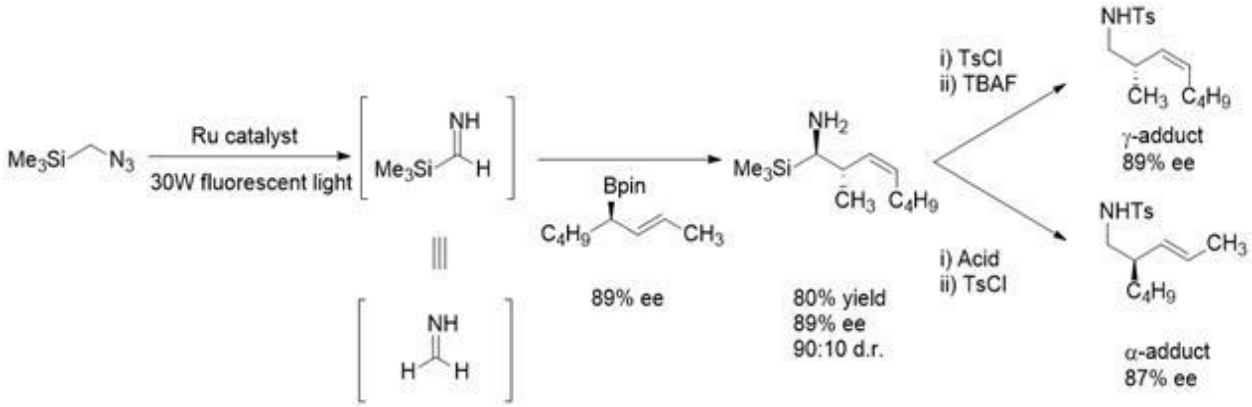

P-483

Development of a synthetic process to optically active heterocyclic fused-ring primary amines

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[1]*Takeda Pharmaceutical Company Limited, Yodogawa-ku/Osaka, Japan*

Poster Session 2

A new synthetic method for optically-active heterocyclic fused-ring amines via rhodium-catalyzed asymmetric hydrogenation of protected ketimines followed by deprotection is presented. In our investigation, (R)-chroman-4-amine (R-CA), was selected as a target compound for two reasons: firstly, it was a core structure of one of our candidates for an active pharmaceutical ingredient, and secondary, there were some drawbacks in the previously reported asymmetric synthesis of R-CA. Relatively high catalyst loadings are required for metal-catalyzed hydrogenation of ketimines,[sup]1 [/sup] while conversion is not a problem when ω-transaminazes are used.[2] To develop an industrial process that will contribute to improved productivity and be applicable for scale-up, we decided to use a ketimine substituted by benzoylhydrazine,[3] CIBH, that is easily obtained in a single step. After extensive screening of the reaction conditions, we found efficient [Rh(cod)2]OTf/ (S)-3,5-Xylyl-BINAP catalysis could afford the corresponding amine, R-CABH, in 77% ee, which was then successfully increased by recrystallization from toluene/heptane to 99% ee. In the subsequent deprotection step, hydrogenolysis mediated by Raney-Nickel containing iron showed good chemoselectivity to give R-CA without loss of enantioselectivity. The present method furnished R-CA in 52% yield from CIBH.

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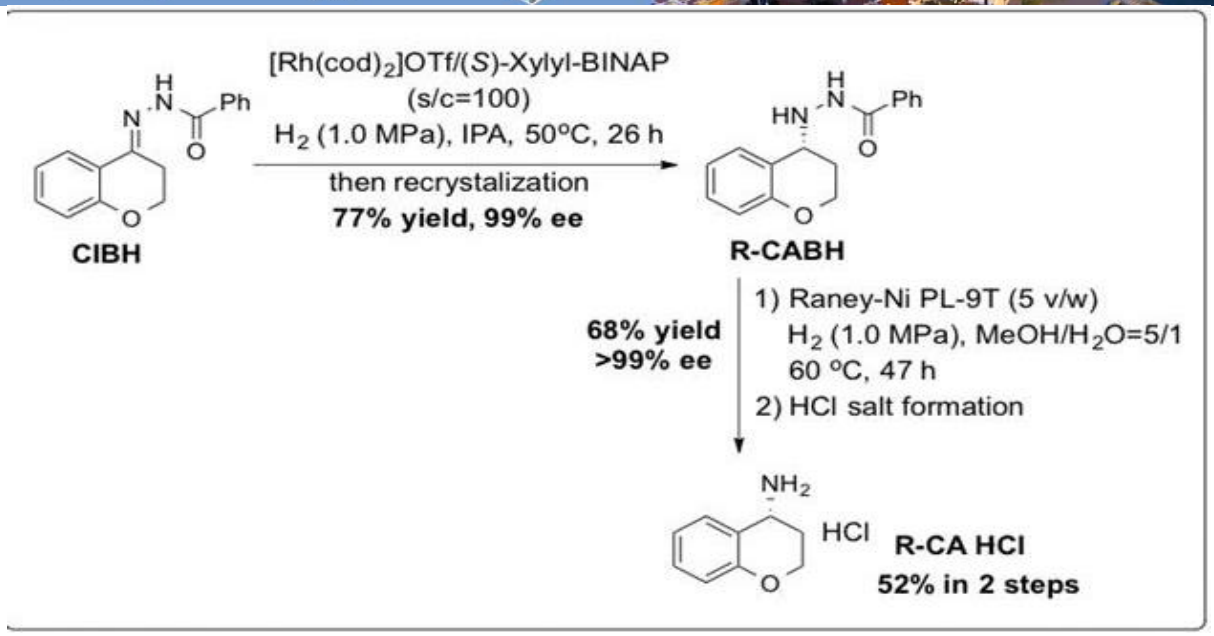
[Rh(cod)2]OTf/(S)-Xylyl-BINAP
(s/c=100)
H2 (1.0 MPa), IPA, 50°C, 26 h
then recrystalization
77% yield, 99% ee
CIBH
R-CABH
68% yield
>99% ee
1) Raney-Ni PL-9T (5 v/w)
H2 (1.0 MPa), MeOH/H2O=5/1
60 °C, 47 h
2) HCl salt formation
HCl
R-CA HCl
52% in 2 steps

P-484

Gold(I)-Catalyzed 1,5-OR Migration / Cyclization: Key Reaction Sequence for the Total Synthesis of Sesquiterpenes

Dr. Óscar Pablo[1], Prof. Dr. Antonio M. Echavarren[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

As part or a program aimed at the synthesis of natural sesquiterpenes, we targeted (+)-schisanwilsonene A (1) which was isolated from Schisandra wilsoniana, a medicinal plan indigenous to southern China.[1] This natural product has shown to be a potent antiviral agent against the hepatitis B displaying higher activity than current over-the-counter drugs (e.g. Epivir-HBV® or Zeffix®).
In 2013 we reported the first total synthesis of (1), where the key reaction sequence 1,5-migration / cyclization was catalyzed by gold.[2] Nevertheless, partial racemization and low yield in the Au-mediated reaction was obtained as a result of a competitive 1,2-shifting of the –OAc migrating group.
Now we are looking for new routes that improve the former features of the synthesis. Preliminary results show –OPNP (p-nitrophenoxy) is a promising migrating group: the use of starting material bearing –OPNP prevents racemization (SM = 89% ee in the starting material leads to 89% ee in the product), and enhances remarkably the chemical yield (78-80%).
Further improvements will be presented in the near future.

Acknowledgments:
We thank MICINN (project CTQ2010-16088/BQU), MINECO (Severo Ochoa Excellence Accreditation 2014-2018, SEV-2013-0319), the European Research Council (Advanced Grant No. 321066), and the ICIQ Foundation for support.

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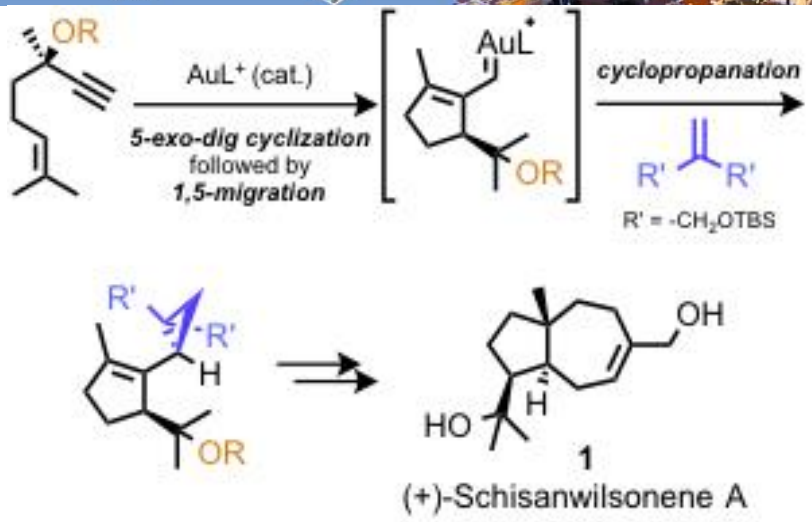
OR
AuL+ (cat.)
5-exo-dig cyclization
followed by
1,5-migration
AuL
OR
cyclopropanation
R'
R'
R' = -CH2OTBS
R'
R'
H
OR
OH
HO
H
1
(+)-Schisanwilsonene A

P-485

Cycloaddition Reactions of Diazoalkane Ruthenium Complexes with Chiral PNNP Ligands

Prof. Antonio Mezzetti[1], Mr. Joël Egloff[1]
[1]*ETH Zurich, Dept of Chemistry & Appl. Biosciences, Zurich, Switzerland*

Poster Session 2

We have recently reported that $[RuCl(OEt_2)(PNNP)]SbF_6$ (2), prepared from $[RuCl_2(PNNP)]$ (1) and $(Et_3O)SbF_6$, catalyzes the asymmetric aziridination of imines in the presence of ethyl diazoacetate (EDA) with the intermediacy of an EDA complex.[1] We find now that complex 2 reacts with dimethyl 2-diazomalonate (3a), methyl 2-diazo-2-phenylacetate (3b), or methyl 2-diazo-3-phenylpropanoate (3c) to give the stable diazoalkane complexes trans-[RuCl(NNCR¹R²)(PNNP)][sup]+[/sup] (4a-c). At –20 °C, cis addition occurs, and the resulting adducts slowly isomerize at room temperature to the trans products, which were isolated as air- and moisture-stable solids. Inspired by a recently reported stoichiometric reaction of such diazoalkane complexes,[2] we have used the methyl 2-diazo-2-phenylacetate adduct $4bBF_4$ to catalyze the dipolar [3+2] cycloaddition of acrylonitrile onto diazoalkane 2b, which gives methyl 3-cyano-5-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate (5b) with low enantioselectivity (ca. 10% ee). More insight into the catalytic reaction will be presented.

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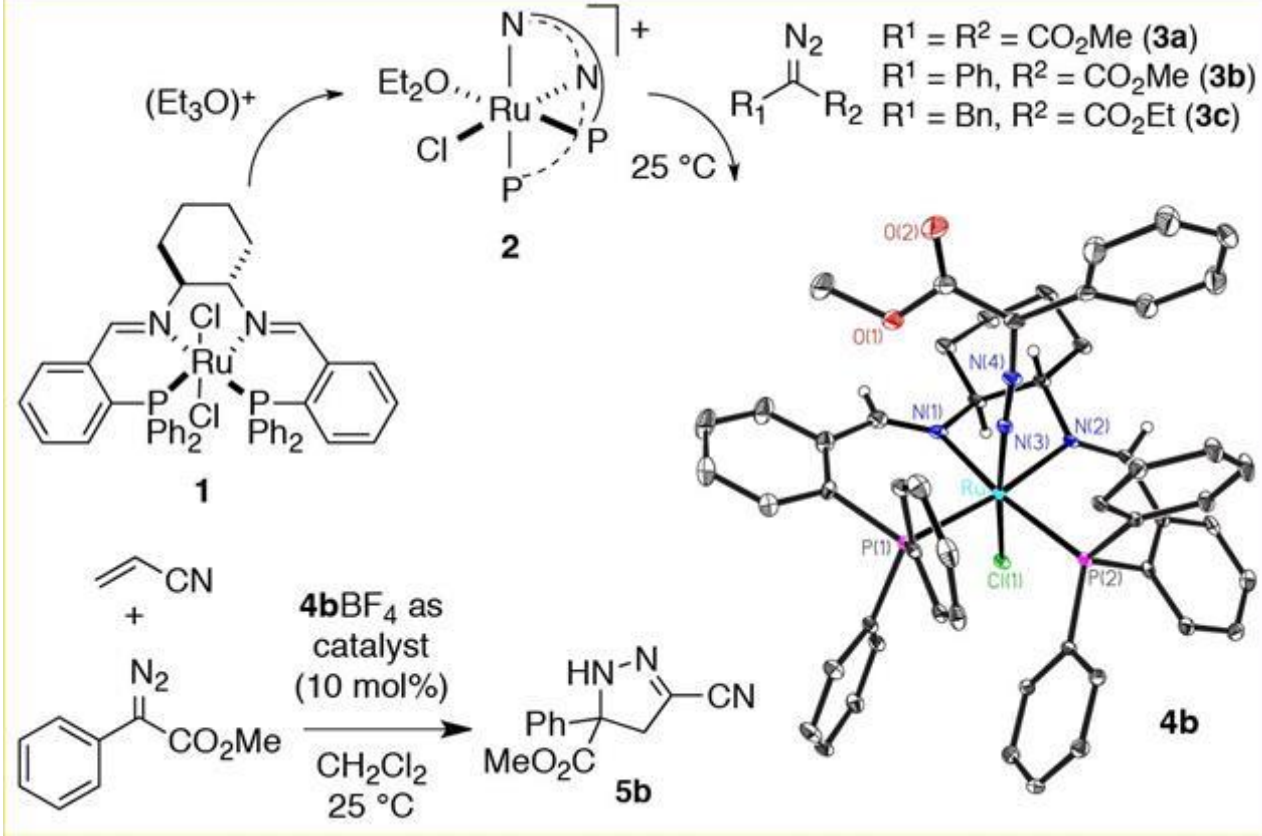


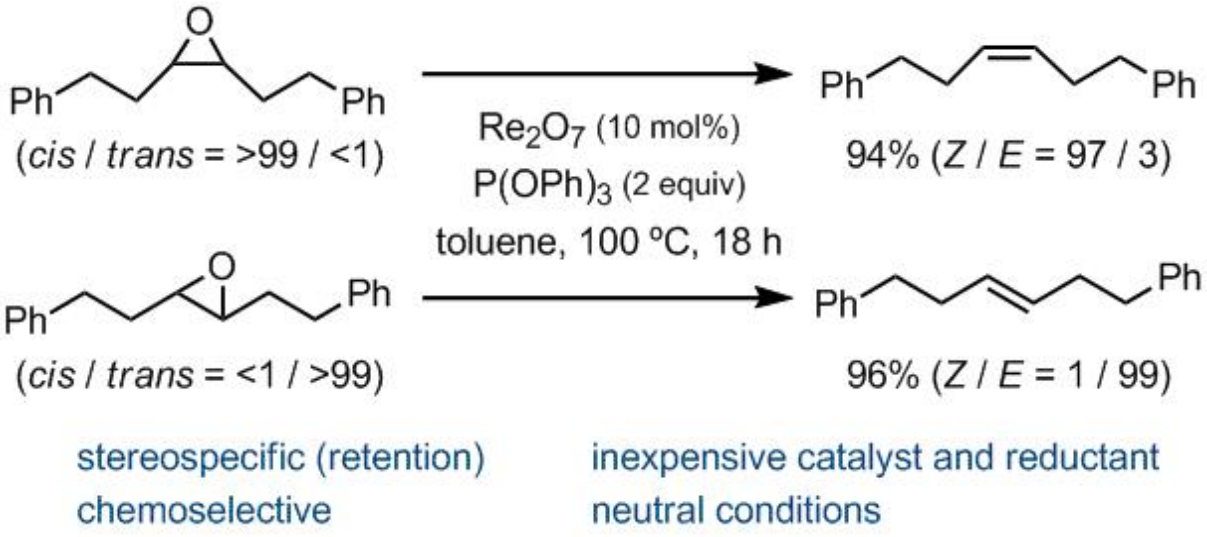
P-255

Stereospecific Deoxygenation of Aliphatic Epoxides to Alkenes under Rhenium Catalysis

Prof. Kazuhiko Takai[1], Dr. Masahito Murai[1], Mr. Takuya Nakagiri[1]
[1]*Okayama University, Okayama, Japan*

Poster Session 1

The combination of a catalytic amount of rhenium(VII) oxide and triphenyl phosphite as a reductant is effective for the deoxygenation of unactivated aliphatic epoxides to alkenes stereospecifically. The reaction proceeds with retention of the configuration of variously substituted epoxides under neutral conditions, and is compatible with various functional groups. Protection and deprotection of a double bond functionality using an epoxide are shown as an example of the current rhenium-catalyzed deoxygenation protocol. The effect of reductants for the stereoselectivity has also been studied, indicating that the use of electron deficient phosphines or phosphites is the key for the stereospecific deoxygenation.



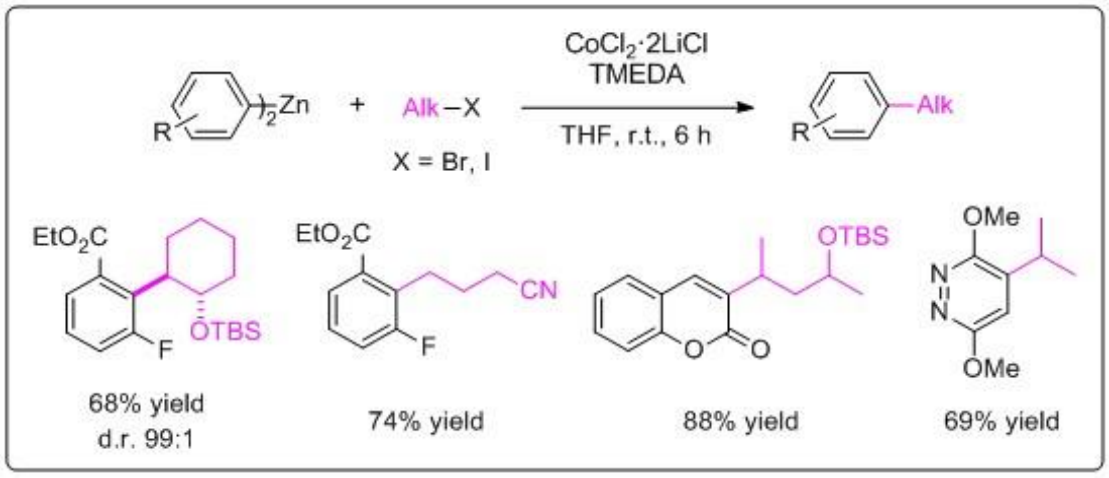
P-486

Co-Catalyzed Negishi Cross-Coupling Reactions of Arylzinc Reagents with Primary and Secondary Alkyl Halides

Diana Haas[1], Jeffrey Hammann[1], Prof. Paul Knochel[1]
[1]*LMU Munich, Munich, Germany*

Poster Session 2

Transition metal-catalyzed cross-coupling reactions are valuable tools for C-C bond-forming reactions and so far, Pd- or Ni-catalyzed cross-coupling reactions dominate this field, but have several drawbacks, such as the metal toxicity or high price, as well as the requirement of sophisticated ligands. The cobalt-catalyzed cross-coupling of di(hetero)arylzinc reagents with primary and secondary alkyl halides using THF soluble $CoCl_2 \cdot 2LiCl$ and TMEDA as a ligand, leads to the alkylated products in up to 88% yield (Scheme 1). A range of functional groups (e.g., COOR, CN, CF_3, F) are tolerated. Remarkably, we do not observe rearrangement of secondary alkyl iodides to unbranched products. Additionally, the use of cyclic TBS-protected iodohydrins leads to trans-2-arylcyclohexanol derivatives in excellent diastereoselectivities (d.r. up to 99:1).



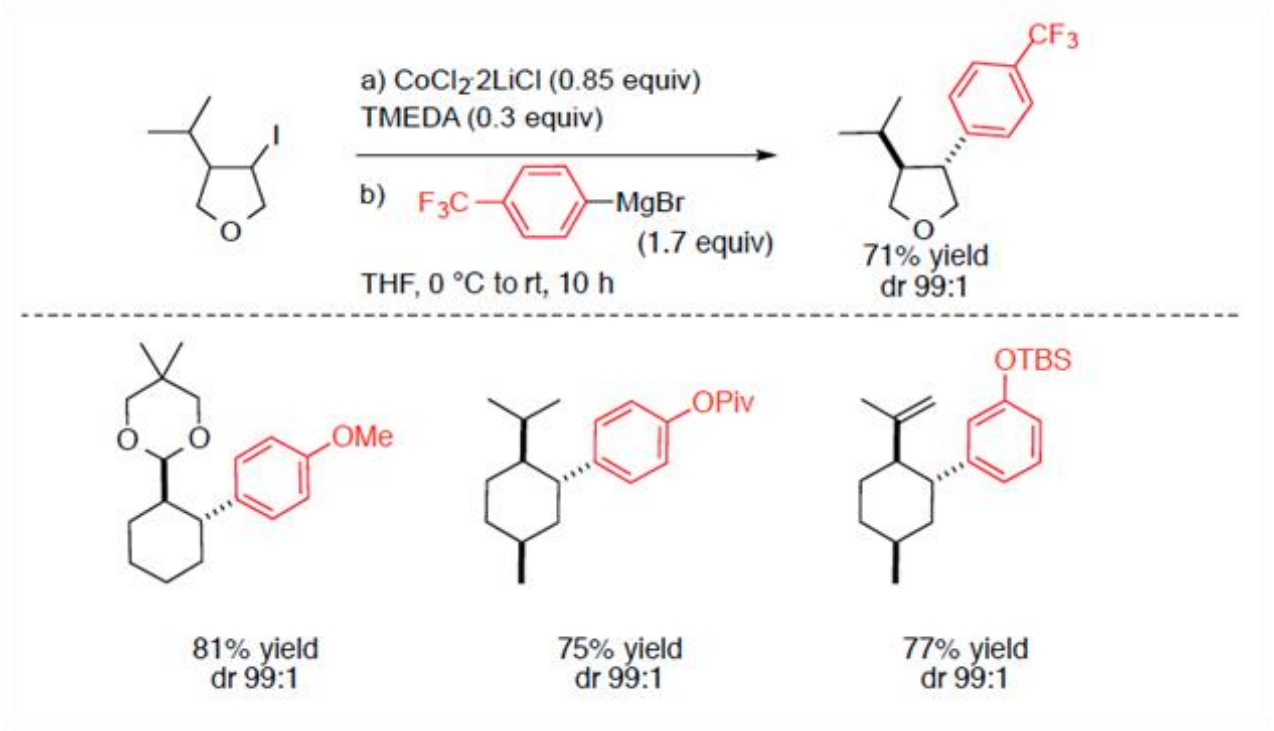
P-487

Cobalt-Mediated Diastereoselective Cross-Coupling Reactions between Alkyl Halides and Arylmagnesium Reagents

PhD Student Jeffrey Hammann[1], Diana Haas[1], Prof. Paul Knochel[1]
[1]*LMU Munich, Munich, Germany*

Poster Session 2

Stereoselective functionalizations of organic molecules are of great importance to modern synthesis. A stereoselective preparation of pharmaceutically active molecules is often required to ensure the appropriate biological activity. Thereby, diastereoselective methods represent valuable tools for an efficient set-up of multiple stereo centers. We report a highly diastereoselective Csp^3–Csp^2 cross-coupling reaction of various 2-substituted alkyl iodides with a broad set of arylmagnesium reagents in the presence of THF soluble $CoCl_2$·2LiCl and TMEDA as a ligand leading to the trans coupling products in good yields and dr up to >99:1. A range of functional groups are tolerated in the Grignard reagent (e.g., COOMe, CN, CF_3, SF_5). Furthermore, heterocyclic alkyl iodides are also excellent substrates for this cobalt-mediated arylation.



P-489

Carboxylative cyclization of propargylamines and allenylmethylamines catalyzed by group 11 metal complexes

Dr. Yoshihito Kayaki[1], Mr. Shun Hase[1], Mr. Kyohei Yamashita[1], Dr. Takao Ikariya[1]
[1]*Tokyo Institute of Technology, Tokyo, Japan*

Poster Session 2

Formation of carbamic acids and their salts from carbon dioxide (CO_2) and amines is a key step leading to a range of urethanes. We recently reported that the carboxylation of propargylamines using CO_2 is promoted by gold(I) complexes bearing an N-heterocyclic carbene (IPr; 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) ligand to afford 5-alkylidene-2-oxazolidones as a 5-exo-dig cyclization product in methanol under neutral and mild conditions.[1] We disclose here that the regioselectivity can be switched to favor the 6-membered cyclic urethanes by using 2,2,2-trifluoroethanol as the solvent in the reaction of primary propargylamines (Scheme 1). As catalytic intermediates, alkenylgold complexes having a 5- or 6-membered urethane moiety were successfully isolated, and the ring expansion on the alkenyl ligand was demonstrated by treatment of 2,2,2-trifluoroethanol. The reverse ring contraction from the alkenyl complex containing the 6-membered urethane did not proceed, and no isomerization from the 5-membered urethane product occurred under the catalytic conditions. These results accommodate a proton-induced isomerization mechanism involving a 1,2-shift of the gold center on the alkenyl ligand to give the 6-endo-dig cyclization product.
For the reaction of allenylmethylamines with CO_2, an IPr-coordinated acetatosilver(I) complex, Ag(OAc)(IPr), showed better catalytic performance than the gold and copper variants, and proved to be beneficial to enhance the chemoselectivity with suppressing the intramolecular hydroamination, leading to 5-alkenyl-2-oxazolidones. The mechanistic aspects will also be discussed.

References
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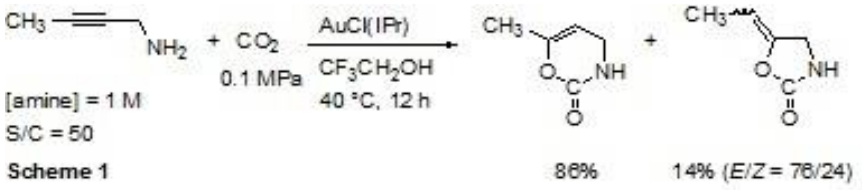

Scheme 1

P-490

Palladium-catalyzed regioselective hydroalkylation of 2-fluoroallyl acetates: Synthesis of vinylmalonic acid ester derivatives

Mr. Ryo Suzuki[1], Ms. Shihori Kuki[1], Mr. Takashi Futamura[1], Mr. Mitsuaki Yamamoto[1], Ms. Maki Minakawa[1], Mr. Motoi Kawatsura[1]

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Poster Session 2

The palladium-catalyzed reaction of allylic substrates with nucleophiles generally provides allylic substituted products or cyclopropane derivatives. However, there is an alternative reaction process for the palladium-catalyzed reaction of 2-fluoroallyl compounds with nucleophiles, and the reaction mainly affords doubly substituted products. Recently, our group also reported double substitution reaction of 2-fuluoroallyl substrates with carbon or oxygen nucleophiles. In line with our palladium-catalyzed reaction of 2-fluoroallyl compounds, we demonstrated the palladium-catalyzed regioselective hydroalkylation reaction of 2-fluoroallyl acetates with malonic esters and triethylsilane, then succeeded in obtaining the vinylmalonic acid ester derivatives in good yield with a high stereoselectivity.

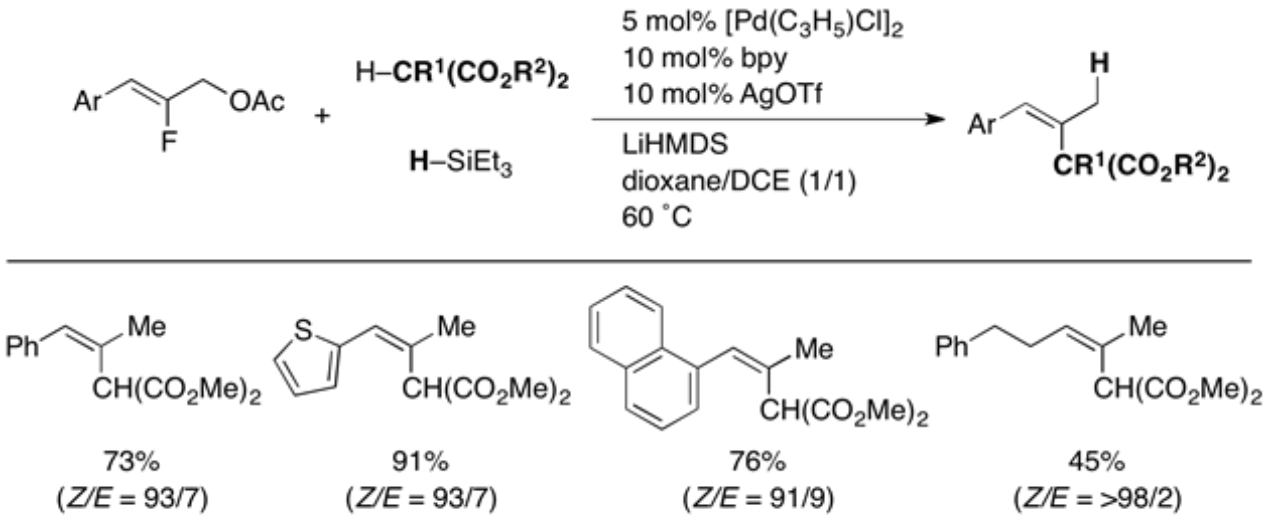

Figure. The palladium-catalyzed hydroalkylation of 2-fluoroallyl acetates.

P-491

Orthogonal Reactivity of Acyl Azides in C-H Activation: Dichotomy Between C-C and C-N Amidations Based on Catalyst Systems

Kwangmin Shin[1]

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[2]*Center for Catalytic Hydrocarbon Functionalization, Institute of Basic Science (IBS), Daejeon, Republic of Korea*

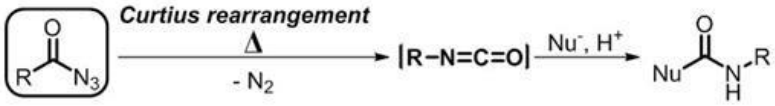
Poster Session 2

Transition metal-catalyzed direct C-H bond functionalization has emerged as a straightforward tool for the construction of carbon-carbon or carbon-heteroatom bonds. Along with the notable advances in the C-H bond activation methods, metal-mediated C-H addition to carbon-carbon multiple bonds have been extensively investigated. On the other hand, C-H addition across unsaturated carbon-nitrogen bonds is still in its infancy. In particular, procedures allowing for the direct insertion of C-H bonds into isocyanates are highly demanding since it can effectively provide synthetically valuable amide moieties.

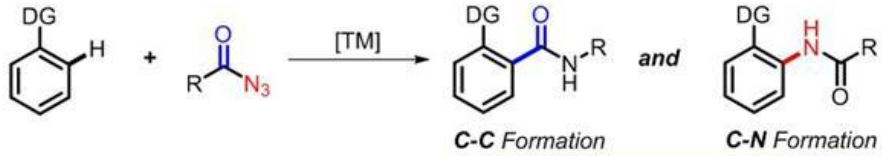
Acyl azides have been widely used in organic synthesis, and, among those examples, the most notable utility is to employ them as precursors for isocyanates via the 'Curtius rearrangement' which can be induced most often thermally. However, to the best of our knowledge, acyl azides have never been applied to the direct C-H functionalization as precursors of isocyanates mainly due to the difficulty of controlling dual reactivity of acyl azides, thus leading to a mixture of C-C and C-N amidated products.

In the context of our studies to utilize organic azides as efficient amino sources in the C-H functionalizations, we were curious about whether acyl azides can be employed in a selective manner, thus serving not only as an amino source but also as a carbon donor. As a proof of concept, we developed the first example of controlling the dual reactivity of acyl azides between C-C and C-N amidations depending on catalyst systems. In addition, mechanistic aspects of this orthogonal selectivity were also investigated.

a) Conventional Utility of Acyl Azides



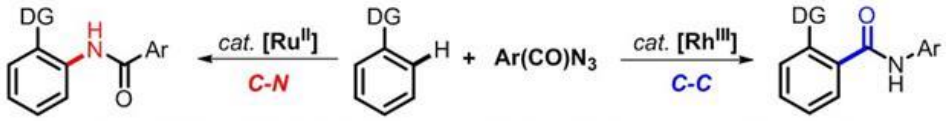
*b) Application to Catalytic C-C Bond Formation - **Selectivity Issue***



***C-C** Formation* ***C-N** Formation*

Mixture of C-C & C-N Products

c) This Work - Controlling Reactivity



- ✓ ***Dual reactivity** of acyl azides: C-C vs C-N Amidations*
- ✓ ***Orthogonal selectivity** based on catalyst systems: Rh vs Ru*
- ✓ ***Mechanistic dichotomy:** Chemoselective Control vs Kinetic Control*

P-492

Ortho-selective palladium catalyzed arylation of anilides via photoredox catalysis

Mr. Balázs Tóth[1], Mr. Zsombor Gonda[1], Mr. Gergő Sályi[1], Dr. Timothy J. Peelen[2], Dr. Zoltán Novák[1]
[1]MTA-ELTE „Lendület" Catalysis and Organic Synthesis Research Group, Eötvös University, Institute of Chemistry, Budapest, Hungary, [2]Lebanon Valley Collage, Department of Chemistry, College Ave Annville, US

Poster Session 2

Our research focused to the study of visible light photocatalytic arylation of anilides via C-H activation in the presence of palladium catalysts. We achieved a regioselective oxidative coupling reaction between acetanilides and aromatic diazonium salts. The desired C-C bond was formed with the aid of organic photosensitizing molecules, ruthenium based photocatalysts, palladium compounds and visible light irradiation. The reaction conditions were studied in order to explore the scope and limitation of this transformation including chemical behaviour of the reactants and technical parameters.
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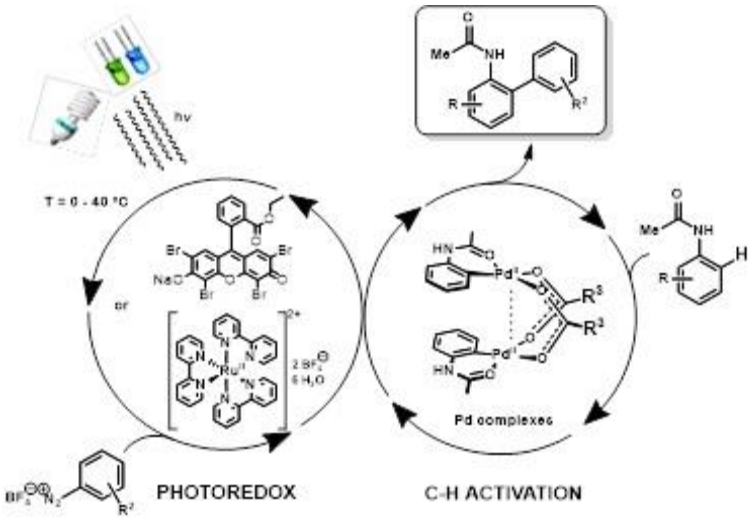


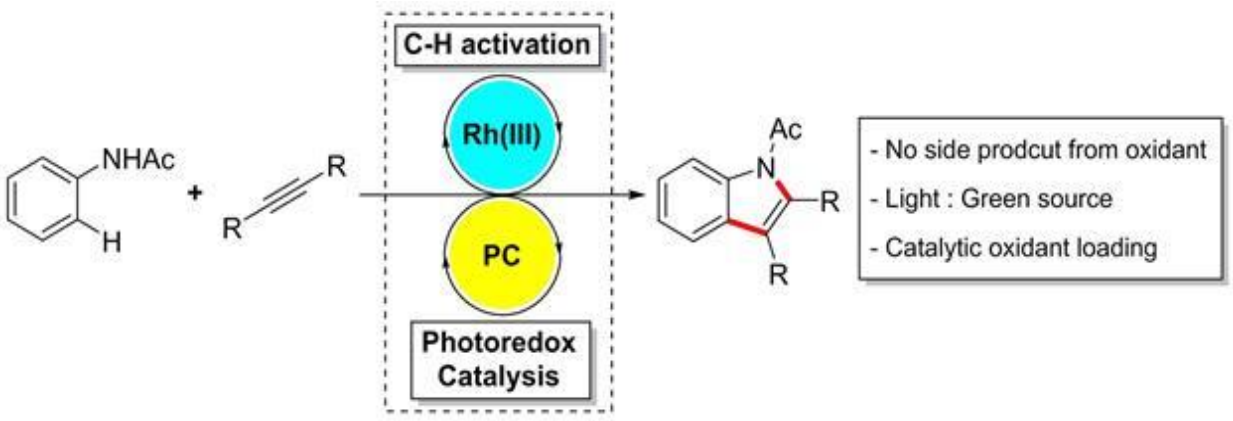
P-493

Assistance of Photoredox Catalysis in C-H Activation for the Synthesis of Nitrogen Containing Heterocycles

Dr. Hyunjin Kim[1], David C. Fabry[1], Steffen Mader[1], Prof. Magnus Reuping[1]
[1]*RWTH Aachen University, Aachen, Germany*

Poster Session 2

The cyclization reaction of acetanilide with alkyne derivatives has been accomplished via direct C-H activation pathway in presence of a photoredox catalysis. The efficient merge of commercially available Rh(III) and photocatalyst under the irradiation of 11 W CFL afforded not only indole but also pyrrole derivatives with acceptable efficiency. The cyclization reaction of acetanilide with alkyne derivatives has been accomplished via direct C-H activation pathway in presence of a photoredox catalysis. The efficient merge of commercially available Rh(III) and photocatalyst under the irradiation of 11 W CFL afforded not only indole but also pyrrole derivatives with acceptable efficiency. Mechanistic studies also provided evidence of the independent role of each catalyst.



P-494

Ruthenium Catalyzed Activation and Amidation of Carboxylic Acids

Thilo Krause[1], Sabrina Baader[1], Benjamin Erb[1], Prof. Dr. Lukas J. Goossen[1]
[1]*TU Kaiserslautern, Kaiserslautern, Germany*

Poster Session 2

Within the last decades the field of amide bond formation has gained more and more attention since a huge number of amides and peptides have shown interesting biological activity. As the direct coupling of carboxylic acids and amines is only possible at highly elevated temperatures with a resulting low tolerance towards functional groups[sup][1][/sup], a broad variety of coupling agents such as DCC and EDC have been developed. However their use leads to high costs and the production of large amounts of waste, which is often hard-to-separate.[sup][2,3][/sup]
As an alternative we have investigated the in-situ activation of carboxylic acids with alkynes to form enol esters. A subsequent aminolysis step would yield the corresponding amides along with an easily-removable ketone as the only byproduct.
Firstly we developed an air- and water-stable Ru[sup]IV[/sup] system that is able to promote the formation of enol esters from 1-hexyne and a variety of carboxylic acids in good to excellent yields. The following aminolysis step can be performed by simply adding the amine to the reaction mixture. This easy applicable one-pot, two-step procedure transforms a broad variety of carboxylic acids with amines to the corresponding amides in good to excellent yields.
Furthermore, by varying the reaction parameters, we were able to activate carboxylic acids in the presence of amines, which yielded the corresponding amides in a shortened and simplified reaction procedure. Ongoing work is directed towards determination of the substrate scope and mechanistic investigations of this reaction.

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[2] E. M. Bradley, Chem. Soc. Rev. 2009, 38, 606
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water, 80 °C, 14 h
60%
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P-495

Spontaneous hydrosilylation in mono-, di-, and tri-iminopyrrolide substituted silanes

MSc Léon Witteman[1], BSc Tim Evers[1], MSc Shu Zhan[1], Dr Martin Lutz[1], Dr Marc-Etienne Moret[1]
[1]*Utrecht University, Utrecht, Netherlands*

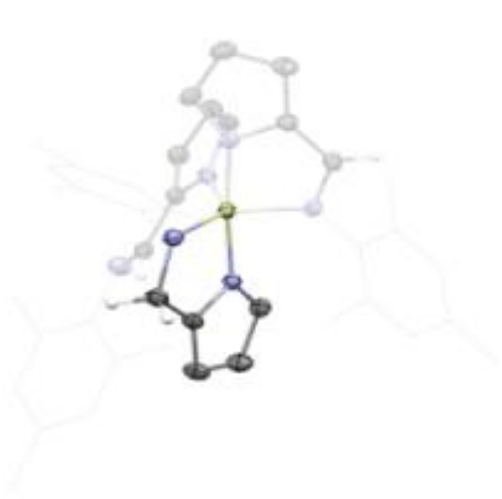
Poster Session 2

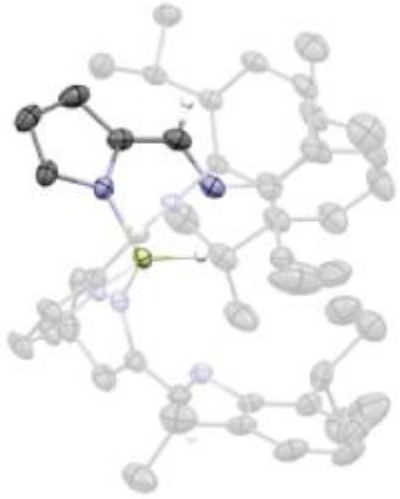
N-substituted silanes are of interest as precursors for strongly donating, high-field silicon(II) ligands such as silylenes and silanides.[1,2] In that context, electron-withdrawing pyrrole substituents are in principle attractive to stabilize reduced silicon species. Here we report on an unusual[3] imine hydrosilylation process discovered during our attempts to synthesize Schiff-base stabilized pyrrolylsilanes. The structural elements that favor or disfavor this process are also investigated.

Reaction of $HSiCl_3$ with iminopyrrole derivatives in the presence of Et_3N yields a range of silanes. In certain cases, hydrosilylation converts the imine ligand into an amido substituents. This reaction is inhibited by factors such as steric bulk, substitution on the imine carbon atom, and increased electron density on Si.

In a tri-substituted silane with mesitylimino moieties hydrosilylation is allowed (Figure 1) in contrast to the diisopropylphenyl (dipp) analogue (Figure 2). In both di- and mono-substituted silanes the dipp moiety does allow hydrosilylation. Substitution of H for Me on the imine carbon atom in a di-substituted silane results in a distinct HCl elimination reaction that keeps the Si-H bond intact. Slow hydrosilylation is observed in mono-substituted $LSiHCl_2$ but not in LSiHMeCl, suggesting that hydrosilylation is inhibited by additional electron density on silicon.

[1] Brück, A. et al., Angew. Chem. Int. Ed. Engl. 51 (2012) 11478
[2] Hübler, K., Roper, W. R., Wright, L. J., Organometallics 16 (1997) 2730
[3] For related examples: Lippe et al. Organometallics 28 (2009) 621 and Novák et al. Chem. Eur. J. 20 (2014) 2542





P-496

Synthesis of Coibacin D and Its Analogues

Mgr. Kristýna Kolská[1], Prof. RNDr. Martin Kotora[1]
[1]*Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Praha, Czech Republic*

Poster Session 2

Development of new asymmetric processes is one of the objectives of catalysis in organic chemistry. These processes can provide access to chiral building blocks applicable in syntheses of various natural substances that can be used for medical purposes. One such process is preparation of chiral homoallyl alcohols, which have been used for syntheses of variety of biologically active compounds. In view of aforementioned, suitably substituted homoallyl alcohols could be used as intermediates in syntheses of coibacins A-D, which have a number of interesting biological properties. Natural coibacins A-D are metabolites isolated from marine cyanobacterium Oscilatoria sp. that exhibits selective anti-leishmanial activity and potent anti-inflammantory properties.[1]

The first asymmetric synthesis of the main intermediate 1 of coibacin D was based on enantioselective allylation of 6-heptenal with allylboronic acid pinacol ester.[2] Further synthetic steps included esterification of the formed homoallyl alcohol with acryloyl chloride and ring closing metathesis in the presence of Grubbs catalyst.[3] Subsequent cross-metathesis of the main intermediate with different alkenes and prepared lipofilic fragment provided analogues of coibacin D 2.

This work was supported by the Czech Science Foundation (No. 207/11/0587).

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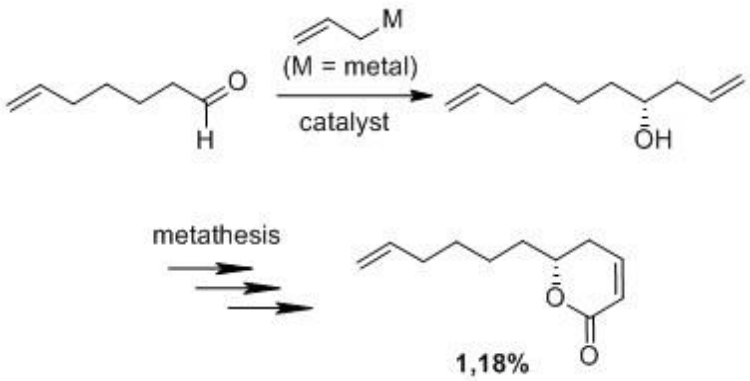


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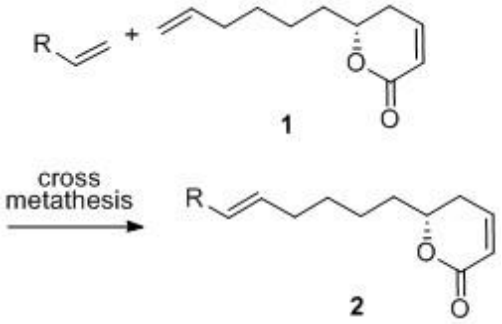
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1
cross
metathesis
R
O
O
2

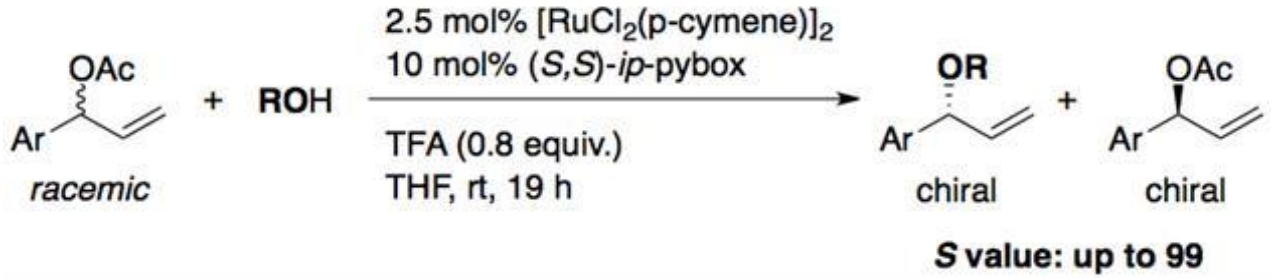
P-497

Kinetic resolution in the ruthenium-catalyzed asymmetric allylic etherification of monosubstituted allylic acetates

Mr Toru Shinozawa[1], Mr Shou Terasaki[1], Ms Maki Minakawa[1], Mr Motoi Kawatsura[1]
[1]*NIHON University, , Japan*

Poster Session 2

We demonstrated the kinetic resolution of the racemic allyl acetates with alcohols by the [Ru/chiral-pybox] catalyzed allylic etherification. The selective kinetic resolution took place at room temperature in 19 h and produced both optically active allyl acetate (substrate) and allyl ether (product) with high S values (up to 99).



P-498

A new approach to Chromeno[4,3-B]Quinolines by copper-catalyzed oxidative ring closure of arylpropynyloxybenzonitriles with iodonium salts

Ms Klara Aradi[1], Dr. Zoltán Novák[1]
[1]*MTA TKI, Budapest, Hungary*

Poster Session 2

Copper-catalyzed syntheses of aromatic and heteroaromatic systems are intensively studied areas of current organic syntheses. Recently, our research group developed a novel copper-catalyzed reaction for the synthesis of iminobenzoxazines from ortho-cyanoanilides and diaryliodonium salts[1] using the concept of aromatic electrophile generation via the intermediacy of Cu(III) species.[2,3]

Based on the theory of these cyclization modes, we developed a new procedure in which arylpropynyloxy-benzonitriles can be straightforwardly transformed to chromeno[4,3-b]quinolines with iodonium salts in the presence of copper-catalyst via the formation of new C-C and C-N bonds. The developed methodology enables the versatile synthesis of chromenoquinoline derivatives with high modularity due to the easily variable functional groups built in the reaction.

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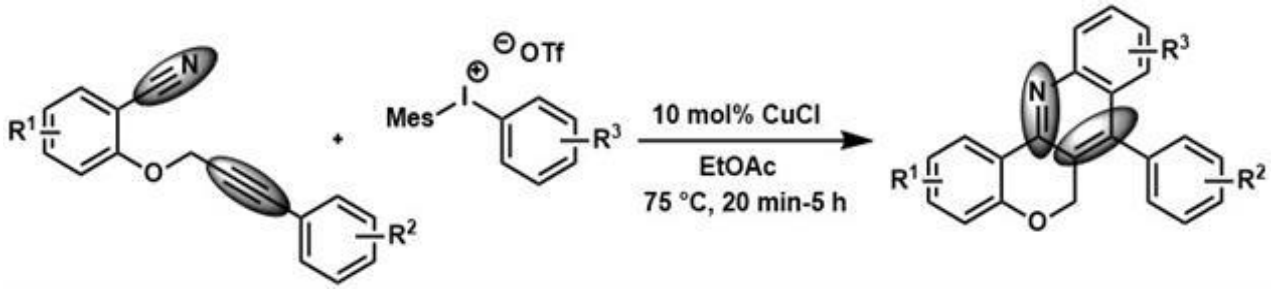
3. (a) Wang, Y.; Chen, C; Zhang, S.; Lou, Z.; Su, X.; Wen, L.; Li, M.; Org. Lett. 2013, 15, 4794–4797; (b) Wang, Y.; Chen, C.; Peng, J.; Li, M.; Angew. Chem. Int. Ed. 2013, 52, 5323–5327.



P-499

Orthogonality in the Hiyama Coupling of Cyclic Alkenylsiloxanes: Mechanistic Insights and Applications Towards Polyene Natural Product Syntheses

Ms Bryony Elbert[1], Dr Edward Anderson[1]
[1]*University of Oxford, Oxford, UK*

Poster Session 2

Organosilanes are highly useful in organic synthesis, particularly in their role as Hiyama-Denmark cross coupling partners, where they offer an attractive, non-toxic alternative to Stille and Suzuki procedures.[1] Cyclic alkenylsiloxanes (such as 1, Scheme 1) represent a valuable class of coupling reagent, and can be synthesised in a straightforward manner from alkynylsiloxanes.[2] They have the potential to install both a Z-double bond and stereogenic alcohol centre, thus generating a motif found in many biologically active natural products (2).

We have uncovered a ring size-dependent orthogonality of cyclic alkenylsiloxanes in palladium-mediated cross coupling: 5-membered species couple under both fluoride- and base-promoted conditions, whilst their 6-membered analogues are inert to the latter (Scheme 1).[2] This poster will present an in-depth exploration of this phenomenon. We have investigated the mechanism of the reaction, leading to insights into the origins of orthogonality, and improved selectivity for productive coupling over deleterious side processes. Further orthogonal couplings, dependent on the variation of the alkyl groups on silicon, will also be discussed, which lead to a uniquely flexible array of silane agents for controlled and selective coupling. The high utility of cyclic alkenylsiloxanes in cross coupling will be demonstrated with applications towards the synthesis of several bioactive polyketide natural products.

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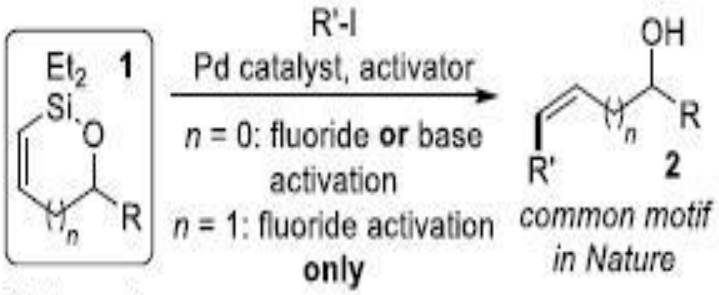

Scheme 1

P-500

Gold-acetonyl complexes: from side-products to valuable synthons

Miss Danila Gasperini[1], Dr. Alba Collado[1], Dr. Adrian Goméz-Suárez[1], Dr. David B Cordes[1], Prof. Alexandra M Z Slawin[1], Prof. Steven P Nolan[1,2]

[1]EastChem, School of Chemistry, University of St Andrews, St Andrews, UK [2]Chemistry Department College of Science, King Saud University, Riyadh, Saudi Arabia

Poster Session 2

The serendipitous discovery of the first Au(I)-N-heterocyclic carbene (NHC) acetonyl complex is presented.[1] This complex, [Au(IPr)(CH_2COCH_3)] (IPr = N, N'-bis(2,6-diisopropylphenyl)imidazole-2-ylidene), first observed as side-product from the synthesis of [Au(NHC)(Cl)] from NHC HCl salts,[2] could be isolated as a single species and turned into a useful gold synthon. A library of gold acetonyl complexes bearing the most common NHC was synthesised by straightforward procedures, starting from easily and commercially available precursors. These new derivatives, bearing an acetonyl fragment, belong to the family of organogold-enolates,[3] organometallic compounds proposed to be involved as short-lived intermediates in organic transformations.

We demonstrated that the complexes bearing the most commonly used IPr and IMes ligands, are versatile precursors of a variety of organogold complexes. Furthermore, their ease of preparation renders them attractive alternatives for the well-known [Au(NHC)(Cl)] or [Au(NHC)(OH)] complexes.

Furthermore, [Au(IPr)(acetonyl)] was tested in common gold(I) catalysed reactions, with satisfying results: the complex is a useful pre-catalysts for the hydration of alkynes to ketones[4] and the rearrangement of propargylic acetates to selectively obtain substituted allenes or indenes.[5]

The investigation of these intriguing species is just at the beginning. Further studies will reveal the potentiality and applicability of these promising Au-acetonyl complexes.

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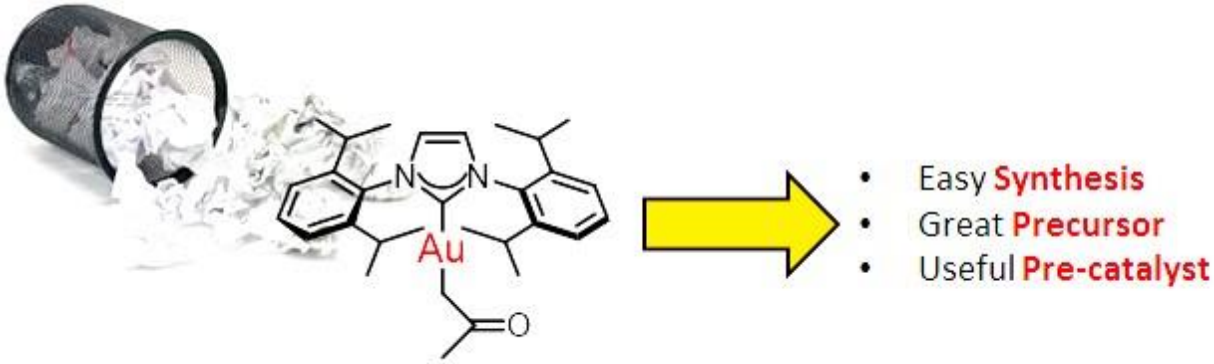
N
N
Au
O
Easy Synthesis
Great Precursor
Useful Pre-catalyst

P-501

Towards the Enantioselective Intermolecular [2+2] Cycloaddition of Alkynes with Alkenes

Cristina García-Morales[1], Imma Escofet[1], Dr Laura López[1], Prof Antonio Echavarren[1]
[1] *Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

Several asymmetric gold(I) catalyzed transformations have been discovered the last few years.[1] Although these major advances, the development of enantioselective intermolecular cycloadditions of alkynes is still challenging.[2] In 2010, our group reported the formation of regioselective cyclobutenes by a gold(I)-catalyzed cycloaddition of alkynes with alkenes.[3] Recently, we found that cationic gold complexes with BAr_4^{F-} as counterion are superior catalysts for this reaction.[4]
In order to develop an asymmetric [2+2] cycloaddition of alkynes with alkenes, many chiral gold complexes were examined by using the HTE. Josiphos digold(I) complexes were found to be the most efficient catalysts giving moderate to excellent yields and good enantiomeric excesses.

Acknowledgments:
We thank MINECO (project CTQ2010-16088/BQU, Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319), the European Research Council (Advanced Grant No. 321066), Cellex Foundation, and the ICIQ Foundation for financial support. CG acknowledges the MINECO for a FPI fellowship.

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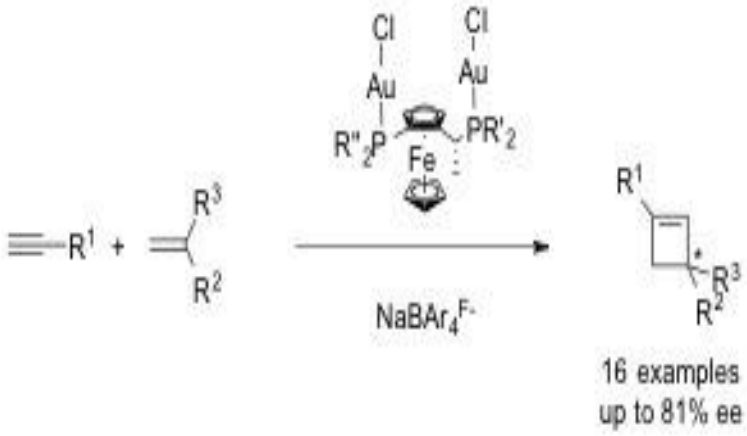

P-502

Synthesis and Characterization of Schiff Base and Metal Complexes Containing Sulphonic Acid Group

Msc Gizem Gümüşgöz[1], Prof. Dr. Bilgehan Güzel[1], PhD Seda Kozay[1], Prof. Dr. Selahattin Serin[1]
[1]*Çukurova University, Adana, Turkey*

Poster Session 2

Polydentate ligands and solubility of their metal complexes are of high importance as it gives catalytic activity to these substances in various mediums. Existence of various functional groups bonded to these ligands is one of the factors affecting solubility of the ligand. Particularly those which contain sulphonic acid and their metal complexes are known as having a soluble form in water and basic medium as well as high stability and different UV/Vis properties. This study aims to synthesize ONO-type tridentate Schiff base.

In this work, tridentate ligands that contain sulpho group and that have high solubility and stability have been synthesized by way of condensation reactions using 3-amino-4-hydroxy-benzenesulfonic acid, with 5-chloro salicylaldehyde (Figure 1), 2-hydroxy-3-methoxybenzaldehyde (Figure 2) and 5-bromo salicylaldehyde, respectively. As a result, Zn(II), Cu(II) and Ni(II) complexes of these ligands have been obtained (Figure 4). The structures synthesized have been characterized with the help of various instrumental analysis methods including IR, 1H NMR and Elemental Analysis, and their thermal stability has been determined by employing TG/DTA. Furthermore, catalytic activities of synthesized complexes have been investigated.

Acknowledgment: This study is sponsored by Scientific And Technological Research Council Of Turkey (TUBITAK) (No: 113Z280)

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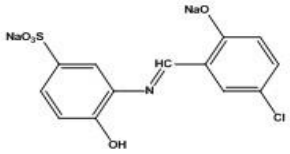

Figure 1

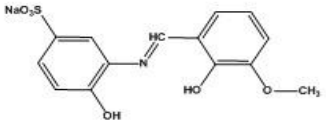

Figure 2

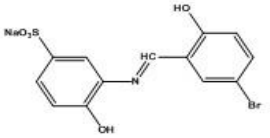

Figure 3

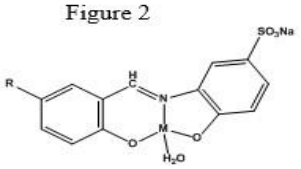

Figure 4.M=Ni(II), Cu(II), Zn(II)

P-503

Functionalization of Phospha-Thiahelicenes and application of their Gold(I) Complexes in Enantioselective Catalysis

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Poster Session 2

Helically chiral structures are known to display peculiar properties and applications in many fields, including asymmetric catalysis. However, both the synthesis of helical phosphorus ligands and their uses in enantioselective organometallic catalysis have been underdeveloped so far [1].
In the course of our studies on helical phosphane derivatives as potential chiral ligands in asymmetric organometallic catalysis [2], we have recently reported the synthesis of a new chiral phospha-thiahelicene based gold (I) complex, which is an excellent and selective pre-catalyst for the enantioselective cycloisomerization of N-tethered enynes [3].
On the basis of these very promising results we have effectively functionalized the phospha-thiahelicene scaffold to obtain new gold (I) complexes, which are then tested as pre-catalysts in other challenging enantioselective cycloisomerization reactions.

References:
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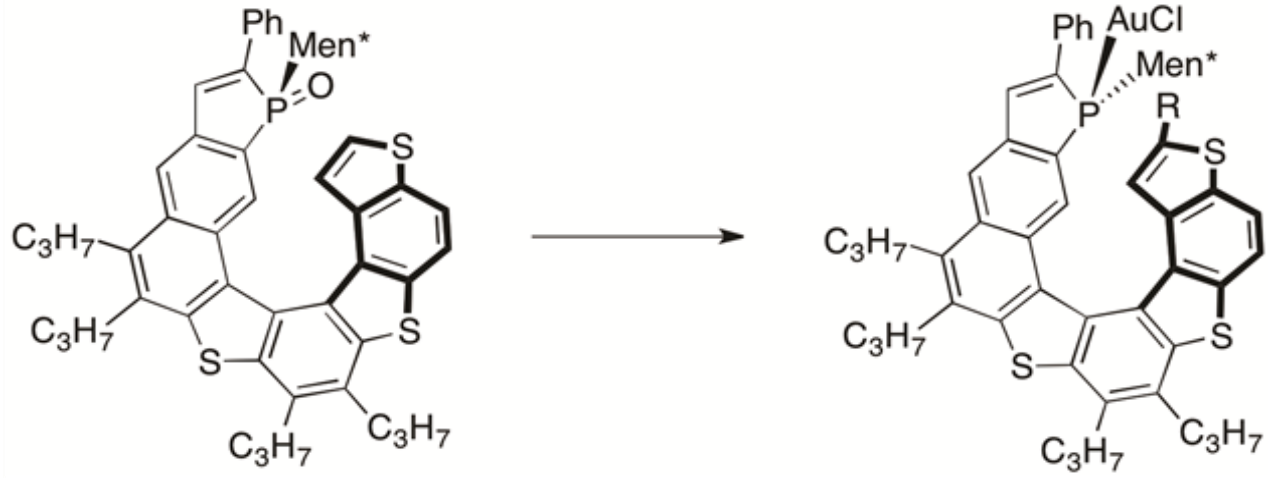
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P-504

Application of β-boration reaction to the synthesis of bioactive compounds

Mr Enrico La Cascia[1,2], Prof Andy Whiting[1], Prof Elena Fernández[2]
[1]*Durham University, Durham, UK* [2]*Rovira I Virgili University, Tarragona, Spain*

Poster Session 2

The β-boration reaction has been demonstrated to be an important tool in organic chemistry in order to functionalize molecules in accordance for a number of applications [1]. In fact, the C-B bond can be easily transformed into different functional groups such as C-C, C-N, C-O and C-X.

This β-borylation reaction typically occurs on electron deficient α,β-unsaturated systems where the β-position is activated by an electon withdrawing group (Scheme 1). To achieve the desired product, a Cu(I)-catalyst is required but in some cases, it can be also performed in a metal free context [2].

With this background of knowledge we investigated some applications of this chemistry to the synthesis of bioactive compounds. In the last years, new synthetic routes towards the synthesis of enantioenriched aminoalcohols has been widely explored by Whiting and Fernández et al. [3]. In this presentation, we present our current research involving in new pathways for the synthesis of bioactive compounds, including Tramadol (Figure 1), an γ-amino alcohol with analgesic properties.

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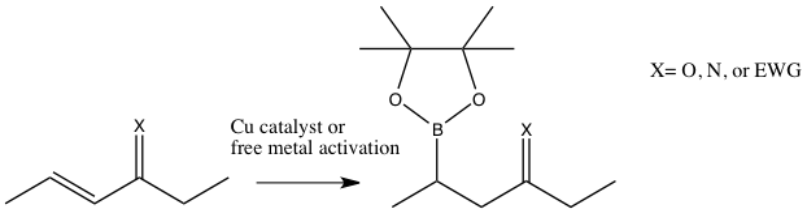

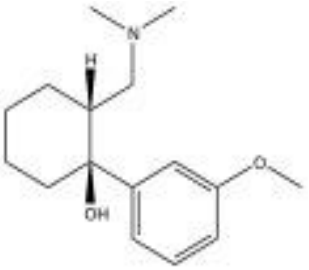

P-505

Asymmetric Transfer Hydrogenation: An Efficient Tool to Access Industrially Relevant Targets

Mr Marc Perez[1], Dr Zi Wu[1], Dr Laure Monnereau[1], Dr Damien Cartigny[1], Dr Michelangelo Scalone[2], Dr Tahar Ayad[1], Dr Virginie Vidal[1]

[1]PSL Research University, Chimie ParisTech - CNRS, Institut de Recherche de Chimie Paris, Paris, France, [2]Process Research and Development, CoE Catalysis, F. Hoffmann-La Roche AG, Basel, Switzerland

Poster Session 2

Asymmetric transfer hydrogenation [1] was applied to a wide range of racemic substituted-α-alkoxy-β-ketoesters in the presence of chiral Ru(II)-TsDPEN and Rh(III)-tethered precatalysts and a 5:2 mixture of formic acid and triethylamine as a hydrogen source. Under the above conditions, dynamic kinetic resolution was efficiently promoted to provide the corresponding syn-α-alkoxy-β-hydroxyesters with a high level of diastereoselectivity (>99:1) and enantioselectivity (>99%). [2] Moreover, the asymmetric transfer hydrogenation of dihydroisoquinolines was also studied to access tetrahydroisoquinolines with high enantiofacial discrimination up to 99% ee. [3]

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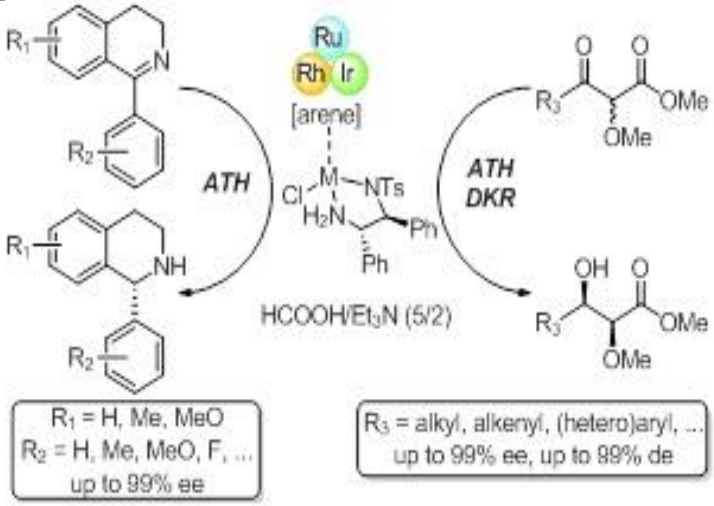
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OH
O
OMe
OMe
R1 = H, Me, MeO
R2 = H, Me, MeO, F, ...
up to 99% ee
R3 = alkyl, alkenyl, (hetero)aryl, ...
up to 99% ee, up to 99% de

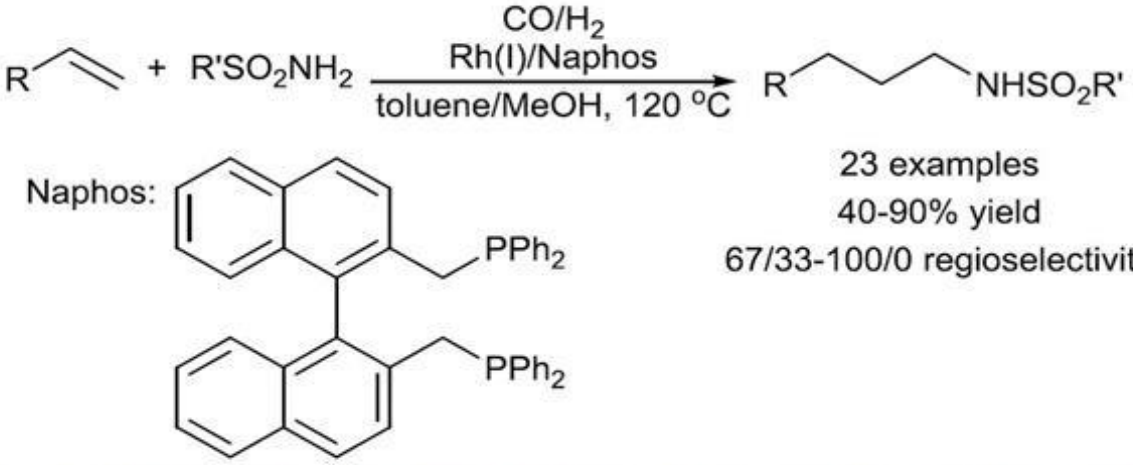
P-506

A Novel Rhodium-Catalyzed Domino-Hydroformylation-Reaction for the Synthesis of Sulphonamides

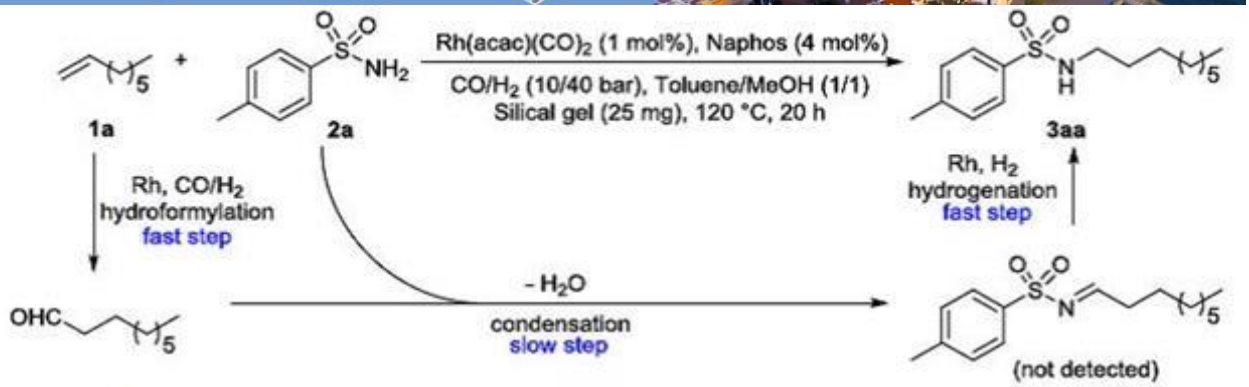
Dr. Kaiwu Dong[1], Dr. Xianjie Fang[1], Dr. Ralf Jackstell[1], Prof. Dr. Matthias Beller[1]
[1]*Leibniz Institute for Catalysis, Rostock, Germany*

Poster Session 2

Hydroformylation, constitutes the largest homogeneous catalytic reaction in industry, and has been widely explored for the production of aliphatic aldehydes and follow-up products. Extension of hydroformylation towards multistep one-pot transformations allows for the development of powerful synthetic methods. Among the different domino hydroformylation reactions, hydroaminomethylation of olefins is a typical addition reaction of aldehydes with amines and has been extensively applied in organic synthesis and industry. Meanwhile, other nitrogen sources such as amides and sulphonamides have been rarely explored as nucleophiles in tandem hydroformylation reactions. Obviously, the weaker nucleophilicity of these nitrogen sources compared to that of amines impedes the condensation step with the aldehydes formed via hydroformylation. Hence, the search for advanced catalytic systems for hydro(sulphon)amidomethylation of olefins is still a challenging but rewarding task.
Sulphonamides are extensively used as antibacterials, diuretics, anticonvulsants, hypoglycemics, and even HIV protease inhibitors. In addition, they represent valuable intermediates and final products in the bulk and fine chemical industries. So far, condensation of sulfonyl chlorides with amines in the presence of base represents the typical method for the synthesis of sulphonamides. Although several other synthetic methods such as the reaction of activated sulphonate esters with amines, cross-coupling of sulphonamides with aryl halides or alcohols have been reported, too. Unfortunately, all these procedures create at least stoichiometric amounts of unwanted side-products or/and suffer from limited substrate scope. Compared to the above-mentioned methods, the tandem hydroformylation–reductive sulphonamidation (this work) is attractive due to its atom economy and the possibility to use diverse olefins. Various olefins and sulphonamides are converted into the desired products in good yields and with excellent selectivities in the presence of a rhodium/Naphos catalyst.



Scheme 1 Rh(I) catalyzed hydroformylation-reductive sulphonamidation of olefins



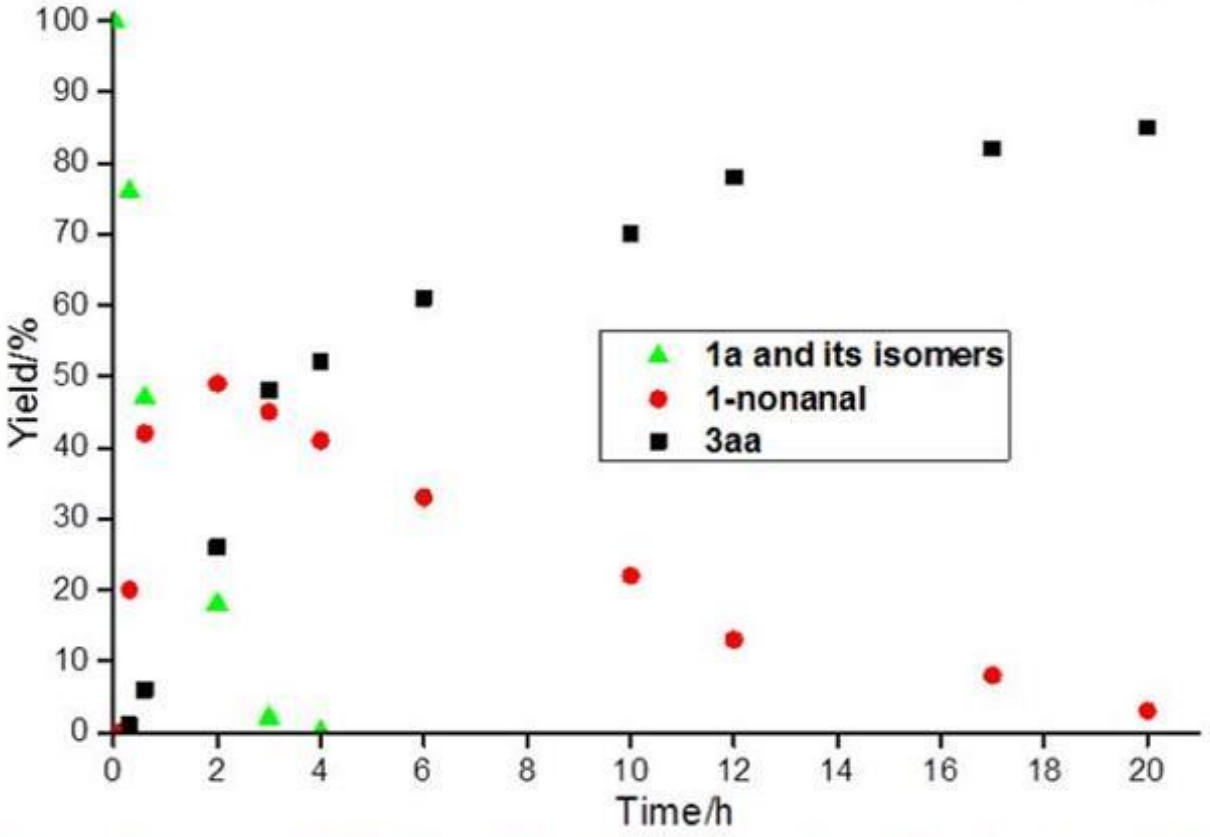


Figure 1 Compound distribution in the hydrosulphonamidomethylation of **1a** with **2a**.

P-507

Synthesis of indene derivatives involving a catalytic and synergistic σ-gold(I) activation-acetylide addition and consecutive σ- and π-gold(I) alkyne activations

Mr. Jairo González[1], Dr. Javier Santamaría[1], Prof. Alfredo Ballesteros[1]
[1]*University of Oviedo, Oviedo, Spain*

Poster Session 2

Among the large number of gold(I) catalyzed organic transformations,[1] gold(I) carbenoids[2] have been proposed as key intermediates for several of them. A variety of methods to generate gold carbenoids has been described, such as decomposition of diazocompounds, 1,2-acyloxy migrations of propargyl esters, cyclization of enynes or oxidation transfer reaction of alkynes, among others.

In this work, we present a catalytic and a simple methodology to obtain indene derivatives through a C-H functionalization, from acylsilanes and silylacetylenes. This transformation is proposed to involve a new methodology to generate Au(I) carbenoids in an intermolecular cascade reaction initiated by a synergistic[3] σ-gold(I) activation-acetylide addition and involving a consecutive double σ- and π-gold(I) alkyne activation.

References:
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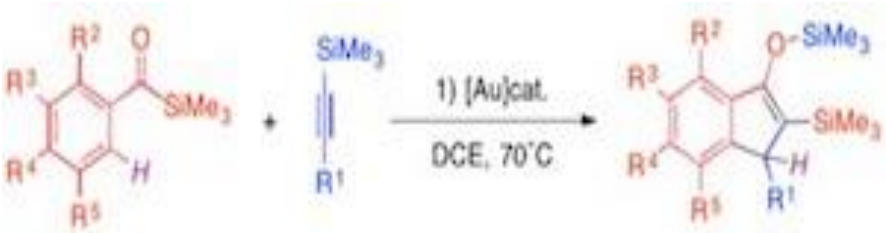
[3] For a reaction in our group involving a synergistic σ-gold(I) alkyne addition, see: Rubial, B.; Ballesteros, A.; González, J. M. Adv. Synth. Catal. 2013, 355, 3337.



P-508

Ni-catalyzed Divergent Cyclization/Carboxylation of Unactivated Primary and Secondary Alkyl Halides with CO2

PhD Xueqiang Wang[1], Dr. Yu Liu[1], Prof. Ruben Martin[1,2]

[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain*

Poster Session 2

Catalytic reductive carboxylation reactions of organic halides have evolved as mature tools in organic synthesis. At present, the reactions remain essentially confined to bond-formation events at the initial reaction site.[1] Intriguingly, the ability to trigger multiple C–C bond-formations via cascade cross-electrophilic reactions in which CO_2 fixation is promoted at distal reaction sites has been unexplored. [2] If successful, such protocols would offer a unique opportunity to increase our chemical portfolio for rapidly preparing carboxylated carbocyclic skeletons from simple precursors. Herein, we report a mild and user-friendly reductive cyclization/carboxylation of unactivated alkyl halides with CO_2 en route to elusive tetrasubstituted olefins in which the nature of the ligand and/or substrate dictates the selectivity pattern. [3]

References:
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P-509

Decarboxylative Cross-Coupling of Non-ortho-substituted Potassium Benzoates with Aryl Chlorides

Jie Tang[1], Agostino Biafora[1], Prof. Dr. Lukas J. Gooßen[1]
[1]*Technische Universität Kaiserslautern , Kaiserslautern, Germany*

Poster Session 2

Within recent years, decarboxylative coupling reactions have emerged as a powerful new strategy for C-C and C-heteroatom bond formation.[1] Their key advantage over couplings of organometallic reagents is that the carbon nucleophiles are generated in situ from widely available carboxylate salts by extrusion of CO_2. In the presence of a suitable catalyst, usually a bimetallic copper/palladium or silver/palladium system, various aromatic carboxylic acids have been successfully coupled with a broad range of (hetero)aryl halides.[2] These protocols were limited to ortho-sustituted or heterocyclic carboxylic acids. By using aryl triflates or aryl tosylates as carbon electrophiles, the reaction is applicable to all kinds of aromatic carboxylic acids, including meta- and para-substituted derivatives.[3] However, the substrate scope of known catalyst systems did not include the coupling between non-ortho-substituted carboxylic acids and ubiquitous aryl halides.

We now found a customized Pd(II)/Cu(I) bimetallic catalyst system, which for the first time is able to efficiently mediate the decarboxylative cross-coupling of non-ortho-substituted aromatic carboxylates with aryl chlorides.[4] This is the first step to extend decarboxylative cross-coupling of aryl halides to the full range of carboxylic acids, including meta- and para-substituted derivatives.

References:
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FG = NO2, 51%,
CN, 54%,
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SO2Me, 69%,
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FG = NO2, 60%,
F, 43%,
CN, 50%,
SO2Me, 53%
FG
R
NO2
R = CN, 68%,
CF3, 60%,
t-Bu, 66%,
n-Bu, 57%,
H, 63%,
SMe, 42%,
F, 57%,
SO2Me, 44%

P-510

Green synthesis of new chiraltripodal bismuth compounds

Prof. Claudia María Herrera Bahena[1], Lic.Daniela Guiérrez Arguelles[1], Prof. Guadalupe Hernández Téllez[1], Dra. Gloria E. Moreno Morales[1], Dra. Manju Sharma Sharma[2], Dr Pankaj Sharma Sharma[3], Dr René Gutiérrez Pérez[1], Dr. Oscar Portillo Moreno[1]

[1]Lab. Síntesis de Complejos. Fac. Ciencias Químicas,.Universidad Autonóma de Puebla, Puebla, México [2]Ingeniería Bioquímica, Instituto Tecnológico Superior de Atlixco, Atlixco, México [3]Instituto de Química UNAM, Coyoacán, México

Poster Session 2

Abstrac. Green Chemistry pursues the aim to design compounds and chemical processes that reduce or eliminate the generation of hazardous substances to the environment, providing improvements , better security and economic benefits simultaneously.

On the other hand, due to the unique features of Bismuth as their minimum levels of toxicity along with inexpensiveness and other interesting features, this element has been considered as a "green element". New compounds containing at its core Bismuth atoms have managed drug development with interesting biological activity.

The literature review has shown that there are no reports on the synthesis of Bi(III) complexes by using green chemistry methods such as the use of microwaves, solvent-free synthesis ,etc., In this work, five new bismuth-based tripodal ligand were synthesized by the “solvent free” technique. The bismuthines obtained have been fully characterized and their structure was confirmed by X-Ray diffraction studies

References:

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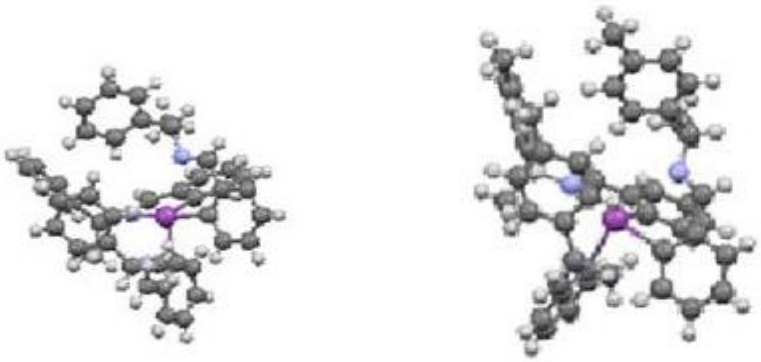


P-511

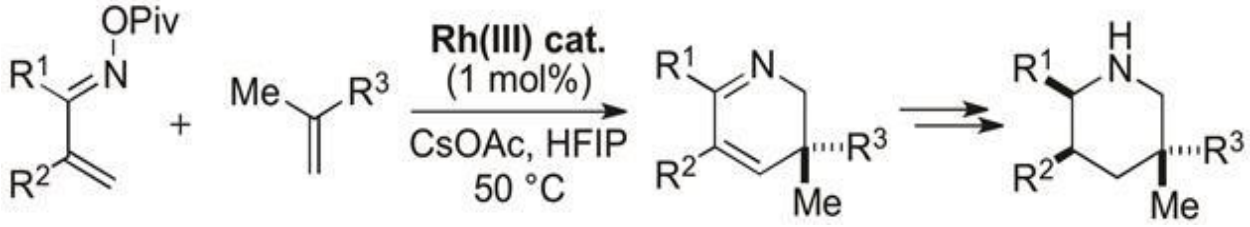
Synthesis of 2,3-Dihydropyridines via Rh(III)-Catalyzed C-H Activation

PhD Fedor Romanov Michailidis[1], Undergraduate Research Assistant Kassandra Sedillo[1], Prof. Dr. Tomislav Rovis[1]

[1]*Colorado State University, Fort Collins, USA*

Poster Session 2

Unsaturated oxime pivalates undergo reversible C-H activation with cationic Rh(III) complexes to afford five-membered metallacycles. In presence of 1,1'-disubstituted olefins, these metallacycles participate in migratory insertion to give, after reductive elimination, 2,3-dihydropyridines. The title reaction tolerates a broad substrate scope and affords products in high yields and exquisite regioselectivities. Mechanistically, olefin insertion was shown to be the rate-limiting step as manifested by a large inverse secondary kinetic isotope effect. The synthetic utility of the method was demonstrated by reductive conversion of the 2,3-dihydropyridine products to highly-substituted piperidines, which are pharmacologically important structures.



P-512

Non-stabilized Nucleophiles in Copper-Catalyzed Dynamic Kinetic Asymmetric Allylic Alkylation

Mr Hengzhi You[1], Dr Stephen P. Fletcher
[1]*Oxford University, Oxford, UK*

Poster Session 2

The development of reliable asymmetric methods to construct stereogenic centres from racemic starting materials would be powerful in synthetic organic chemistry. Over the past decades, the use of stabilized nucleophiles in dynamic kinetic asymmetric carbon-carbon formations, where both enantiomers of a starting material are converted to a single product, has proven to be an a fruitful method.[1] [2] There have been significant difficulties in using non-stabilized nucleophiles in such progresses and this remains a key challenge. [3] [4]

Recently, we described a copper-catalysed enantioselective addition of alkyl zirconium reagents to racemic cyclic allylic chlorides. The reaction uses readily available starting materials and catalysts, tolerates a variety of functional groups and operates under convenient conditions. (Figure 1) .[5] Here we will describe experimental work aimed at better understanding the mechanisms of these reaction and at extending the scope of this chemistry.

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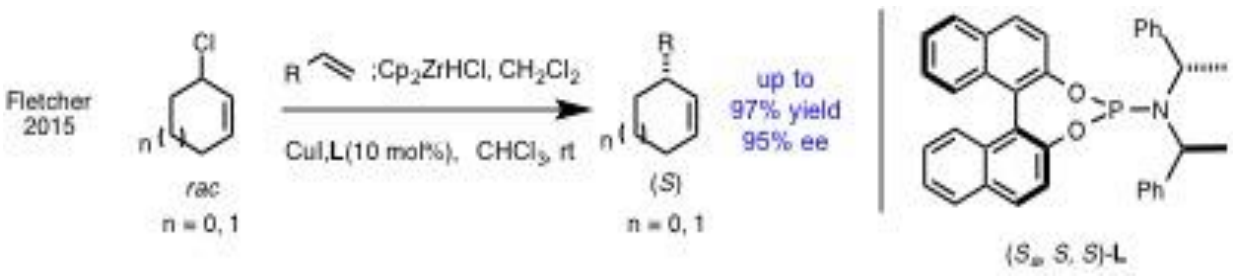

P-513

Bottom-up approach towards distorted graphene nanoribbons containing seven-membered carbocycles

Irene Rodriguez Marquez[1], Francisco J. Herrera[1], Duane Choquesillo-Lazarte[3], Luisa Marcos[2], Luis Crovetto[1], Teresa González[4], Rubén Martín[5], Araceli G. Campaña[1], Juan M. Cuerva[1]

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Poster Session 2

Graphene is considered one of the most promising materials in nanotechnology. Graphene samples with high perfection of the atomic lattice exhibit unique electronic and mechanical properties. However, structural defects can significantly modify its properties.[1] Thus, understanding the influence of each topological defect[2] represents the commencement for the construction of new materials based on the controlled inclusion of imperfect nanographenes into the graphene lattice.

Within this context, we designed a versatile route to construct a graphene nanoribbon that incorporates a single heptagon in one edge. This route is based on a Co(0)-mediated intermolecular cyclotrimerization reaction followed by a cyclodehydrogenation reaction (Scheme 1). In this way we obtained compound 4 presenting a seven-membered ring core partially surrounded in a hexagonal lattice. X-Ray crystal structure confirmed the distortion caused by the odd-membered ring, enhancing solubility drastically. Compound 4 also showed very promising optical properties and redox behaviour. Moreover, 4 is strategically functionalized to further expand the hexagonal sheet in two different directions, that we can combine or not: i) functionalization of the ketone moeity with nucleophiles; ii) application of the recently developed Ni(0)-catalyzed Kumada-type cross coupling reaction by using the methoxy groups as electrophiles.[3] In both cases, the subsequent cyclodehydrogenation reaction would lead to differently expanded distorted nanographenes. By combining both strategies we aim to construct a variety of distorted graphene nanoribbons including a 7-membered carbocycle.

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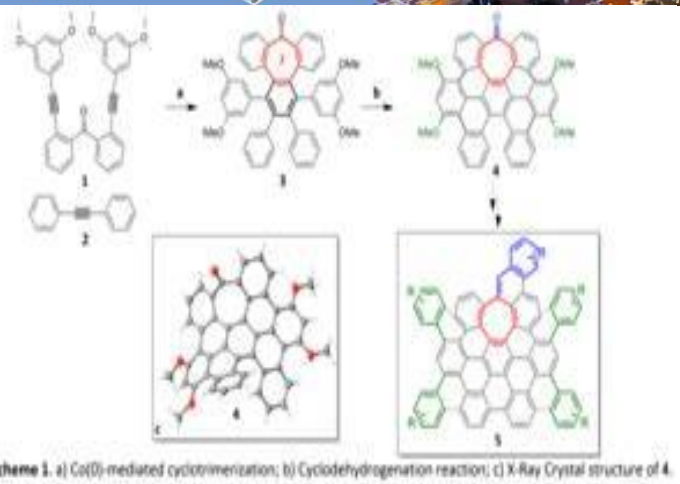

Scheme 1. a) Co(0)-mediated cyclotrimerization; b) Cyclodehydrogenation reaction; c) X-Ray Crystal structure of 4.

P-514

Z-Selective Olefin Synthesis via Iron-Catalyzed Reductive Coupling of Alkyl Halides with Terminal Arylalkynes

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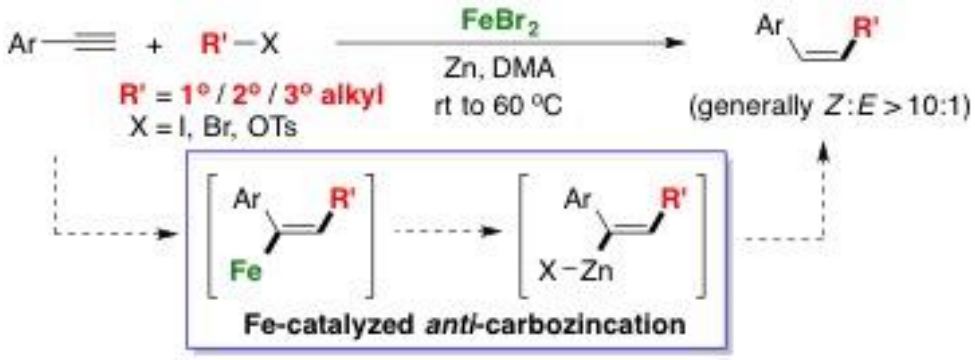
Poster Session 2

Selective catalytic synthesis of Z-olefins has been challenging. Here we describe a method to produce 1,2-disubstituted olefins in high Z selectivity via reductive cross-coupling of alkyl halides with terminal arylalkynes. The method employs inexpensive and non-toxic catalyst (iron(II) bromide) and reductant (zinc). The substrate scope encompasses primary, secondary, and tertiary alkyl halides, and the reaction tolerates a large number of functional groups. The utility of the method is demonstrated in the synthesis of several pharmaceutically relevant molecules. Mechanistic study suggests that the reaction proceeds through an iron-catalyzed anti-selective carbozincation pathway.



P-515

Visible light reduction of ketones and aldehydes catalyzed by complexes based on earth abundant elements and water as source of hydrogen atoms

Mr. Arnau Call[2], Mr. Ferran Acuña-Parés[2], Dr. Julio Lloret Fillol[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*Universitat de Girona, Girona, Spain*

Poster Session 2

The development of alternative greener synthetic methods of high-value chemicals and energy carriers is a requeriment for a more sustainable society. Among different opportunities to this end, the use of solar light-driven reactions has become one of the most ambitious and challenging approaches.1 In this regard, during the last years a spectacular increase of efforts devoted to understand and mimic natural photosynthetic processes with the aim to generate solar fuels has been pursuit.2 Despite the significant advances on the reduction of organic substrates using homogeneous catalytic systems based on Ru, Rh, Ir, Fe or Co,3 the reduction of synthetic molecules using visible light as driving force and water as hydrogen source, has only rarely considered by using a combination of novel-metals and enzymes.4 Herein, we present, a new photocatalytic system based entirely on Earth-abundant elements that reduces ketones and aldehydes to alcohols with excellent yields (up to 1200 TON) making use of water as source of hydrogen atoms in aqueous phase. Based on kinetic studies we showed that water reduction to H2 and reduction of carbonyls are competing reactions, supporting strongly that both share a common well-defined intermediate. The reactivity toward H2 or alcohol formation can be tuned simply by modulating the electronic nature of the ligand. The results based on reactivity, electronic effects and labelling studies exclude free radical mechanism, suggesting a cobalt hydride as intermediate responsible for the carbonyl reduction. This work opens up newer and greener avenues for the selective transformations of organic substrates by artificial photosynthetic schemes.

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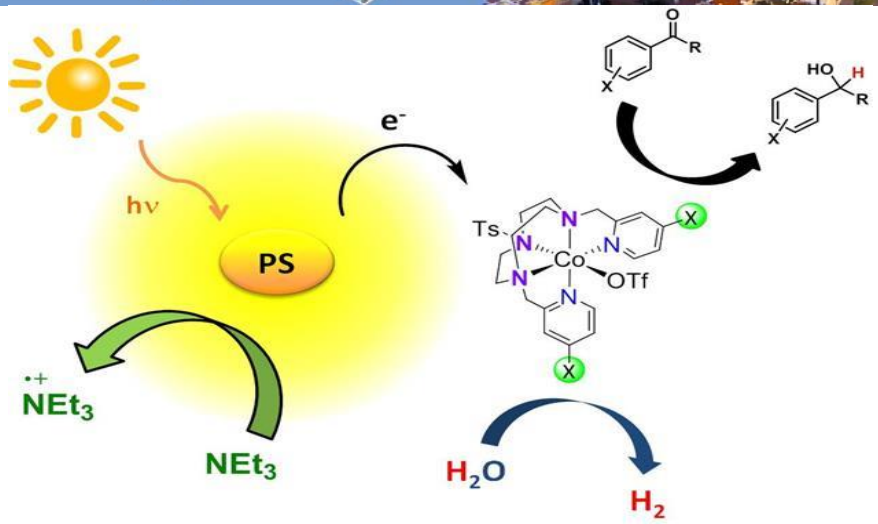
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P-516

Mechanistic Insights into Catalytic Enantioselective Synthesis of 3-Substituted Morpholines and Piperazines by Tandem Sequential Hydroamination and Asymmetric Transfer Hydrogenation

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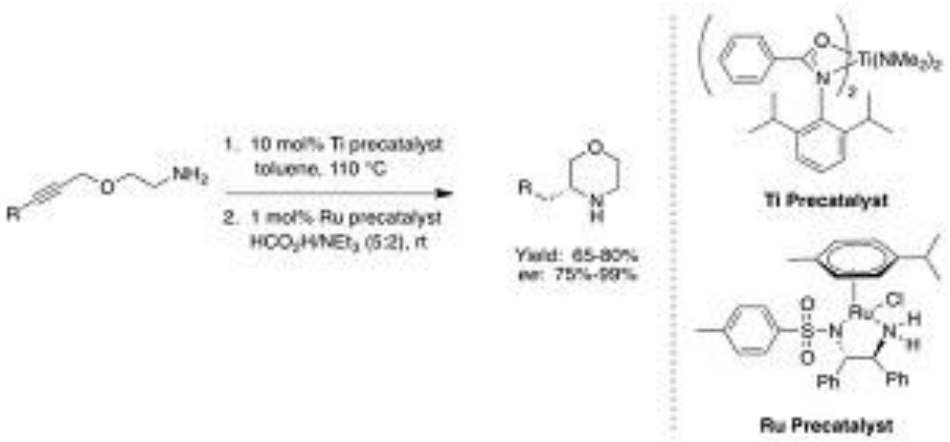
[1]*University of British Columbia, Vancouver, Canada*

Poster Session 2

The synthesis of enantioenriched N-heterocycles typically requires the use of enantiopure starting materials, such as amino acids. We have recently disclosed the first catalytic approach for the enantioselective synthesis of 3-substituted morpholines through a tandem sequential one-pot reaction employing both hydroamination and asymmetric hydrogen transfer reactions. Using aminoalkyne substrates, we utilize a commercially available bis(amidate)bis(amido)Ti precatalyst to yield a cyclic imine, which is subsequently reduced using commercially available RuCl [(S,S)-Ts-DPEN] (p-cymene). For the synthesis of morpholines, excellent yields and enantioselectivities (up to 99%) were achieved. Mechanistic investigations suggest that hydrogen bonding interactions between the oxygen in the backbone of the imine substrate and the [(S,S)-Ts-DPEN] ligand of the Ru catalyst are crucial for obtaining high ees. Using this mechanistic proposal, we were able to extend this methodology to the enantioselective synthesis of another important class of N-heterocycles, 3-substituted piperazines.



P-517

Development of High Throughput Screening for Metal-Catalyzed the Coupling Reactions

Mr. Han-Sung Kim[1], Prof. Min Su Han[2], Prof. Sunwoo Lee[1]

[1]*Chonnam National University, Gwangju, South Korea* [2]*Gwangju Institute of Science and Technology, Gwangju, South Korea*

Poster Session 2

The development of efficient reaction methodology is one of the most important parts in the pharmaceutical and fine chemical industries. To find a new reaction tool, a variety of conditions are tested by changing parameters such as substrate, additive, temperature, and solvent. As demanding the fast analysis of reaction results in the development of organic synthesis, a number of high throughput screening methods have been developed. The employment of gas chromatography, high performance liquid chromatography, mass spectrometry and NMR spectroscopy which are operated by automatic equipment is good in convenience because they do not require pre-functionalization for analysis. However, their analysis times highly depend on the automatic system and still take minutes per a sample. To address these problems, we had developed the colorimetric analysis methods by gold nanoparticle and paper–based iodide sensor. Although these methods were proved as efficient tools for the screening of transition metal-catalyzed coupling reactions, they are limited to aryl iodide substrates. In the coupling reactions of aryl halides, aryl bromide is the most frequently employing substrate and aryl chloride is the cheapest and challenging substrate. Therefore, the development of high throughput screening method for the coupling of aryl halides such as iodide, bromide and chloride is highly needed. Here in we report high throughput screening methods for the coupling reaction of aryl halides and C-H activation.

P-518

Decarboxylative coupling of propiolic acids for the synthesis of allyl amines and allenes

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[1]*Chonnam National University, Gwangju, South Korea*

Poster Session 2

We developed an additive-free decarboxylative coupling of cinnamic acid and propiolic acid derivatives with formaldehyde and amines to afford the corresponding allyl amines and propargyl amines. These decarboxylative coupling reaction is highly environmentally friendly because the reaction was conducted in H_2O and without any additives, releasing only CO_2 and H_2O as the by-products. The electron-donating substituents of cinnamic acids play a key role in the metal-free decarboxylative coupling reaction. It provided the products with retention of the stereochemistry of the double bond of cinnamic acid and showed a broad substrate scope including cyclic and acyclic amines and high functional group tolerance. In addition, we developed the synthesis of allene from the copper-catalyzed decarboxylative coupling of propiolic acid with formaldehyde and amines.

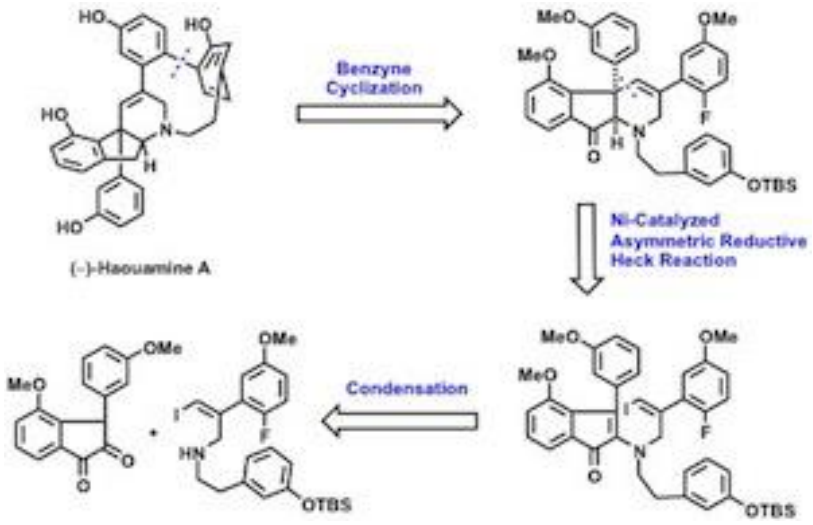
P-519

Convergent Approach to the Total Synthesis of (−)-Haouamine A

Eunhye An[1], Jaehoon Jung[1], Sean H. Wiedemann[2], Chulbom Lee[1]
[1]*Seoul National University, Seoul, South Korea,* [2]*Princeton University, USA*

Poster Session 2

Presented in this poster are our efforts toward the total synthesis of haouamine A, an anticancer marine alkaloid possessing a novel molecular architecture. The molecule features an indenotetrahydropyridine moiety that contains a diaryl quaternary center and an anti-bredt double bond. This tetrahydropyridine ring is further fused to a highly strained 11-membered paracyclophane that includes a bent aromatic ring. The marine alkaloid has an exquisitely selective anticancer activity against the human colon carcinoma cell line HT-29 with an IC_{50} of 0.1 μg/ml and against human prostate cancer cells with IC_{50} of 14.5 μg/ml. Highlights of our strategy are the convergent assembly of building blocks using Pd-catalyzed reactions and the construction of the tetrahydropyridine by the Ni-catalyzed asymmetric reductive Heck reaction. With successful synthesis of the paracyclophane precursor, we are investigating the prospect of constructing the paracyclophane by connecting unactivated arylfluoride and phenolic part via a cross-coupling reaction or a benzyne intermediate. Details of the recent progress in our synthetic investigation will be described.



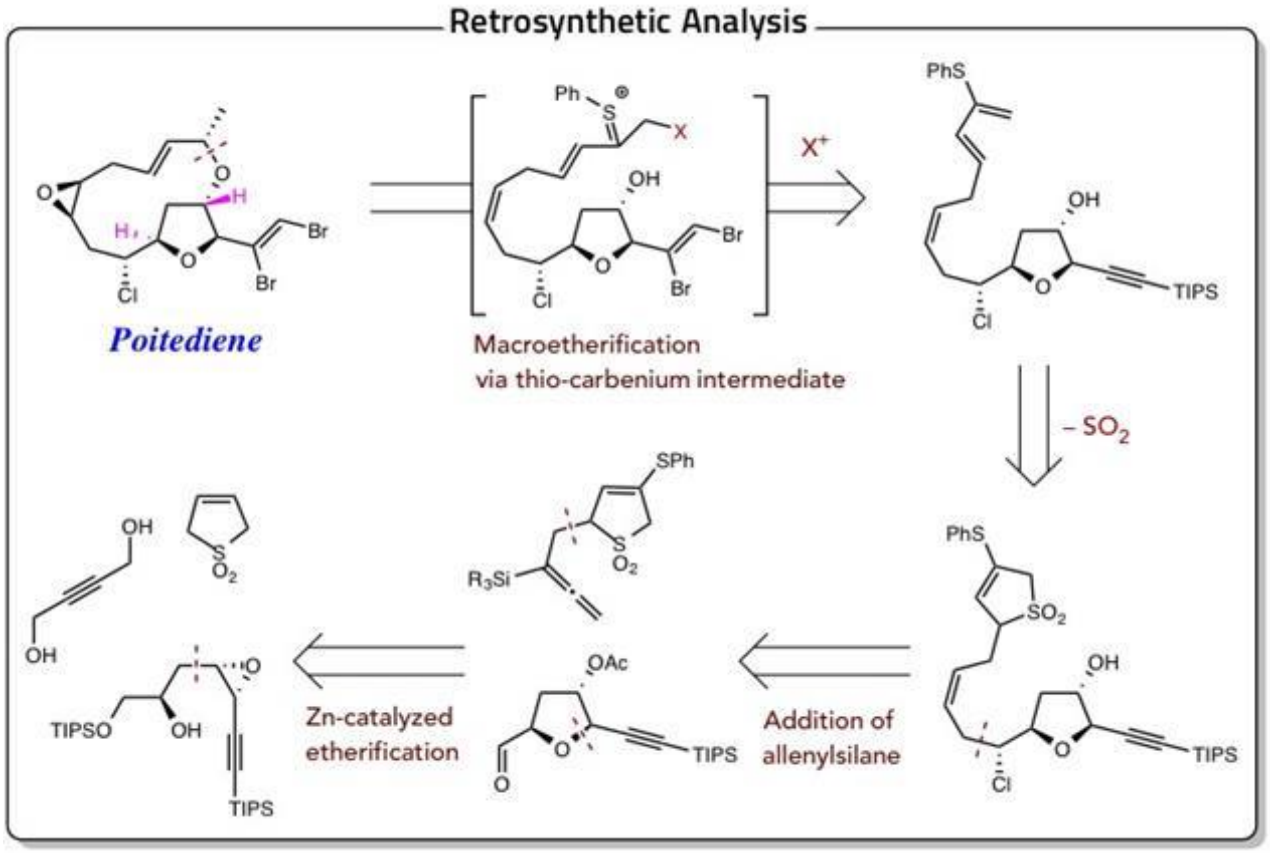
P-520

Studies toward the Total Synthesis of Poitediene

Mr. Seonwoo Kim[1], Ms. Sinae Kim[2], Dr. Robert Matunas[2], Prof. Dr. Chulbom Lee[1]
[1]*Seoul National University, Seoul, South Korea,* [2]*Princeton University, Princeton, USA*

Poster Session 2

We present here a novel approach to the enantioselective total synthesis of poitediene, a metabolite of red algae possessing a unique “in-out” bridged cyclic structure. We envision that the highly strained 12-membered macrocyclic ether is constructed by etherification using a hetero atom-stabilized carbocation intermediate. The oxolane core was built from epoxy alcohol by zinc-catalyzed etherification, which took place via stereospecific cycloisomerization. Described in this poster are the details of our synthetic route that provides efficient access to the highly functionalized 2,12- dioxabicyclo[9.2.1]tetradecane system.



P-521

Ni-catalyzed Linear-selective Alkylation of Benzene with Olefins

Mr. Akito Ohgi[1], Dr. Teruhiko Saito[1], Prof. Kazuhiko Semba[1], Prof. Yoshiaki Nakao[1,2], Prof. John F. Hartwig[3]
[1]Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan, [2]CREST, Japan Science and Technology Agency (JST), Saitama, Japan, [3]Department of Chemistry, University of California, Berkeley, USA

Poster Session 2

Alkylation of benzene is commonly achieved by the Friedel–Crafts reaction with olefins. The methodology gives branched alkylbenzenes exclusively and often suffers from over-alkylation to afford poly-alkylated benzenes. On the other hand, linear- and mono-selective alkylation of benzene has been accomplished by transition-metal catalysis though with modest linear/branch-selectivities.[1] Although a nickel catalyst bearing an N-heterocyclic carbene (NHC) ligand has recently been introduced as a catalyst for the alkylation of trifluoromethyl-substituted arenes with exclusive linear-selectivity, it shows poor reactivity toward non-activated arenes such as benzene.[2]

In this study, we show that the linear-selective alkylation of benzene with olefins can be achieved by a nickel catalyst bearing a sterically hindered NHC ligand (Eq. 1). We have found that the turnover number of the phenylation of sterically less hindered 1-alkenes can be dramatically improved by base additives.

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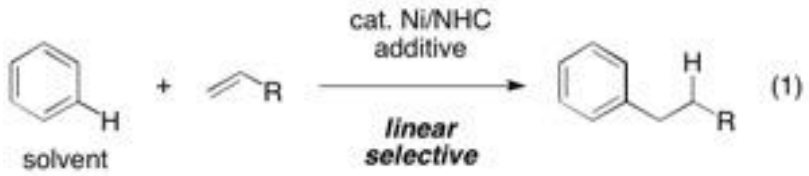

P-522

Copper–Catalyzed Semihydrogenation of Internal Alkynes

Mr. Ryohei Kameyama[1], Prof. Kazuhiko Semba[1], Prof. Yoshiaki Nakao[1,2]

[1]*Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan,* [2]*CREST, Japan Science and Technology Agency (JST), Saitama, Japan*

Poster Session 2

Semihydrogenation of alkynes is an important reaction in organic synthesis. Nevertheless, well-established and effective catalysts such as the Lindlar catalyst often suffer from (Z)/(E)-isomerization, and/or over-hydrogenation to give alkanes. Due to low cost and abundance of copper, it is beneficial to use a copper catalyst in semihydrogenation of alkynes. To date, Cu_2O-catalyzed semihydrogenation of alkynes under 20 atm of H_2 has been the only precedent.[1] We reported that $[(PPh_3)CuCl]_4$, a readily available copper complex serves as a catalyst for semihydrogenation of internal alkynes in the presence of LiOt-Bu and i-PrOH. The reaction proceeds at 100 °C under 5 atm of H_2, giving (Z)-alkenes in high yields and selectivities (Scheme 1).[2] Compared with the previous work[1], this catalytic system works under mild conditions with wide substrate scope.

References
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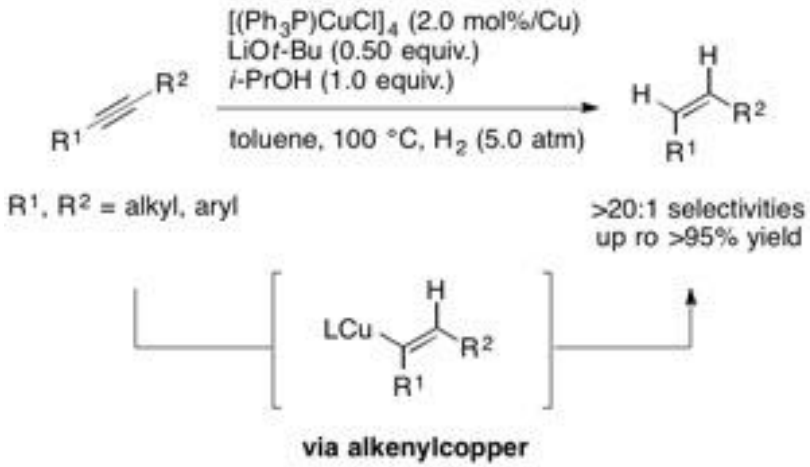
Scheme 1



P-524

Ligand-controlled regioselective ni-catalyzed reductive carboxylation of allyl esters with CO^2

Dr. Toni Moragas[1], Dr. Josep Cornella[1], Prof. Rubén Martín [1,2]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain,* [2]*Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain*

Poster Session 2

The use of CO_2 in chemical syntheses arises as a powerful alternative to existing methodologies for the preparation of carboxylic acids.[1] The direct applicability of this cheap and unlimited source represents a more cost-efficient approach for the synthesis of these valuable compounds. In our continuous efforts towards the catalytic fixation of CO_2 into organic scaffolds,[2] a novel Ni-catalyzed reductive carboxylation of allylic substrates is presented herein. The fine-tuning of the ligand allowed for an exquisite control of regioselectivity, resulting in the formation of linear or branched carboxylic acids. To the best of our knowledge, our study study represents the first time that the nature of the ligand dictates the selectivity pattern in catalytic reductive CO_2 fixation processes.[3] Furthermore, this protocol is characterized by its simplicity and excellent chemoselectivity profile, thus representing a particularly attractive and useful tool in organic synthesis.[4]

References:
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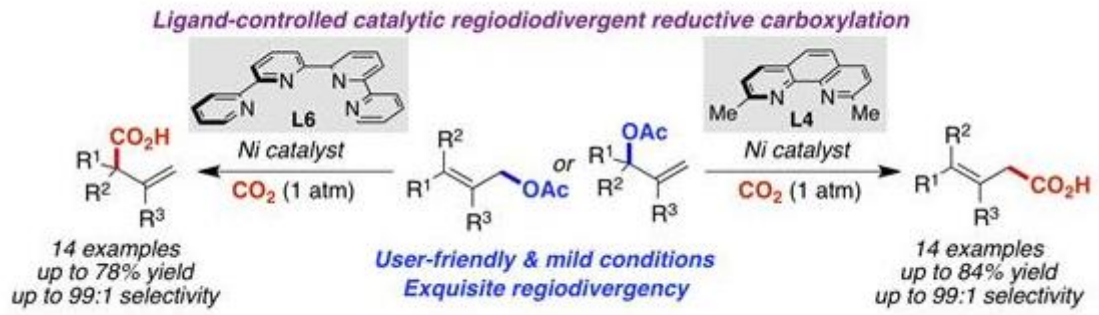

P-525

Design of new backbone-functionalized imidazol-2-ylidenes and its booster effect in Pd-catalyzed Buchwald-Hartwig Amination

YIN ZHANG[1,2], Golo Storch[1,2], Dr. Noël Lugan[1,2], Dr. Vincent César[1,2], Dr. Guy Lavigne[1,2]
[1]*Laboratoire De Chimie De Coordination du CNRS, Toulouse, France* [2]*Université de Toulouse, Toulouse, France*

Poster Session 2

N-heterocyclic carbenes (NHCs) have gained considerable significance as ubiquitous ligands for the design of a variety of highly efficient transition-metal pre-catalysts.[1] Their intrinsic interest is both due to their high steric bulk, mainly determined by the nature of nitrogen substituents, and their strong electronic σ-donor properties. Following our interest in the design of backbone-functionalized NHCs as an efficient strategy to tune the electronic properties of the carbene centre,[2] we now report two new classes of imidazol-2-ylidenes, based on the well-known 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), whose carbenic heterocycles are directly substituted by one or two NMe_2 groups (abbreviated by IRXY with IR = IMes or IPr and X,Y = H or NMe_2).[3]
We successively present here the challenging synthesis of their imidazolium salts precursors, the quantification of their stereoelectronic properties and the evaluation of efficiency as PEPPSI[4] type palladium (II) pre-catalysts in the Buchwald-Hartwig amination.[5]
The results reveal that the performances of the catalyst are correlated with the donor properties of the carbene (see Figure), and the complex $[PdCl_2(3\text{-}ClPy)(IPr(NMe_2)_2)]$ was found to be an extremely efficient pre-catalyst in this reaction.[6]

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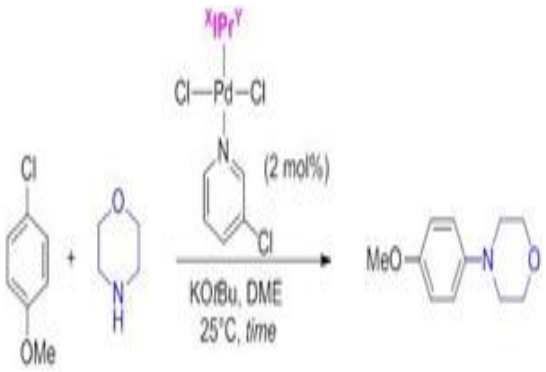
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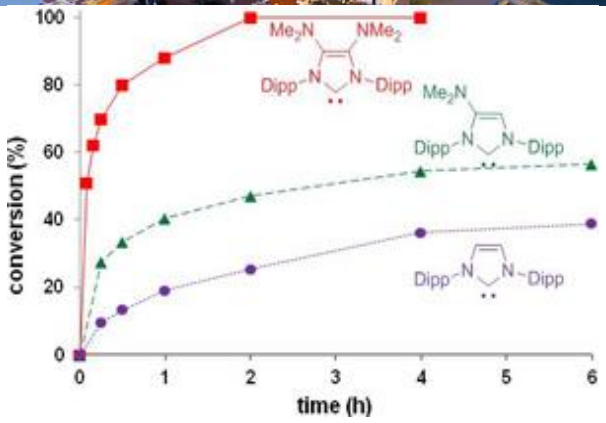
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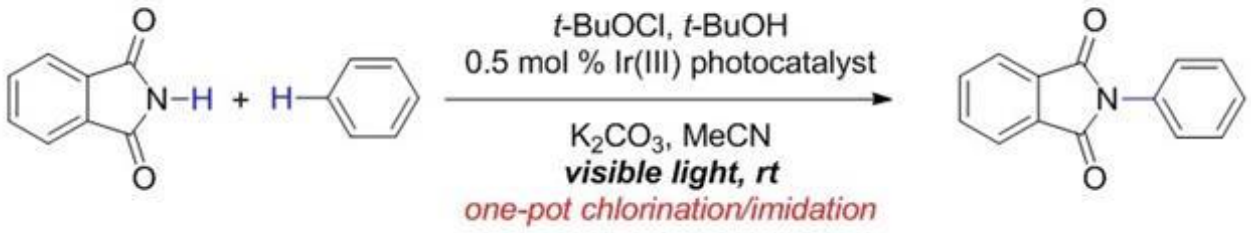
P-526

Visible Light Induced Photocatalysis for C-H Imidation of Arenes and Heteroarenes

Dong Gil Lee[1], Dr. Hyejin Kim[2], Taehoon Kim[1], Sang Weon Roh[1], Prof. Chulbom Lee[1]
[1]*Seoul National University, Seoul, South Korea,* [2]*Max Plank Institute, , Germany*

Poster Session 2

Herein, we present a mild and convenient photocatalytic method for C–H imidation of arenes. The process allows for the formation of N-aryl bonds by introducing a phthalimido group to unfunctionalized arenes via a nitrogen radical mediated aromatic substitution mechanism. An important feature of this imidation is mild generation of the phthalimidyl radical intermediate from N-chlorophthalimide at room temperature via reductive scission of the N–Cl bond using a visible light photoredox catalyst. The present imidation method is operationally simple and can be conducted on a gram scale using only inexpensive, commercially available reagents with very low catalyst loading.



P-527

Ru-Catalysed C-H Arylation of Indoles and Pyrroles with Boronic Acids: Scope and Mechanistic Studies

Carina Sollert[1], Karthik Devaraj[1], Andreas Orthaber[2], Paul Gates[3], Lukasz Pilarski[1]

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Poster Session 2

The transition-metal-catalysed activation of carbon-hydrogen (C-H) bonds has received enormous attention in recent years and has become a fast growing field of research. The coupling of C-H units is highly atom economical and leads to reduction of chemical byproducts and waste. Providing new synthetic strategies in this field offers previously impossible transformations, new selectivities, and shortened routes in the preparation of organic molecules. The importance of indole and pyrrole units in bioactive molecules has fuelled continued efforts to develop new approaches to their selective C-H functionalisation.

A Ruthenium(II)-catalysed C2-H arylation of indoles and pyrroles by using boronic acids under oxidative conditions has been developed.[1] Halide functionalities as iodide and bromide, which are consumed in traditional cross coupling methods are tolerated under our reaction conditions opening up the way for further functionalization of the reaction products and is complementing existing methods.[2,3] New organometallic complexes were described and investigated as possible intermediates in the reaction. Mechanistic studies suggest the on-cycle intermediates do not possess a para-cymene ligand and that the on cycle metalation occurs through an electrophilic attack by the Ruthenium center.

References:

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[2]Ackermann, L.; Lygin, A. V. Org. Lett. 2011, 13, 3332.

[2]Ackermann, L.; Diers, E.; Manvar, A. Org. Lett. 2012, 14, 1154.

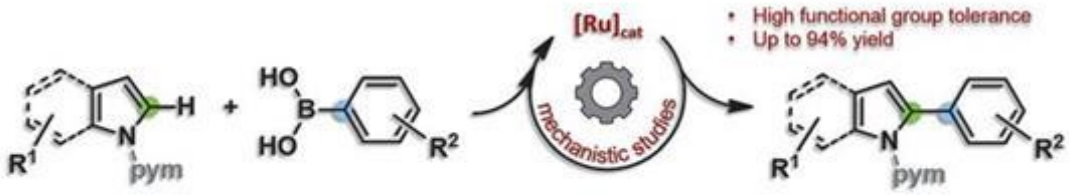


Figure 1: Reaction scheme for Ruthenium(II) catalyzed C2-arylation of indoles and pyrroles with boronic acids.

P-528

Metal-catalyzed 1,2-additional reaction to alkynes

Doctoral Tao XU[1]
[1]*EPFL, Lausanne, Switzerland*

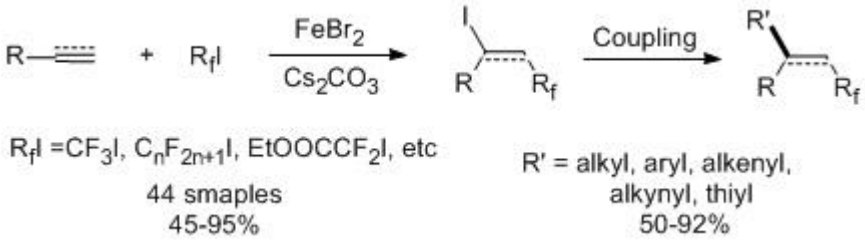
Poster Session 2

Additional reaction is an efficient method to proceed difunctionalization of unsaturated bonds which presents good atom-economical merit. The addition of organic halogen compounds to alkynes will directly produce the products with vinyl-halogen bond and this is a versatile medium for further functionalization, such as coupling reactions.

Herein, iron catalysis has been developed for the intermolecular 1,2-addition of perfluoroalkyl iodides to alkynes and alkenes. A variety of perfluoroalkyl iodides including CF3I can be employed. The resulting perfluoroalkylated alkyl and alkenyl iodides can be further transformed to other bonds. This methodology provides a straightforward and streamlined access to perfluoroalkylated organic molecules.(File1)

Meanwhile, β,γ-unsaturated ketones are synthesized through 1,2-addition of a-carbonyl iodides to alkynes with copper catalyst. The reactions exhibit wide substrate scope and high functional group tolerance. The reaction products are versatile synthetic intermediates to complex small molecules. The method was applied for the formal synthesis of (±)-trichostatin A, a histone deacetylase inhibitor.
(File 2)

References:
[1] Tao Xu, Chi Wai Cheung, and Xile Hu* Angew. Chem. Int. Ed. 2014, 53, 4910-4914.
[2] Tao Xu and Xile Hu* Angew. Chem. Int. Ed. 2015, 54, 1307-1311.

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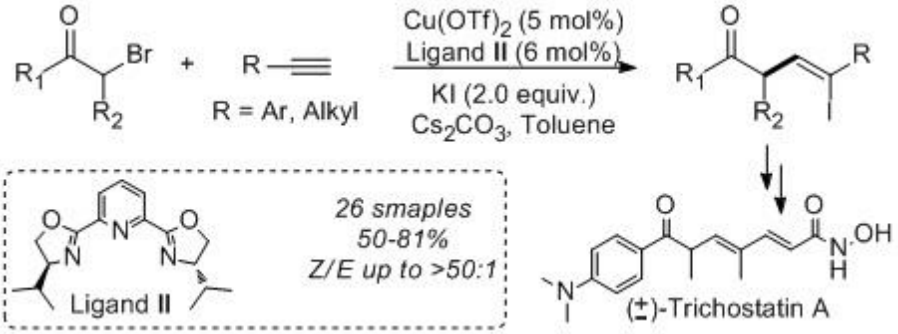
R = Ar, Alkyl
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Ligand II (6 mol%)
KI (2.0 equiv.)
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Ligand II
26 smaples
50-81%
Z/E up to >50:1
(±)-Trichostatin A

P-529

Ni-catalyzed Reductive Amidation of Unactivated Alkyl Bromides with Isocyanates

MSc. Eloisa Serrano[1], MSc. Yangyang Shen[1], Prof. Ruben Martin[1,2]
[1] *Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*ICREA, Barcelona, Spain*

Poster Session 2

In the past decades, important advances have been made on the use of unactivated alkyl halides as electrophiles in cross-coupling reactions.[1] These substrates are highly challenging due to the difficult oxidative addition and their ease to undergo β-hydride elimination and homodimerization reactions. While significant advances have been realized using nucleophile/electrophile regimes,[1] the means to promote catalytic cross-electrophile coupling reactions using unactivated alkyl halides is still at its infancy.[2] Herein, we report the first nickel-catalyzed reductive coupling of unactivated primary and secondary alkyl bromides with isocyanates to afford aliphatic amides.[3] These scaffolds are important building blocks in a myriad of molecules displaying significant biological properties. The protocol is characterized by its robustness, mild conditions and high chemoselectivity profile using simple and available precursors by obviating the need for well-defined organometallic species.

References
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(2) Reviews on reductive cross couplings: (a) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. Chem. Eur. J. 2014, 20, 6828. (b) Everson, D. A.; Weix, D. J. J. Org. Chem. 2014, 79, 4793. (c) Moragas, T.; Correa, A.; Martin, R. Chem. Eur. J. 2014, 20, 8242.
(3) Serrano, E.; Martin, R. In preparation

P-530

Evidence for an Oxygen Evolving Fe–O–Ce Intermediate in Iron-Catalysed Water Oxidation

Dr. Julio Lloret-Fillol[1,2], Dr. Zoel Codolà[2], Dr. Laura Gómez[2], Dr. Scott T. Kleespies[3], Prof. Lawrence Jr. Que.[3], Dr. Miquel Costas[2]

[1]Institut Català d'Investigació Química (ICIQ), Tarragona, Spain, [2]Institut de Química Comptacional i Catalisi, Departament de Química, Universitat de Girona, Girona, Spain [3]Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, USA

Poster Session 2

Water oxidation (WO) catalysis constitutes the bottleneck for the development of energy conversion schemes based on sunlight. State of the art of homogeneous WO catalysis is so far efficiently performed with earth-scarce transition metals. For instance, we recently showed that iridium organometallic pre-catalysts are able to catalyze WO with impressive turnover numbers (TON, up to 400,000).[1] Although abundant and less toxic 3d metal-based complexes are much less established,[2] we have discovered that readily available iron coordination complexes are highly efficient homogeneous WO catalysts. TON > 350 and >1000 were obtained when using cerium ammonium nitrate (CAN), and NaIO4, respectively.[3-4]

We present here one of the few examples of homogeneous WO catalysts based on 1st row transition metals. The non-heme iron complex [FeII(CF3SO3)2(mcp)] (mcp = (N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-cis-diaminocyclohexane) reacts with CeIV to oxidise water to O2, representing an iron-based functional model for the oxygen evolving complex (OEC) of photosystem II. The intermediate has been trapped and characterized by cryospray ionization high resolution mass spectrometry and resonance Raman spectroscopy, which lead to its formulation as the first example of an inner-sphere complex to be formed in CeIV-mediated water oxidation. The identification of this reactive FeIV–O–CeIV adduct also validates mechanistic notions of an analogous MnV–O–CaII unit in the OEC that is responsible for carrying out the key O–O bond forming step

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[4] Z. Codolà, I. Gracia-Bosch, F. Acuña, J. M. Lluis, M. Costas,* J. Lloret Fillol* Chem. Eur. J. 2013, 19, 8042.

P-531

Radical Addition Of 1,3-Dicarbonyl Compounds To Conjugated Dienes Leading To 5-Vinylphenyl-4,5-Dihydrofurans Using Transition Metal Salts

PhD Student Asli Ustalar[1], Prof. Mehmet Yilmaz[1], MS Simge Can[1]
[1]*Kocaeli University, Umuttepe Kocaeli, Turkey*

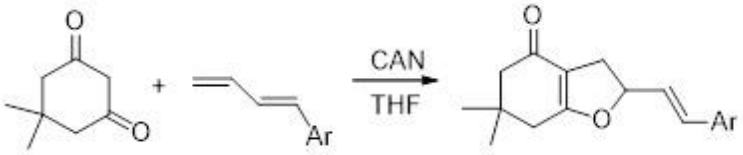
Poster Session 2

It is well known that transition metal salts (Mn+3, Co+3, Ce+4, Ag+ etc.) performing single electron transfer form new C-C bonds in organic compounds. Among these transition metals, manganese(III) acetate and cerium(IV) ammonium nitrate are widely used. These radical oxidants allow the formation of furans, lactones, β-lactams and highly functionalized products such as antibiotic, antitumor and natural products.

In recent years, 4,5-dihydrofurans are obtained from radical addition of 1,3 dicarbonyl compounds to alkenes mediated by manganese(III) acetate or cerium(IV) ammonium nitrate. However, radical addition of 1,3-dicarbonyl compounds to conjugated diens using cerium(IV) ammonium nitrate has not been studied yet in detail. According to results of this study, 5-vinyl substituted 4,5-dyhidrofuran compounds were obtained in good yields. In this work, 5,5-dimethyl-1,3-cyclohexadione (1a), 5-phenyl-1,3-cyclohexadione (1b), 1,3-cyclohexadione (1c), 2,4-pentanedione (1d) and ethyl 3-oxobutanoate (1e) were used as 1,3-dicarbonyl compounds. As conjugated diens, 1-phenyl-1,3-butadiene (2a), 1-pheny-3-methyl-1,3-butadiene (2b) and 1,1-diphenyl-1,3-butadiene were used.

All radical addition were performed under nitrogen atmosphere and basic laboratory conditions. The novel 4,5-dihydrofuran compounds that were obtained in this study were purified by column or preparative thin layer chromatography methods and determination of structures were performed by IR, 1H-NMR, 13C-NMR and mass spectroscopy.

The authors are grateful to the Kocaeli University Science Research Foundations (BAP 2014/18) for financial support.



P-532

Assembly of chromene skeletons by means of a Rh(III)-catalyzed annulation between 2-hydroxystyrenes and allenes

Ms. Karina Del Rio[1], Ms. Noelia Casanova[1], Mr. Andrés Seoane[1], Mr. Felipe Verdugo[1], Dr. Moisés Gulías[1], Dr. Jose Mascareñas[1]

[1]*Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago De Compostela, Spain*

Poster Session 2

In recent years there have been an increasing number of reports on a new type of metal catalyzed annulations that involve as a key step the activation of C−H bonds.[1] Most of the transformations use alkynes, alkenes or carbon monoxide as partners.[2] However the use of allenes have been scarcely investigated.

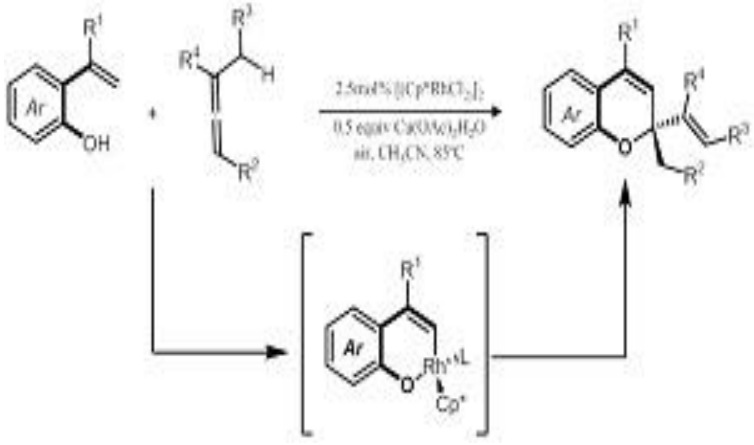
Herein we describe details of a formal [5C+1C] cycloaddition between 2-alkenylphenols and allenes that is catalyzed by Rh (III) under oxidative conditions.[3]

References:

[1] For selected recent reviews of metal-catalyzed C−H functionalizations, see: (a) Wencel-Delord, J.;Glorius, F. Nat. Chem.2013, 5, 369−375. (b) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. Acc. Chem. Res. 2012, 45, 788−802. (c) Yeung, C. S.; Dong, V. M. Chem. Rev. 2011, 111, 1215−1292.

[2] a) A. Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas, M. Gulías, J. Am. Chem. Soc. 2014, 136, 834; b) A.Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas, M. Gulías, J. Am. Chem. Soc. 2014, 136, 7607.

[3] N. Casanova, A. Seoane, J. L. Mascareñas, M. Gulías, Angew. Chem. Int. Ed. 2015, 54, 2374–2377.



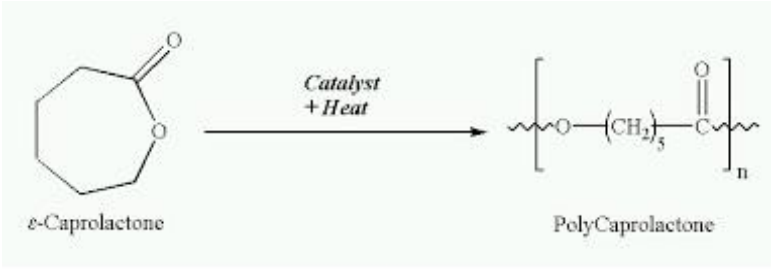
P-533

Synthesis of new and effective catalysts of Sn and their catalytic activity over polymerization of ε-caprolactone

Phd Begum Canan Yildiz[1], Prof Asgar Kayan[1]
[1]*Kocaeli University, Umuttepe Izmit Kocaeli, Turkey*

Poster Session 2

Firstly, 2-((E)-(p-tolylimino)methyl)phenol (TIMPH) precursor was prepared by reaction between salicylaldehyde and p-Toluidine in ethanol and was let to react for 3 h at reflux temperature. Then it was cooled at room temperature and washed two times with ethanol. After that, it was dried under reduced pressure and orange solid was obtained. This precursor was used in the preparation of (TIMP)2SnClBu catalyst. Secondly, same precursor was reduced by NaBH4 and then was used in the synthesis of (TAMP)2SnClBu catalyst. In order to see their catalytic activity, these compounds were tested in polymerization of ε-caprolactone and were effective. All these compounds were characterized by 1H, 13C NMR, FTIR spectroscopies and elemental analysis. Addition to these, poly-caprolactone (PCL) was also characterized by gel permeation chromatography (GPC).



P-534

Synthesis Of 4,5-Dihydrofuran-2-Carboxyamide and 3-Amino-Chromene-Dione Compounds by Single Electron Transfer Reaction Using Manganese(III) Acetate

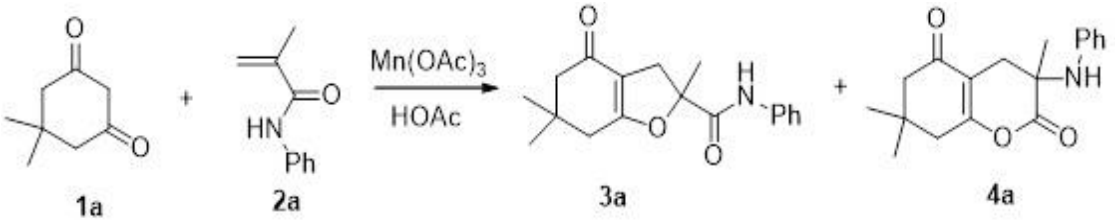
Prof Mehmet Yilmaz[1], PhD Student Asli Ustalar[1], Student Sedanur Birincioğlu[1]
[1]*Kocaeli University, Umuttepe Kocaeli, Turkey*

Poster Session 2

During the last three decades, manganese(III) acetate and cerium(IV) ammonium nitrate have been used as efficient radical oxidants for the synthesis of C-C bond formation. These oxidants are well known for formation of dihydrofurans by radical cyclization of 1,3-dicarbonyl compounds with alkenes. Dihydrofurans are important class of compounds since they show a wide range of biological activities (antibacterial, antifungal, antitumor) and form the basic structure of many natural compounds.

Here we report radical addition-cyclization reactions between 1,3-dicarbonyls (1a) and acrylamide derivatives (2a) by using manganese(III) acetate resulting 4,5-dihydrofuran-2-carboxyamide (3a) and 3-amino-chromene-2,5-dione (4a) compounds. In this work, 5,5-dimethyl-1,3-cyclohexadione (1a), 2,4-pentanedione (1b) and ethyl 3-oxobutanoate (1c) were used as 1,3-dicarbonyl compounds; and N-phenylmethacrylamide (2a), methacrylamide (2b), N-phenylacrylamide (2c), N-ethylmethacrylamide (2d) and S-phenyl 2-methylprop-2-enethioate (2e) were used as acrylamide derivatives.

Oxidative cyclization reactions were performed under nitrogen atmosphere and basic laboratory conditions. Obtained all compunds were purified by column or preparative thin layer chromatography. All compounds were characterized by spectroscopic techniques.



P-535

Palladium-catalyzed Amination 2,3,3-Trifluoroallyl Acetates with amines, and Synthesis of Trifluoromethylenamines

Mr. Taisyun Hanakawa[1], Mr. Kazuki Isa[1], Ms. Maki Minakawa[1], Mr. Motoi Kawatsura[1]
[1]*Nihon University, Japan*

Poster Session 2

The palladium-catalyzed reaction of allylic compounds with nitrogen nucleophiles is well known as an allylic amination reaction. However, we found that the reaction of 2,3,3-trifluoroallyl esters 1 with amines 2 didn't provide any allylic amines, and selectively produced trifluoromethylenamines 3, which was formed by the attack of amines on to C-2 carbon and migration of fluorine atom from C-2 position to C-3 position. We also confirmed that several types of amines are tolerated in this amination reaction, and obtained the trifluoromethylenamines up to 93% isolated yield.

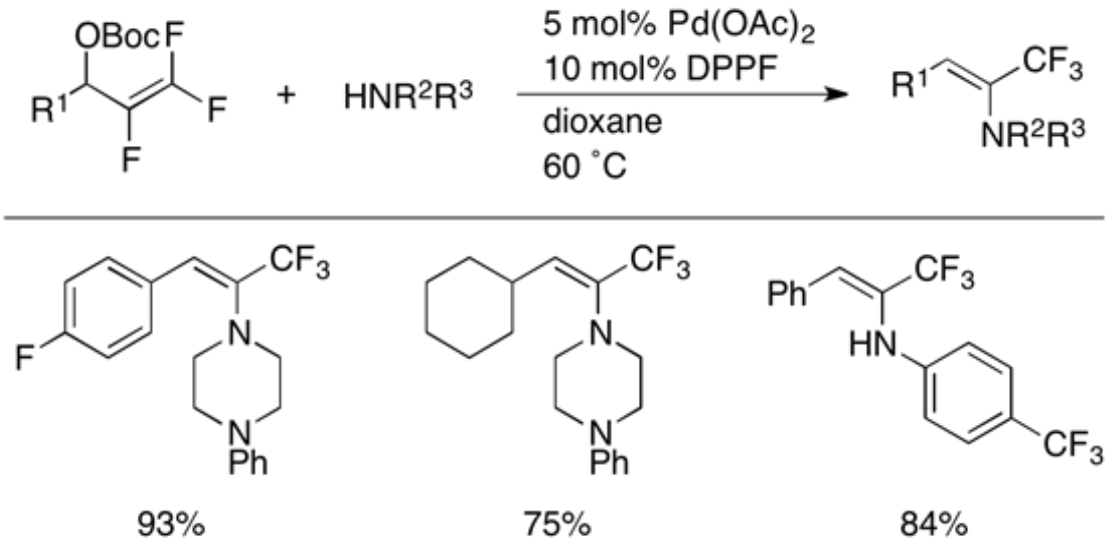


Figure. The palladium-catalyzed reaction of 2,3,3-trifluoroallyl esters with amines.

P-536

Novel strategy for the assymmetric synthesis of gamma,delta-lactones containing multiple contiguous stereocenters

M.S. Maria Isabel Alvarado-Beltrán[1], M.S. Mariana Lozano González[1], Dr. Eddy Maerten[2], Dr. R. Alfredo Toscano[1], Dr. José G. López-Cortés[1], Dr. Antoine Baceiredo[2], Dr. Cecilio Álvarez-Toledano[1]

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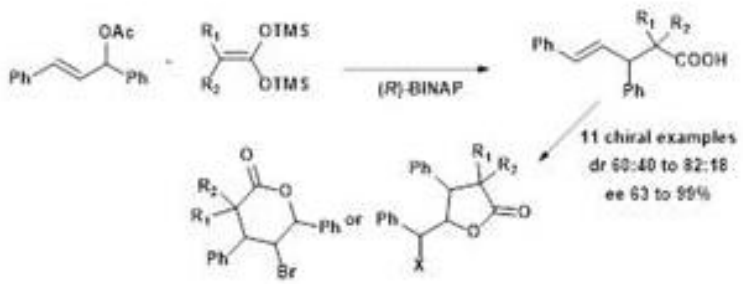
Poster Session 2

The γ- and δ-lactones skeleton appears as an important moiety in several natural products that exhibit a wide range of biological activity. Some of these lactones contain multiple contiguous stereocenters, which means that their asymmetric synthesis can represent a significant challenge. Consequently, the development of new methods for the synthesis of lactones, particularly in a stereocontrolled fashion, has received considerable attention; however, their synthesis involves several steps and low overall yields. Asymmetric halolactonization is a common method for the formation of highly substituted stereocontrolled lactones. Nevertheless, the procedure is quite complicated because it requires a long multi-step catalytic synthesis the use of a catalyst and involves several steps in their synthesis. A straightforward precursor for chiral γ- and δ-lactones could be the corresponding chiral 4-alkenoic acids, but to date, their enantioselective synthesis had not been broadly studied.

On the other hand, bis(TMS)ketene acetals have emerged as very convenient 1,3-dinucleophiles, noteworthy for the synthesis of lactones among a variety of substrates. Indeed these bis(TMS)ketene acetals are easily prepared and very convenient to manipulate. Moreover their high thermal stability allows their storage under inert atmosphere for months. Surprisingly, the use of ketene acetals in allylic substitution reactions has been poorly explored to date.

Herein, we report the use of bis(TMS)ketene acetals as nucleophiles in asymmetric allylic alkylation to prepare 4-alkenoic acids in good yields with high enantioselectivities. The scope of the reaction was studied using symmetric and prochiral ketene acetals, affording several unsaturated acids with one or two consecutive stereogenic centers, respectively. Finally, one of these acids was converted into functionalized halolactones containing three contiguous stereocenters with an excellent level of stereocontrol.



P-537

Design of chiral nucleophilic organocatalysts

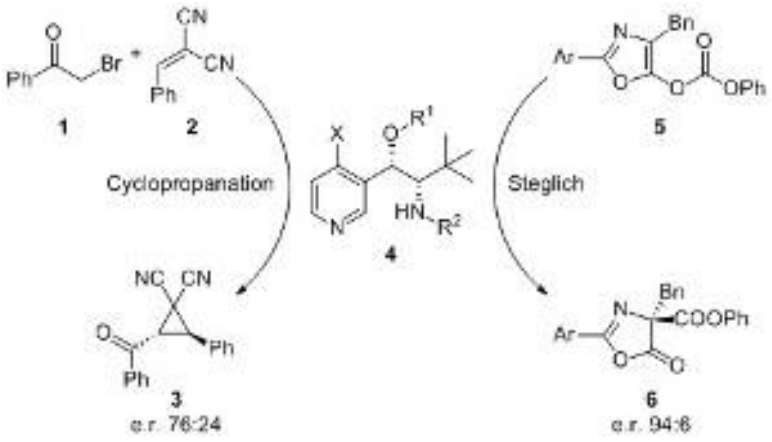
Artis Kinens[1], Dr. Chem. Edgars Suna[1], Dr. Chem. Edwin Vedejs[1,2]
[1]*Latvian Institute of Organic Synthesis, Riga, Latvia,* [2]*University of Michigan, Ann Arbor, USA*

Poster Session 2

Pyridine derivatives are widely used as nucleophilic organocatalysts and as ligands in transition metal catalysis. Herein we report versatile synthesis of chiral pyridine organocatalysts and their use in cyclopropanation and Steglich reactions (Scheme 1). A series of nucleophilic organocatalysts was obtained by the late-stage derivatization of chiral pyridine building block, which was obtained from ortho-litiated pyridines and azidoaldehyde.

Chiral nucleophilic organocatalysts 4 were successfully employed in cyclopropanation reaction. Cyclopropanes with enantiomeric ratio up to 76:24 were obtained using pyridine 4 with electron-donating groups in the

para-position. Likewise, electron-donating substituents in pyridine influenced enantioselectivity of Steglich rearrangement. Fine-tuning of reaction conditions and catalysts 4 structure allowed us to obtain oxazolone 6 with enantiomeric ratio up to 94:6.



P-539

Missing-linker defects in Zr-MOFs as platform for catalysts anchoring

Dr Oleksii Gutov[1], Dr Alexandr Shafir[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

Porous materials with a periodic 3D structure have come to the forefront of catalysis. In this context, research into regular metal-organic frameworks (MOFs) has experienced a spectacular growth, due, in part, to the property control possible via a judicial choice of just two structural building units: linkers and nodes. In 2008, a new family MOFs based on Zr_6-oxo clusters connected by carboxylate linkers was introduced by Lillerud and co-workers. These Zr-MOFs have shown promise for a wide range of applications including gas storage and catalysis, due, in large part, to the elevated stability of such materials. An interesting feature of this type of MOFs is the tolerance towards rather high defect content, made possible by the unusually high connectivity in the system. The defect formation is due to the use of acid modulation in their synthesis, with some of the modulating acid retained at the node (Figure 1), and occupying the place of the linker. The presence of such missing linker defects has been demonstrated to have a dramatic effect on material's properties.

We will present a broad study on defect formation control in Zr-MOFs using a variety of modulating acids, and will discuss the possibility of using the resulting linker vacancies as anchoring point for catalyst introduction.

$Zr_6O_4(OH)_4F_{12}$

Missing-linker defect in UiO-67

Figure 1. I - Proposed scheme for defect Zr-MOF formation using H_2bpdc (biphenyl-4,4`-dicarboxylic acid) as a ligand in the presence of excess formic acid modulator. II – Replacing of anions, capping defects, with catalytically active specie. (F = formate).

P-540

New reactivities in the deprotonation of {Mo(hapto^3-allyl)(CO)$_2$(N-RIm}-containing complexes: A theoretical mechanistic investigation

Dr. Ramón López[1], Dr. Jesús Díaz[2]
[1]*Universidad de Oviedo, Oviedo, Spain,* [2]*Universidad de Extremadura, Cáceres, Spain*

Poster Session 2

The imidazole moiety is of importance mainly due to its presence in the side chain of the amino acid histidine, and its role as a metal binding site in metalloenzymes. The relatively small size and the electronic properties (σ-donor and π-aceptor) make imidazole and its derivatives good ligands for a variety of metal fragments. As a consequence, the coordination chemistry of imidazoles has been extensively studied. However, little attention has been paid to the analogy between cationic metal complexes with N-alkylimidazole (N-RIm) ligands and N,N'-dialkylimidazolium salts instead. This has encouraged interest in investigating, among other reactions, the deprotonation of transition metal complexes with N-RIm ligands in order to generate a new type of N-heterocyclic carbene species (NHC) with a metal fragment as substituent of one of the imidazole nitrogen atoms.
A current study has reported that the deprotonation of [Mo(η^3-C_4H_7)(CO)$_2$(N-MeIm)(py-2-CH=N-R')]OTf (R'=C_6H_5, C_6H_4-4-Me, C_6H_3-3,5-Me2, iPr, tBu) leads to C-C coupling species between the deprotonated central carbon atom of the imidazole ligand (Cimidazole) and the imine carbon atom of the py-2-CH=N-R' ligand. This contrasts with that previously found for the analogous 2,2´-bipyridine (bipy) compounds [Mo(η^3-allyl)(CO)$_2$(bipy)(N-RIm)]OTf (R= Me, Mes) which afforded imidazol-2-yl complexes via the attack of Cimidazole on a cis-CO ligand. Aiming at understanding the reasons of the difference, we investigated the deprotonation mechanism of [Mo(η^3-C_4H_7)(CO)$_2$(N-MeIm)(py-2-CH=N-C_6H_3-3,5-Me2)]OTf at the CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + f for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + f for Mo) level of theory. Our computations uncover that the reactivity of the imine carbon atom along with its ability to delocalize electron density are responsible for the new reactivity pattern found for this kind of molybdenum complexes.

P-541

Os-Catalyzed Cyclization of o-(Alkynyl)Phenethylamines by Osmacyclopropenation: An Easy Entry to Dopaminergic 3-Benzazepines

Ms Andrea Álvarez-Pérez[1], Dr Carlos González-Rodríguez[1], Dr Cristina García-Yebra[2], Dr. Jesús A. Varela[1], Dr Miguel A. Esteruelas[2], Dr Carlos Saá[1]

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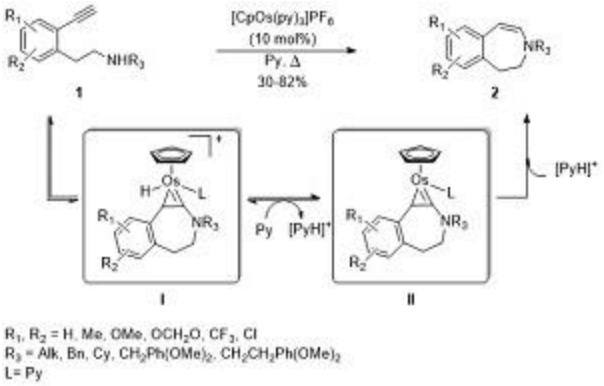
Poster Session 2

Heterocyclic derivatives containing phenethylamine units have shown important dopaminergic properties.[1] In particular, seven-membered 3-benzazepines remain as one of the most reliable structural scaffold in terms of the affinity and selectivity against the D1 receptor of mammalian brains.[2] Tipically, metal-mediated intramolecular hydroamin(d)ations of alkynylamin(d)es have been employed for their preparation.[3] However, no 7-endo dig cyclization of terminal o-(alkynyl)phenthylamines to 3-benzazepines has been described.

Based on our recently developed Os-catalyzed cyclization of terminal bis-homopropargylic alcohols,[4] we now report the novel Os-catalyzed 7-endo dig cyclization of terminal o-(alkynyl)phenethylamines 1 to 3-benzazepines 2 via the formation of new osmacyclopropene intermediates I and II, which have been characterized by X-Ray analysis (L=P[sup]i[/sup]Pr_3).



Acknowledgements: This work was supported by MICINN (project CTQ2011-28258 and ORFEO-CINQA CTQ2014-51912-REDC), Xunta de Galicia and European Development Fund (projects GRC2014/032 and EM 2012/051). A.A-P. thanks MINECO (Spain) for a FPI fellowship (BES-2012-054798).

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P-542

Development of Fe-catalysed Kumada type alkyl-alkyl cross-coupling using NHC ligands

Dr. Irene Ortín[1], Graduate Natalia Cabrera[1], Prof. Elena Buñuel[1], Full Prof. Diego J. Cárdenas[1]
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Poster Session 2

Transition metal-catalyzed cross-coupling reactions are some of the most utilized transformations in synthetic organic chemistry, both in research and development and industrial settings.[1] In this field, iron has received much attention in recent years as a catalyst for cross-coupling reactions; besides attractive features such as wide availability, low cost and negligible toxicity, irons shows a unique reactivity that allows cross-coupling to proceed under mild reaction conditions with high chemoselectivity. Formation of $C(sp^3)$-$C(sp^3)$ bonds by cross-coupling reaction is still considered a challenging reaction[2] because alkyl halides resist oxidative addition and because the resulting alkyl-metal intermediates have proclivity for β-hydride elimination.

In our group, considerable advances in this field have been achieved. We have developed the first Fe-catalysed Kumada-type alkyl-alkyl cross-coupling under mild reaction conditions that has allowed us to avoid side reaction products as the formation of β-elimination compounds; being a general reaction that tolerates several functional groups (esters, carbamates, nitriles, ketals…) having as the only limitation the Grignard reagent that must contain a cyclic acetal in the structure to provide reasonable yields.[3]

In order to extend our previous results of the Fe-catalysed Kumada alkyl-alkyl cross-coupling reaction regardless the Grignard reagent type, and taking into account the advantages of Fe, we have synthesized different imidazolium salts containing coordinating groups such as cyclic acetal or sulfoxide function, as well as bisimidazolium cores as ligands with the aim of blocking an extra coordination site and preclude β-elimination of hydrogen in the alkyl-metal intermediate. (Scheme1)

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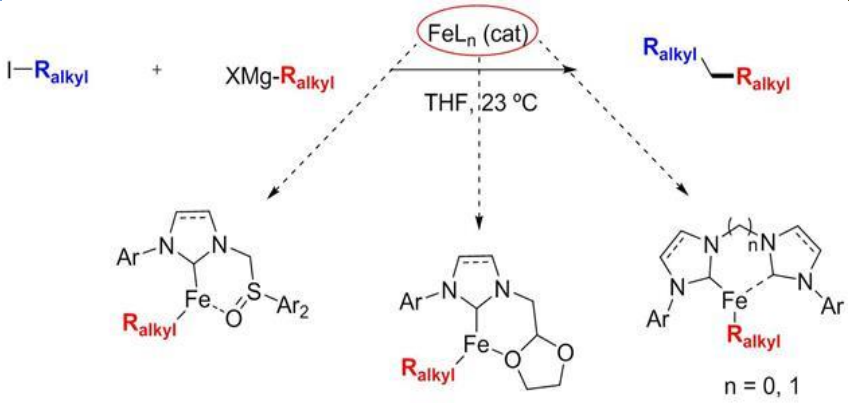
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n = 0, 1

P-543

Ni-catalyzed cross-coupling reaction of propargylic bromides with alkyl zinc halides: synthesis of trisubstituted allenes

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Poster Session 2

Nickel catalyzed cross-coupling reactions constitute a highly efficient method for the formation of C-C bonds from alkyl halides and alkyl metal nucleophiles,[1] avoiding typical problems associated to this kind of couplings, such as the difficult oxidative addition of the alkyl electrophiles and the fast β-elimination of hydrogen on the alkyl–metal intermediates.[2] The use of alkyl zinc halides as nucleophiles also makes this procedure compatible with several functional groups. Surprisingly, the use of propargyl halides as coupling partners in Ni-catalyzed reactions has not been extensively studied.[3] These electrophiles can give rise to either allenes or propargyl derivatives upon cross-coupling reactions. Pd and Cu complexes have been used as catalysts for coupling reactions to afford propargylic or allenylic species.[4] Ni has been recently reported to provide propargyl coupling compounds employed in reactions of propargylic compounds.

In this work trisubstituted allenes have been synthetized through nickel catalyzed cross-coupling of propargylic bromides with alkyl zinc halides achieving excellent yields and high functional group tolerance. Preliminary studies suggest that these reactions seem to follow a different mechanism that those described for Pd and Cu catalyzed process. Furthermore, the reaction exhibits a complementary regiochemistry to previous works.[5] (Scheme 1)

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P-544

Unexpected Pyridine Dearomatization Through Double Ru-Metal Carbenes Insertion

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Poster Session 2

CpRu complexes are interesting alternatives to copper and dirhodium species for the catalyzed decomposition of diazo compounds.[1] Our group has shown that combinations of $[CpRu(CH_3CN)_3][PF_6]$ and diimine ligands catalyze the decomposition of α-diazo-β-ketoesters and allow further condensation, O-H and 1,3-C-H insertion reactions.[2] Recently, using the same catalytic combination, new dioxene motifs were synthetized by enantiospecific syn-opening of epoxides.[3]
In a new development that uses electron-poor pyridines and quinolines as substrates, we describe the direct formation of unique oxazine moieties 1, via a tandem addition of two carbenes and a dearomatization of the azaaromatics. The process is possible through ruthenium cyclopentadienyle catalysis as, under Rh(II)-mediated reactions, pyridinium ylides 2 are the major products.[4] Mechanistic insights will be presented.

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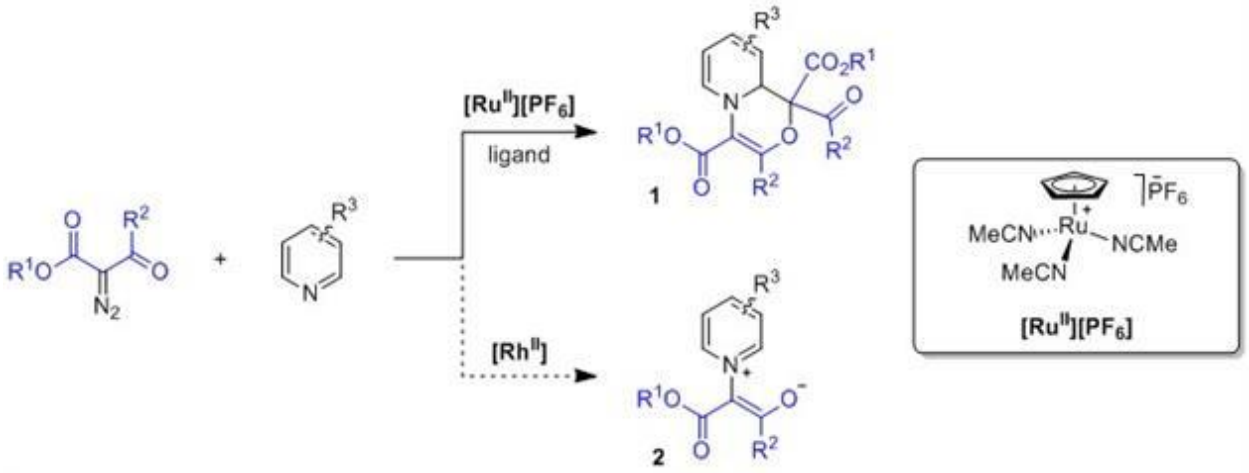

P-545

Efficient Ru-catalyzed N-methylation of Amines using Methanol

Dr. Thanh Tuan Dang[1], Dr. Balamurugan Ramalingam[1], Dr. Abdul Majeed Seayad[1]
[1]*ICES, Singapore, Singapore*

Poster Session 2

Methylation is one of the most widely used reactions in fine chemical and pharmaceutical industries.[1] Classical procedures for methylation often use toxic methyl halides as alkylating agents.[2] Recently, H-borrowing strategy for N-alkylation has been developed using alcohols as green and non-toxic alkylating agents instead of using toxic halides.[3] Herein, [RuCp*Cl2]2 in the combination with a bidentate ligand is reported as an efficient and high turnover catalyst for N-methylation of amines using methanol under neat conditions at 100-120oC following hydrogen borrowing strategy.[4] Practical and green methods for N-monomethylation of aromatic amines and N-doublemethylation of aliphatic amines with methanol are developed.

P-546

Combined Experimental and Computational Studies on Dinuclear Pd (I) Complexes as Versatile Catalysts in C-X Bond Formation

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Poster Session 2

Although much less known and employed in catalysis, palladium in odd oxidation states (I, III) stands out in reactivity from the more common even oxidation state (0, II, IV) palladium chemistry. Especially dinuclear complexes of Pd(I) offer novel possibilities in catalysis by providing a platform for cooperativity at their multiple metal sites.
Recent studies in our group revealed that Pd(I) dimers may directly react with aryl halides leaving the Pd(I)-Pd(I) bond intact. In this context, we have shown that the Pd(I)-Pd(I) unit in [$Pd_2(\mu\text{-}I)_2$(P[sup]t[/sup]$Bu_2)_2$] facilitates direct halide exchange of aryl iodides to form aryl bromides (Figure 1).[1,2] Our combined computational and experimental mechanistic study supported the direct involvement of dimeric Pd(I) species, whereas Pd(0) species were found to be ineffective under the employed reaction conditions. Moreover, we found the employed Pd(I) catalyst to be air-stable and easy-to-recover, thus presenting a promising alternative to more sensitive Pd(0) catalysis. Based on this alternative coupling concept at dinuclear Pd(I) sites, we are exploring novel Pd(I)-catalysed protocols for C-X bond formation (Figure 1, X = Nu) employing a combined experimental and computational approach.[3,4]

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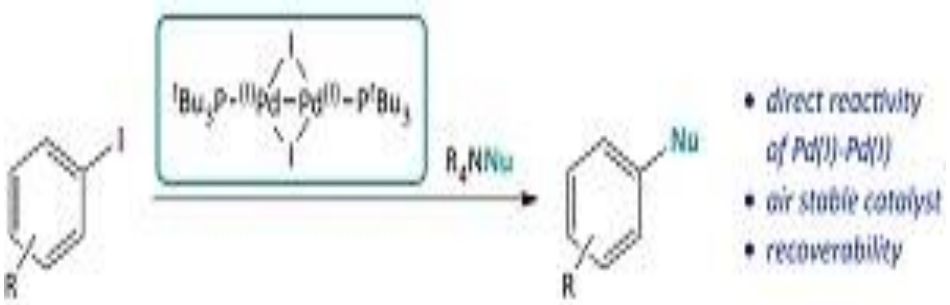

P-547

Nickel-Catalyzed Trifluoromethylthiolation of Aryl Chlorides: Fundamental Studies Revealing the Active Catalytic Species and the Key Roles of Ligand and Additive

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Poster Session 2

Continuous efforts to develop new catalytic systems are being made in order to reach new levels of efficiency in chemical synthesis. A strong fundamental understanding is essential for discovering new transformations and for fine-tuning known systems. Nickel as historically been recognized as a more reactive counterpart of palladium, but many factors have so far suppressed its wide applicability. The possibility of multiple reaction pathways (i.e., Ni(0)/Ni(II) or Ni(I)/Ni(III) catalytic cycles), numerous potential active species and the difficulties in controlling the selectivities and reactivities illustrate the diverse nature of Ni catalysis. Fundamental studies are therefore often required to overcome these issues.

In that regard, this poster will present a specific case where computational and experimental tools were combined to gain a deeper understanding of the key factors. As a result, the importance of ligand properties and its implications on the active species of the catalyst, along with the role and beneficial effect of an additive and the characterization of key intermediates are highlighted. These studies also led to the development of an unprecedented metal-catalyzed trifluoromethylthiolation protocol for aryl chlorides [1]. Furthermore, this methodology is shown to be applicable in the late-stage modification of compounds of pharmaceutical relevance.

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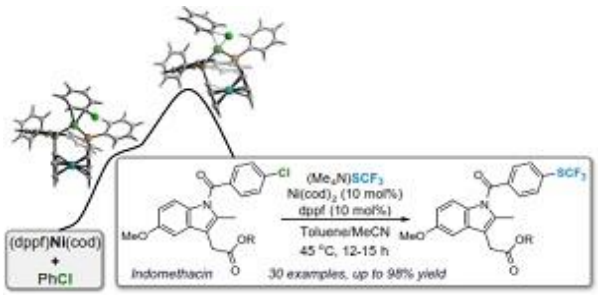

P-548

Synthesis and bioactivity studies of berkelic acid and analoges

Tamara Arto[1], Prof. Francisco Javier Fañanás[1], Prof. Félix Rodríguez[1]
[1]*University of Oviedo, Oviedo, Spain*

Poster Session 2

Berkelic Acid is a stereochemically dense secondary metabolite isolated by Stierle and co-workers in 2006 from an extremophile Penicillium species found in the hostile environment of Berkeley Pit Lake, Montana (USA). [1] This lake was formed when an abandoned copper mine was filled with infiltrating ground water to give an extremely acidic (pH= 2.5) and metal-contaminated ecosystem. Berkelic acid is one of the increasing numbers of novel secondary metabolites isolated from extreme dwelling microorganisms that have been found to present unique structure and bioactivity. Specifically, isolation team reported high and selective biological activity towards the human ovarian cancer line OVCAR-3 for this molecule and also it was found to inhibit the cysteine protease caspase-1 and matrix metalloprotease MMP-3. However, studies run with synthetic berkelic acid showed no antitumoral activity. [2] We have recently published a practical total synthesis of this natural product based on a strategy where the polycyclic core of (-)-berkelic acid was constructed in just one step with a high control of the stereoselectivity and from very simple starting materials. [3] Following this highly stereoconvergent and modular strategy we were able to synthetize up to 15 structurally analogous compounds to berkelic acid. We evaluated the activity of some of these molecules as well as berkelic acid itself, against ovarian cancer cell line OVCAR-3 and SCC38PWZL head and neck adenocarcinoma.

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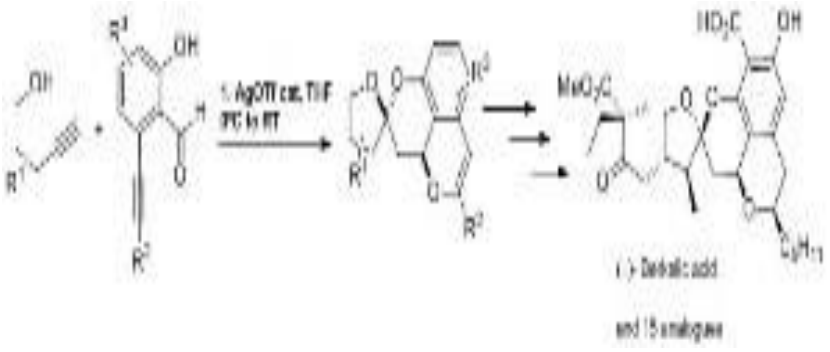

P-363

Asymmetric Pd-catalyzed allylic substitutions using P-S ligands

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Poster Session 2

Enantioselective Pd-catalyzed allylic substitution is one of the most powerful and versatile tools for the construction of new chiral carbon-carbon and carbon-heteroatom bonds.[1] In order to achieve high levels of enantioselectivity, two different strategies have been used. In the first strategy, C2 –symmetrical scaffolds are used to restrict the number of diasteromeric transition states. The second one, consists in the use of ligands that can differenciate the two carbon allyl terminus, by means of either a secondary ligand-nucleophile interaction or an electronic differentiation2. In this latter strategy, the use of heterodonor ligands allows the ability to electronically distinguish between the two allylic terminal carbons due to the distinct trans influences of the donor atoms.[2] Although these strategies have led to the discovery of several privileged ligands that provide high levels of enantioselectivity[1,2], asymmetric induction is highly dependent on the steric demands of the substrate. Thus, the search of new ligands which tolerate a broad range of substrates still remains a challenge. With this purpose, we have prepared a family of phosphite-thioether ligands and applied them in the Pd-allylic substitution of several substrates.

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P-549

Domino Reaction to Access Alkynylated Heterocycles: -A Complementary Method to C-H Functionalization

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[1]*Ecole Polytechnique Federale De Lausanne, Lausanne, Switzerland*

Poster Session 2

Molecules containing heterocycles and alkynes play an important role in medicinal chemistry and material science. A well-established method – the Sonogashira reaction- has dominated the introduction of alkynes onto heterocycles. Due to several shortcomings of the Sonogashira reaction, such as stoichiometric waste production and poor stability or accessibility of starting materials, a more direct but still regioselective method to access alkynylated heterocycles is highly desirable.

Based on previous work in our group, a direct alkynylation method was first developed to access C2 alkynylated furans and benzofurans using a gold catalyst and triisopropylsilyl ethynyl benziodoxolone (TIPS-EBX) reagent. In the case of benzofurans, Zn(OTf)2 was discovered as an efficient Lewis acid to activate EBX reagents.

Starting from 2012, we spent intensive effort on developing a cyclization-alkynylation domino reaction to access C3-functionalized furans. We discovered that bistrifluoromethyl benziodoxole reagent is an exceptionally efficient reagent for this process together with a gold (III) catalyst. Then we turned our interest to the synthesis of C5- and C6-alkynylated indoles. In this case, the advantages of the domino approach will become fully apparent, as the benzene ring of indoles is much less reactive than the pyrrole part for direct functionalization. A platinum (II) catalyst showed superior reactivity starting from pyrrole homo-propargylic alkynes. C5- or C6- alkynylated indoles can be accessed selectively depending on the substitution pattern of the pyrrole starting materials.

Based on either direct C-H functionalization or a domino approach, a series of alkynylated heterocycles could be rapidly accessed. Further functionalization of these compounds gave access to unprecedented building blocks for organic materials. Future work will focus on developing new domino processes with different metal catalysts and electrophilic reagents.

P-550

In Situ Diazomethane Generation and the Palladium-Catalysed Cyclopropanation of Alkenes

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[1]*University of Edinburgh, Edinburgh, UK*

Poster Session 2

The cyclopropanation of alkenes with diazomethane under palladium catalysis, first discovered in the 1960s,[1] is a versatile method for the synthesis of cyclopropanes from terminal, strained and electron-deficient alkenes. However, the necessity of using the acutely toxic and explosive diazomethane has undoubtedly limited its use. Although methods for the in situ generation of diazomethane from the commonly-used N-methyl-N-nitroso precursors have been reported,[sup]2,3[/sup] these require strongly alkaline conditions to proceed, thereby limiting the substrate scope.

We present an alternative strategy; the catalytic protodesilylation of trimethylsilyldiazomethane (Me_3SiCHN_2) under mild conditions affords diazomethane, which engages in the palladium-catalysed alkene cyclopropanation reaction. As well as representing a practical means for effecting this transformation, this method for in situ diazomethane generation has also enabled the study of aspects of the reaction mechanism – particularly relating to the nature and origins of side products – allowing for the rational optimisation of the reaction conditions.

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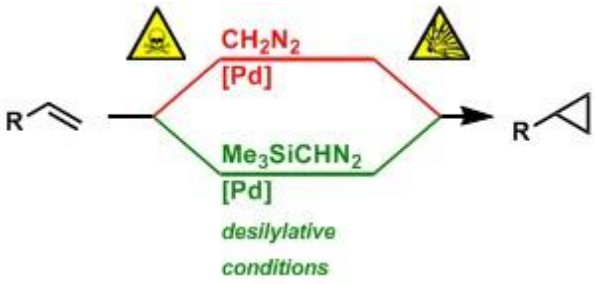

P-551

Rhodium (I)-N-Heterocyclic Carbene Catalyst for Selective Coupling of Aromatic Heterocycles with Olefins and Alkynes by C-H Activation

BsC. Ramón Azpíroz Latre[1], Dr Ricardo Castarlenas[3], Dr Luis A. Oro[3]

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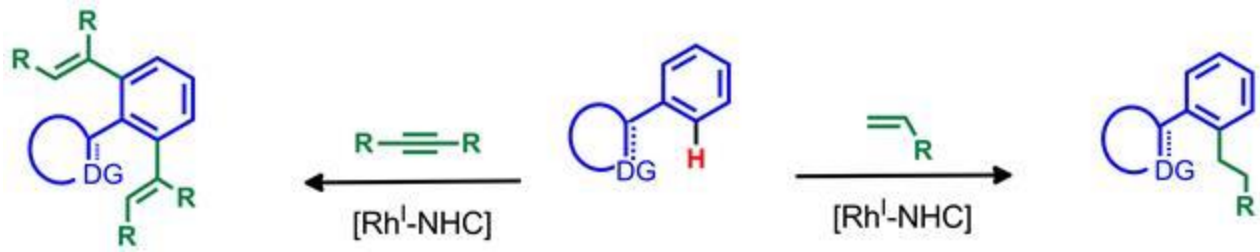
Poster Session 2

The development of new and selective catalytic methodologies has been the focus of intense research. Particularly, rhodium catalyzed C-C bond formation via C-H activation continues to be a powerful tool in organic shynthesis. Substitution of classical ligands such as phosphines by NHC carbene ligands in the metal center has a significant influence on the selectivity control over the catalytic outcome.[1] Herein, we present the selective coupling of heteroarenes with alkenes and alkynes mediated by a Rh[sup]I[/sup]-NHC catalyst. The proposed mechanism involves C-H activation, migratory insertion reactions and reductive elimination steps (Scheme 1 - Control of selectivity in the aromatic heterocycles functionalization).



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1 (a) Rubio-Pérez, L.; Azpíroz, R.; Di Giuseppe, A.; Polo, V.; Castarlenas, R.; Pérez-Torrente, J.; Oro, L. A. Chem. Eur. J. 2013, 19, 15304-15314. (b) Azpíroz, R.; Rubio-Pérez, L.; Di Giuseppe, A.; Passarelli, V.; Lahoz, F. J.; Castarlenas, R.; Pérez-Torrente, J. J.; Oro, L. A. ACS Catal. 2014, 4, 4244-4253. (c) Azpíroz, R.; Rubio-Pérez, L.; Castarlenas, R.; Pérez-Torrente, J.; Oro, L. A. ChemCatChem 2014, 9, 2587-2592.

P-552

Selective C-H Bond Functionalization of 2-(2-Thienyl)-pyridine by a Rhodium N-Heterocyclic Carbene Catalyst

Dr Laura Rubio-Pérez[1], Dr Manuel Iglesias[1], Dr Luis A. Oro[1]
[1]*Instituto De Síntesis Química Y Catálisis Homogenea-ISQCH, Zaragoza, Spain*

Poster Session 2

Thiophene moieties are present in a great number of natural and synthetic organic molecules, which include pharmacologically active heterocyclic compounds and thiophene-based materials.[1] The development of new transition-metal catalyzed C-C bond formation via C-H activation has been revealed as a very powerful, selective an atom-economical transformation that has pushed forward organic synthesis in the last decade. We have developed a Rh-catalyzed functionalization of 2-(thiophen-2-yl)pyridine with unactivated internal alkynes and terminal olefins by directed C-H activation. This reaction renders moderate to excellent yields and high selectivities for the hydroarylation of a wide range of internal alkynes and terminal alkenes under relatively mild conditions. (Scheme 1).[2]

Scheme 1. Hydroarylation of 2-(thiophen-2-yl)pyridine with alkenes and alkynes by Rh-NHC catalyst.

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1. Kishbaugh, T. L. S. in Progress in Heterocyclic Chemistry, Vol. 14 (Eds.: G.W. Gribble, T. L. Gilchrist), Elsevier, Oxford, 2002, Chap. 5.1, pp. 319 –355.
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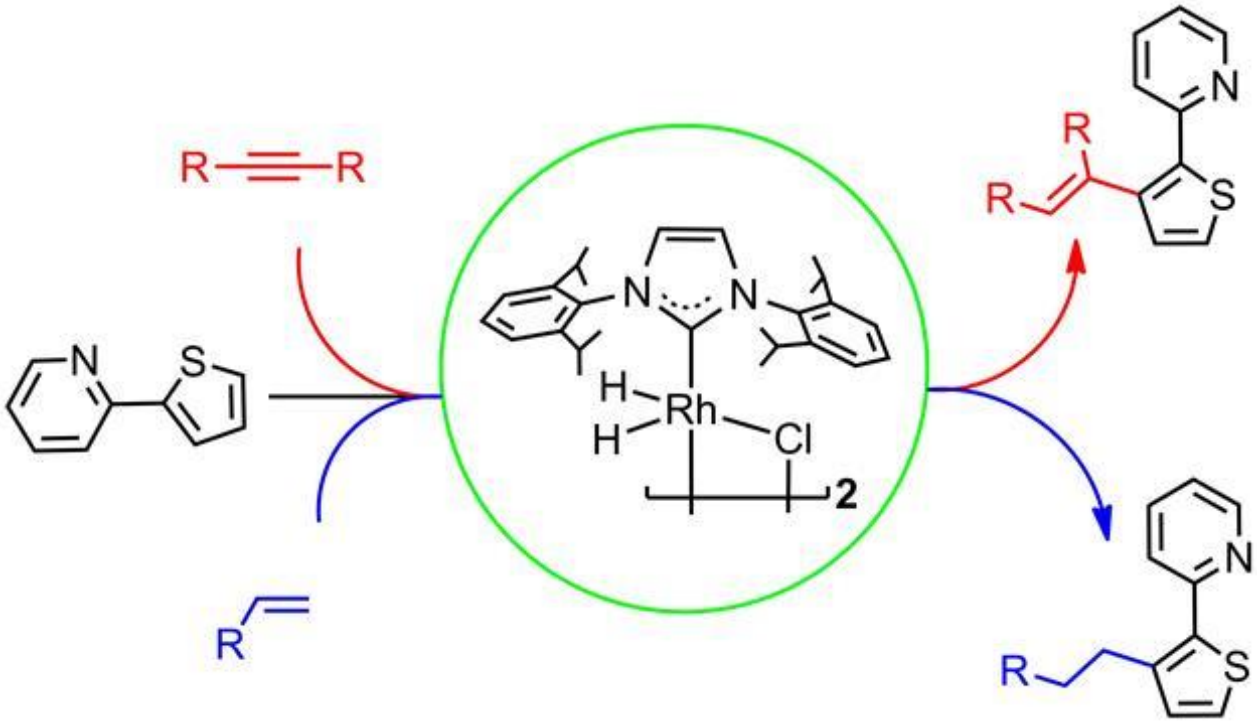
R
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N
S
H
Rh
H
Cl
2
R
R
N
S
R
N
S

P-553

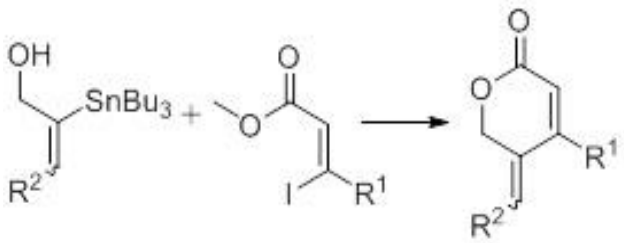
Metalic palladium catalyzed ligand-free Migita-Stille coupling

Master of Pharmacy Zbyněk Brůža[1], Master of Pharmacy Jiří Kratochvíl[1], Master of Pharmacy Zdeněk Novák[1], PhD. Mukund Ghavre[1], Associate Prof. Jiří Kuneš[1], Prof. Milan Pour[1]
[1]*Faculty of Pharmacy in Hradec Králové, Charles University in Prague, Hradec Králové, Czech Republic*

Poster Session 2

Migita-Stille reaction is well known cross-coupling of organostannanes and different electrophiles using Pd^0 species with various ligands.
Palladium black in DMF catalyzes cross-coupling between α-stannyl allylic alcohols (1) and (Z)-β-iodoacrylates (2) to produce polysubstituted pyranones (3) in high yields without the need for ligands, additives or solid support. This method is also applicable to other substrates which promises access to a cheaper coupling procedure.[1]

References:
[1] Kratochvil, J. et al. Org. Lett. 2015,17, 520-523



1 2 3

P-554

Cyclic Sulfamidates as Versatile Building Blocks for the Synthesis of Novel BACE 1 Inhibitors

Ana I de Lucas[1], Juan A. Vega[1], Andrés A. Trabanco[1], Henricus J.M. Gijsen[2], Gregor J. Macdonald[2]
[1]Neuroscience Medicinal Chemistry, Janssen Research & Development, Janssen-Cilag S.A., Toledo, Spain, [2]Neuroscience Medicinal Chemistry, Janssen Research & Development, Janssen Pharmaceutica N.V., Beerse, Belgium

Poster Session 2

Alzheimer's disease (AD) is a neurodegenerative brain disorder and the major cause of dementia. Despite massive investments, there are no effective treatments and the currently available therapies are limited to a symptomatic relief. The cost of caring for an increasing number of patients continues to rise; in 2011 there were an estimated 30 million people with dementia worldwide, with numbers expected to further increase to 80 million by 2040. Pathologically, AD is characterized by the existence of two features namely amyloid plaques containing Aβ peptides and neurofibrillary tangles. The Aβ plaques are generated by the cleavage of the membrane-associated amyloid precursor protein (APP) by aspartyl proteases, β- and γ-secretase. Thus, inhibition of β-secretase (BACE) represents a strategy for the development of disease-modifying therapeutics for the treatment of AD.
1,2-Cyclic sulfamidates represent a versatile class of functionalized electrophiles. These compounds can undergo regiospecific ring opening with several nucleophilic reagents. In this communication we report on the ring opening of cyclic sulfamidates with nucleophiles containing a pendant nitrile or ester function, which after a subsequent intramolecular amidine formation or lactamization reaction provide novel scaffolds with BACE-1 inhibitory activity.

References:
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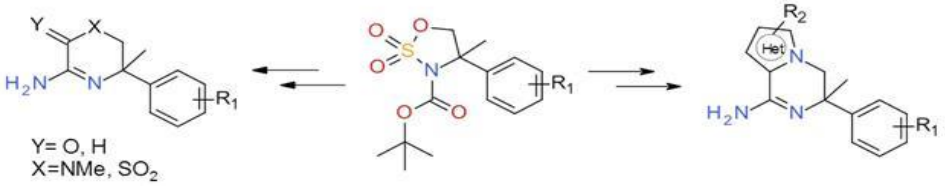
Y
X
H2N
N
R1
Y= O, H
X=NMe, SO2
O
S
N
O
O
O
R1
R2
Het
N
H2N
N
R1

P-555

Nickel-Catalyzed Reductive Carboxylation of Benzylic C-N Bonds with CO2

Dr. Morgane Gaydou[1], Dr. Toni Moragas[1], Prof. Rubén Martín [1,2]

[1]Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain [2]Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain

Poster Session 2

In the past years a significant progress has been made for the carboxylation of aryl and benzyl halides with CO_2.[1] More recently, our group described a challenging activation of C-O bonds providing a new tool for accessing carboxylic acids.[2] With the aim of expanding the scope of coupling partners we now report a new protocol that deals with the carboxylation of C-N bonds.[3] This new method does not only represent an extension of previously reported carboxylation reactions, but also constitute the first time that a cross-electrophilic event can be conducted via C-N bond cleavage.

References:

[1] (a) Correa, A.; Martin, R. J. Am. Chem. Soc. 2009, 131, 15974. (b) León, T.; Correa, A.; Martin, R. J. Am. Chem. Soc. 2013, 135, 1221. (c) Fujihara, T.; Nogi, K.; Xu, T.; Terao, J.; Tsuji, Y. J. Am. Chem. Soc. 2012, 134, 9106. (d) Tran-Vu, H.; Daugulis, O. ACS Catal. 2013, 3, 2417.

[2] Correa, A.; León, T.; Martin, R. J. Am. Chem. Soc. 2014, 136, 1062.

[3] Manuscript submitted.


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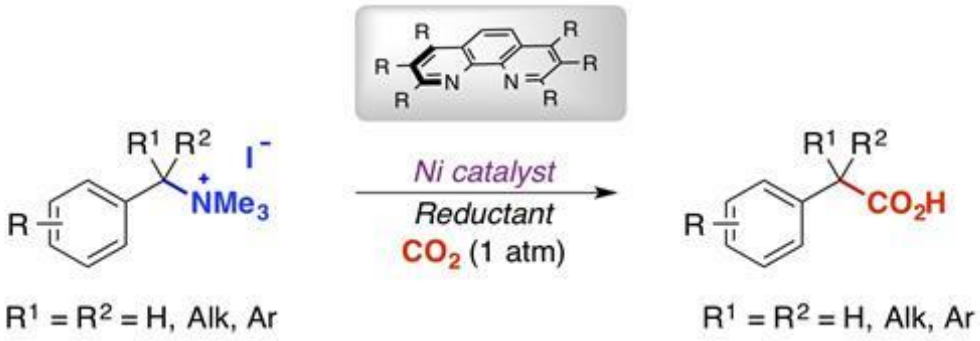

R
R
R
R
N
N
R
R
R1 R2
I-
+
NMe3
R
Ni catalyst
Reductant
CO2 (1 atm)
R1 R2
CO2H
R
R1 = R2 = H, Alk, Ar
R1 = R2 = H, Alk, Ar

P-556

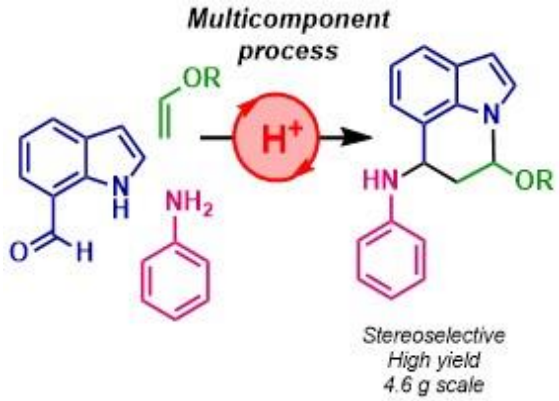
A New Catalytic Multicomponent Coupling Reaction for the Synthesis of Pyrrolo[3,2,1-ij]quinoline Derivatives

Raquel Fontaneda[1], Alicia Galván[1], Prof. Félix Rodríguez[1], Prof. Dr. Francisco Javier Fañanás[1]
[1]*Universidad De Oviedo, Oviedo, Spain*

Poster Session 2

The pyrrolo[3,2,1-ij]quinoline structural motif is found in numerous pharmaceuticals and natural products. Extensive studies have demonstrated that pyrrolo[3,2,1-ij]quinolines are lead candidates in potential treatments for diseases. For example, derivatives 1 and 2 possess good anticonvulsant properties. This system is also present at the core of the lilolidine (3) alkaloids, which have been explored as therapeutics and fungicides.
In this context we have developed a stereoselective multicomponent Brønsted acid catalyzed reaction of 1H-indole-7-carbaldehyde derivatives, anilines and enol ethers affording interesting pyrrolo[3,2,1-ij]quinoline compounds in high yields and as single diastereoisomers. This process involves the in situ generation of N-arylimine derivatives and their subsequent reaction with enol ethers.

References:
R. J. Bass, R. C. Koch, H. C. Richards, J. E. Thorpe, J. Agric. Food Chem., 1981, 29, 576.
M. Isaac, A. Slassi, A. O'Brien, L. Edwards, N. MacLean, D. Bueschkens, D. K. H. Lee, K. McCallum, I. D. Lannoy, L. Demchyshyn, R. Kamboj, Bioorg. Med. Chem. Lett., 2000, 10, 919.

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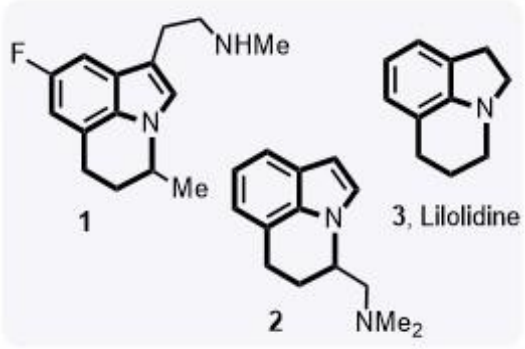
F
NHMe
N
Me
1
N
3, Lilolidine
N
2
NMe2

P-557

Ni-catalyzed Direct Borylation of Aryl Fluorides via C–F Cleavage

Sr. Javier Echavarren[1], Mr. Rubén Martín[1,2], Xiang Wei Liu[1], Cayetana Zarate[1]

[1]Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain, [2]Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain

Poster Session 2

Over the past decade the utilization of Ni catalysts has gained considerable recognition in the scientific community. The electropositive character of nickel greatly facilitates the oxidative addition step within the catalytic cycle as this elementary step entails the loss of electron density around the metal. This allows the use of cross-coupling electrophiles that can be considered quite challenging in palladium catalysis such as aryl fluorides. These are less reactive than any of the aryl halide series due to the higher C□F bond bond dissociation energy. As part of our interest in activation of inert bonds, we describe herein the Ni-catalyzed borylation of aryl fuorides via C(sp2)–F cleavage (Scheme 1). The transformation is distinguished by a broad substrate scope including challenging substrate combinations, thus representing a straightforward alternative to the well-established borylation techniques reported in the literature.

Scheme 1. Ni-catalyzed C(sp2)–F borylation

References:

S. Z. Tasker, E. A. Standley, T. F. Jamison, Nature, 2014, 509, 299.

T. T. Tsou, J. K. Kochi, J. Am. Chem. Soc. 1979, 101, 6319.

For a Suzuki-Miyaura coupling of aryl fluorides, see: M. Tobisu, T. Xu, T. Shimasaki, N. Chatani, J. Am. Chem. Soc. 2011, 133, 19505.

Selected recent references: (a) C. Zarate, R. Martin, J. Am. Chem. Soc. 2014, 136, 2236. (b) A. Correa,R. Martin, J. Am. Chem. Soc. 2014, 136, 7253. (c) T. Moragas, J. Cornella, R. Martin, J. Am. Chem. Soc. 2014, 136, 17702. (d) J. Cornella, E. Goḿez-Bengoa, R. Martin, J. Am. Chem. Soc. 2013, 135, 1997.

J. F. Hartwig, Chem .Soc. Rev. 2011, 40, 1992.

P-622

A new access to alpha-iodoenones by IPyBF4 triple bond activation of propargylic esters.

Miss Tatiana Suarez-Rodriguez[1], Dr Alfredo Ballesteros Gimeno[1], Dr Angel Luis Suarez Sobrino[1]
[1]*University of Oviedo, Oviedo, Spain*

Poster Session 2

Propargylic alcohol derivatives constitute an interesting class of organic compounds. They are easily accessible from terminal alkynes and aldehydes or ketones, and have been extensively used as synthetic intermediates due to their particular reactivity. For instance, propargylic rearrangement by electrophile triple bond activation of the corresponding ester derivatives has been applied in the past years as an access to other organic functionalities. (1)

Within this context, there are several examples in the literature to obtain α-haloenones, an important class of synthetic intermediates, by propargylic rearrangement using a metal catalyst and an external source of halogen. (2) However, apart from the low generality of most methods, there are few examples in which the triple bond activation is directly exerted by the electrophilic halogen without the use of a carbophilic metal catalyst. (3)

In this regard we describe an easy new access to α-iodoenones from propargylic esters using IPy2BF4 both as carbophilic triple bond activator and electrophilic iodine source. The reaction takes place with good yields in the presence of an acid and under mild conditions. It also has demonstrated group tolerance, since it goes well for primary, secondary or terciary propargylic alcohol derivatives containing either alkyl, aryl or heteroaryl groups.

In summary, we have developed an efficient synthesis of α-iodoenones by the use of propargylic esters and IPy2BF4 as both carbophilic activator and iodine source.

References:
(1) ACS Catal. 2014, 4, 1911-1925
(2) a) Org. Lett, Vol. 12, No. 9, 2010; b) Org. Lett, Vol. 9, No. 11, 2007
(3) Org. Lett. 2014, 16, 5246−5249

P-558

In situ Hypervalent Activation as Key Step in Direct ortho-Coupling of Iodoarenes

Miss Yichen Wu[1], Ismael Arenas[1], Alexandr Shafir[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

The α-aryl ketone is an important building blocks in the preparation of a variety of pharmaceuticals and bioactive molecules. Many effective methods have been developed for their synthesis, including the metal-catalyzed C-C coupling protocols made practical by Miyuara, Buchwald, Hartwig, etc.[1] Alternative routes using diaryliodonium salts as aryl transfer agents have also been found suitable in several applications.[2] Nevertheless, challenges still remain, and the development of new methods continue.
We recently reported a protocol for direct metal-free α-arylation of activated carbonyl compounds employing PIFA [phenyliodine bis(trifluoroacetate)] to construct the product with the iodine conserved ortho to the new C-C bond.[3] Now we present the recent findings on the ortho CH functionalization of iodoarenes through a direct C-C coupling via in situ hypervalent activation in the presence of the suitable oxidant (Oxone or m-CPBA). The reaction shows good functional group compatibility with respect to the iodoarene partner, and Oxone appears to play a double role as both the initial oxidant of ArI and promoter of the subsequent dehydrogenative C-C coupling.

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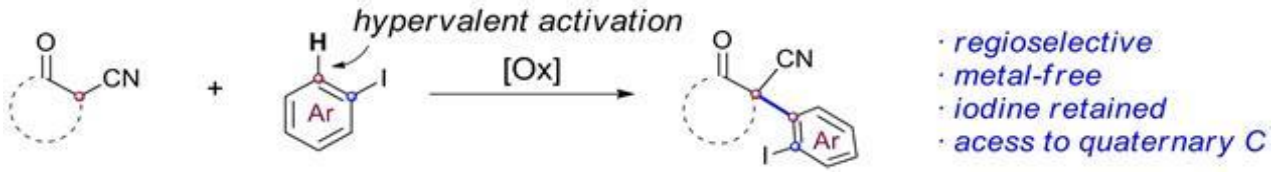

P-559

Borylphosphanes and Boryl(organyl)phoshanes Gold(I) Complexes: Transmetallation and beyond

PhD Student Ekaterina Smirnova[1], Dr. Juan Sarria Toro[1], Dr. Nuno Bandeira[1], Prof. Carles Bo[1], Prof. Antonio Echavarren[1]

[1] *Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

Cationic hexanuclear gold cluster 1 was previously obtained by chloride abstraction with $AgSbF_6$ from neutral gold(I) complexes bearing ortho-boronylphosphine ligands.[1] Herein we report the most recent insight obtained in the chemistry of this type of gold clusters. Mechanistic studies supported by DFT calculations have revealed that an associative ligand substitution is the rate-determining step on the 1,6-enyne isomerization catalysed by gold cluster 1. Two additional hexanuclear gold clusters bearing cyclohexyl 2 and 2-furyl 3 substituents on phosphorous atom have been synthesized. These new clusters will aid the understanding of the influence of the phosphine's electronic properties in the reactivity of the corresponding gold clusters. In an attempt to supress Au-B transmetallation and favour the formation of cationic mononuclear gold complexes, boryl(organyl)phospnanes of the type 4 were used. Ligands 4 were obtained by the reaction of chiral diols with precursor ortho-$Ph_2PC_6H_4CH_2B(NMe_2)$.[2]

Acknowledgments.
We thank MINECO (project CTQ2010-16088/BQU), Severo Ochoa Excellence Accreditation (SEV-2013-0319), European Research Council (Advanced Grant No. 321066), and the ICIQ Foundation for financial support.

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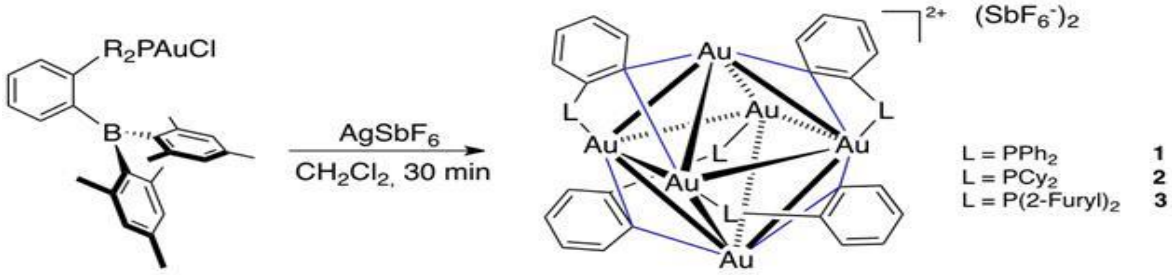

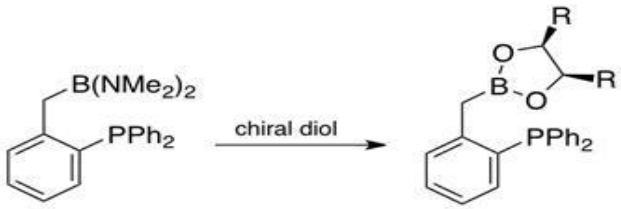

4

R = Me, Ph or $Me_2N(O)C$

P-560

An Approach Towards the Total Synthesis of Repraesentin F

Sofia Ferrer[1], Tania Jiménez[1], Prof. Dr. Antonio Echavarren[1,2]

[1]Institut Català de Investigació Química (ICIQ), Tarragona, Spain [2]Departament de Química Analílitca i Orgànica, Universitat Rovira i Virgili, Tarragona, Spain

Poster Session 2

The natural product repraesentin F is a protoilludane-related sesquiterpene isolated from the fungus Lactarius repraesentaneus, whose biological activity is related to regulation of plant growth.[1] Its characteristic octahydrocyclobuta[a]pentalene skeleton with an anti- fusion of the rings is highly attractive and challenging, and up to date no total synthesis has been reported. Our approach towards the synthesis of this natural product exploits the ability of cationic gold(I) complexes to promote a wide variety of enyne cyclizations.[2] The key reaction involves a tandem gold-catalyzed enyne cyclization/ring-expansion/Prins reaction with the appropriate cyclopropyl enyne, yielding the tricyclic skeleton in single step.[3] Details on this cyclization and functionalization of the tricyclic core to synthesize repraesentin F will be presented.

Aknowledgements:
We thank MINECO (project CTQ2010-16088/BQU, Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319), the European Research Council (Advanced Grant No. 321066), Cellex Foundation, and the ICIQ Foundation for financial support.

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3 E. Jiménez-Núñez, C. K. Claverie, C. Nieto-Oberhuber, A. M. Echavarren, Angew Chem. Int. Ed. 2006, 45, 5452-5455.


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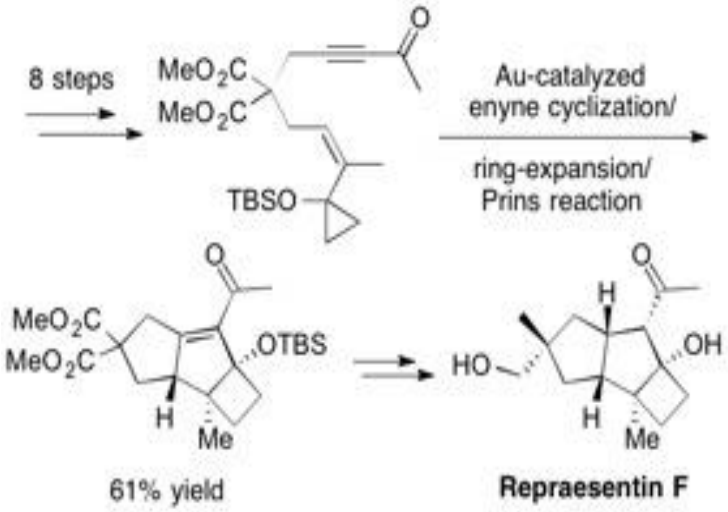
8 steps
MeO2C
MeO2C
TBSO
O
Au-catalyzed
enyne cyclization/
ring-expansion/
Prins reaction
MeO2C
MeO2C
OTBS
H
Me
61% yield
HO
OH
H
H
Me
Repraesentin F

P-561

Digging into the Gold(I)-Catalyzed Intermolecular Reaction of Alkynes with Alkenes: Cyclobutene or Diene Formation

M. Elena De Orbe[1], Laura Amenós[1], Prof. Feliu Maseras[1], Prof. Antonio M. Echavarren[1]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

Despite many advances in homogeneous gold catalysis [1], intermolecular reactions between alkynes and alkenes giving functionalized alkenes are still a challenge owing to the competition of the final products with the starting materials leading to oligomers or polymers [2]. In the gold(I)-catalyzed [2+2] cycloaddition of meta- and para-substituted ethynylbenzenes with a wide variety of alkenes, cyclobutenes are formed as the major or exclusive products. However, in the case of ortho-subtituted ethynylbenzenes, we discovered that both cyclobutenes and 1,3-dienes are formed [3].
The ortho-substituent of the arylalkyne was found to play a very important role, as different ratios of cyclobutene and diene products are obtained in the reaction between diverse ortho-subtituted ethynylbenzenes and the same alkene. Furthermore, subtle differences in the nature of the alkene also affect the selectivity of this kind of transformations, dramatically changing the products ratio in the reaction with the same alkyne.

Acknowledgments.
We thank MINECO (project CTQ2010-16088/BQU, Severo Ochoa Excellence Accreditation SEV-2013-0319 and Severo Ochoa fellowship), European Research Council (Advanced Grant No. 321066), and the ICIQ Foundation for financial support.

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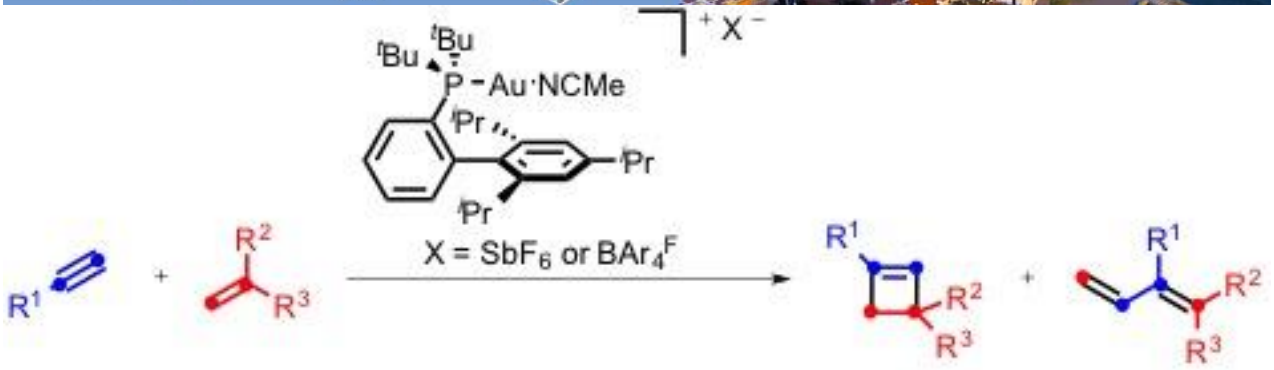
Directed Towards Organic Synthesis
IUPAC International Symposium
Sitges - Barcelona
From June 28th to July 2nd
2015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R1
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R1
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P-562

Gold(I)-catalyzed multicomponent [2+2+2] cycloaddition of allenamides, alkenes and aldehydes

Mr. Iván Varela[1], Mr Hélio Faustino[1], Mr. Jaime Fernández-Casado[1], Mr. Ronald Nelson[1], Mr. David Cagiao[1], Mr. José L. Mascareñas[1], Mr. Fernando López[1,2]

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Poster Session 2

During the last decade there have been extraordinary advances in the development of Au-catalyzed processes. Our group has demonstrated the possibility of using allenamides as two carbon-atom components in intermolecular Au-catalyzed [4 + 2] and [2 + 2] cycloadditions with dienes and alkenes, respectively.[1] We have also developed a simple and highly versatile cascade cycloaddition between allenamides and carbonyl-tethered alkenes that affords oxa-bridged seven-, eight- and even nine-membered carbocycles.[2]

More recently we have also demonstrated that it is possible to achieve annulations between allenamides, alkenes and carbonyl derivatives in a fully intermolecular way.[3] The three-component assembly is better carried out by using a phosphite-gold complex as catalyst, and takes place with high regioselectivity and, in many cases, with good diastereoselectivities. The reaction works with different types of allenes, alkenes and aldehydes and provides a straightforward entry to 2,6-disubstituted tetrahydropyrans. We will also disclose relevant mechanistic aspects and preliminary results of an enantioselective variant.

[Figure 1]

References:

[1] (a) H. Faustino, F. López, L. Castedo, J. L. Mascareñas, Chem. Sci. 2011, 2, 633–637. (b) J. Francos, F. Grande-Carmona, H. Faustino, J. Iglesias-Sigüenza, E. Díez, I. Alonso, R. Fernández, J. M. Lassaletta, F. López, J. L. Mascareñas, J. Am. Chem. Soc. 2012, 134, 14322–14325. c) S. Montserrat, H. Faustino, A. Lledós, J. L. Mascareñas, F. López, G. Ujaque, Chemistry 2013, 19, 15248–15260. d) H. Faustino, P. Bernal, L. Castedo, F. López, J. L. Mascareñas, Adv. Synth. Catal. 2012, 354, 1658–1664.

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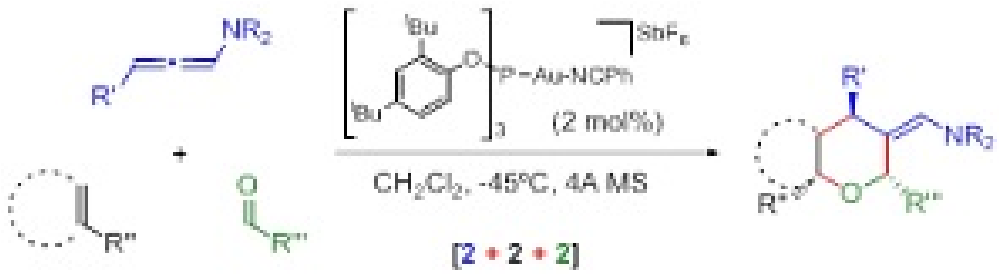
[3] H. Faustino, I. Varela, J. L. Mascareñas, F. López, Chem. Sci. 2015, DOI 10.1039/C5SC00295H.



P-563

A gold(I)-catalyzed oxidative rearrangement of lactam derived 1,3-enynes provides an efficient and selective route to cyclopentenones under mild conditions in the presence of pyridine-N-oxides as external oxidants

Prof. Cristina Prandi[1], Dr. Gabriele Prina Cerai[1], PhD Alberrto Oppedisano[1], Mrs Gizem Kaleoglu[1], Prof. Ernesto G. Occhiato[2]

[1]University of Turin, Department of chemistry, Turin, Italy, [2]University of Florence, Department of Chemistry, ,

Poster Session 2

We have previously demonstrated that the gold(I)-catalyzed reaction of N-Boc-protected 6-alkynyl-3,4-dihydro-2H-pyridines affords synthetically useful vinylogous amides (□-enaminones). The reaction has been studied in detail in order to optimize the reaction conditions, enlarge the scope and have insights into the mechanism and the structural features that selectively favor the 6-endo dig oxyauration of the triple bond.1

When the substrates are N-tosyl-protected 6-alkynyl-3,4-dihydro-2H-pyridines the intramolecular cyclization is prevented and an intermolecular reaction with an external oxidants can be featured.2 The reaction has been conducted on a model substrate in the presence of pyridin N-oxide as an oxidant and PPh3AuCl/Ag OTf (5% mol) as a catalyst in DCE at room temperature. The formation of the oxo carbenoid specie is reported to be a highly selective process based on the preferred approach of the oxidant to the less hindered end of the triple bond2 as a consequence of steric factors involved. In our case we observed a complete regioselectivity, being the highly conjugated system formed as a product one of the main factors involved. Furthermore, depending on the reaction conditions either conjugated dienones or cyclopentenones can be obtained, these ones as a result of the Nazarov cyclization on the open products formed.

References:

1. (a) Scarpi, D., Begliomini, S., Prandi, C., Oppedisano, A., Deagostino, A., Gómez-Bengoa, E., Fiser, B. and Occhiato, E. G. , Gold-Catalysed Synthesis of Exocyclic Vinylogous Amides and β-Amino Ketones: A Detailed Study on the 5-exo/6-endo-dig Selectivity, Methodology and Scope. Eur. J. Org. Chem 2015; (b) Oppedisano, A.; Prandi, C.; Venturello, P.; Deagostino, A.; Goti, G.; Scarpi, D.; Occhiato, E. G., Synthesis of Vinylogous Amides by Gold(I)-Catalyzed Cyclization of N-Boc-Protected 6-Alkynyl-3,4-dihydro-2H-pyridines. Journal of Organic Chemistry 2013, 78 (21), 11007-11016.

2. Zhang, L., A Non-Diazo Approach to α-Oxo Gold Carbenes via Gold-Catalyzed Alkyne Oxidation. Accounts of Chemical Research 2014, 47 (3), 877-888.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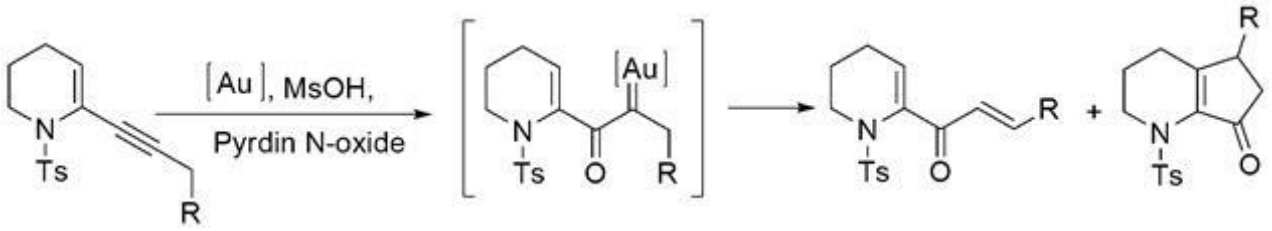

[Au], MsOH,
Pyrdin N-oxide
N
Ts
R
O
[Au]

P-564

Computational evaluation of the η6-arene during the ATH of imines on Noyori's RuII catalyst

MsC Miguel Ángel Soriano Lendínez[1], Dr. Petr Kačer[1], MSc Jakub Januščák[1], BSc Petr Šot[1], MSc Jan Pecháček[1], Dr. Marek Kuzma[1]

[1]*University of Chemistry and Technology of Prague, Prague, Czech Republic*

Poster Session 2

Asymmetric hydrogenation ranks to the most intensively researched way of preparation of enantiomerically pure compounds. In the field of asymmetric transfer hydrogenations (ATH) of C=N and C=O double bonds Noyori's ruthenium (II) complexes represent significant breakthrough. This catalytic system consists of three integral parts - chiral monotosylated diamine, η6-coordinated aromatic molecule and halogen. Aforementioned fragments/ligands offer countless possibilities for structural modifications. – e.g. alkylation of amino group, usage of diversely substituted η6-aromatic molecule, employment of different aryls within arylsulfonyl fragment etc. Systematic evaluation of these modifications has multilateral benefits because it not only helps to clarify mechanistic phenomena but also contributes to the deeper understanding of relationship between structure and catalytic activity. With sufficiently big data base it should be possible to tailor catalyst's properties specifically for given substrate and reaction conditions. Our research is focused on comprehension of role of the η6-aromatic molecule during asymmetric transfer hydrogenation of imines. This ligand plays very important mechanistic role because its structure allows asymmetric course of the reaction. Arene ligand can in certain cases form stabilizing CH/π interaction between aromatic part of substrate and therefore lower energy of transition state. This led us to the hypothesis that alteration of its structure could strongly affect enantioselectivity and reaction rate. This hypothesis has been brought up and discussed but only in case of ATH of C=O bonds, which dramatically differs from hydrogenation of C=N bonds. In our study we have prepared and compared catalysts with different aromatic ligands (benzene, p-cymene, mesitylene, 1,2,3,4,5,6-hexamethylbenzene) according to their performance (reaction rate, enantioselectivity) during hydrogenation of variously substituted 3,4-dihydroisoquinolines and tried to interpret obtained results via means of computational chemistry.

Acknowledgement: This work has been financially supported by the Grant Agency of the Czech Republic (Grant GACR 106/12/1276).

P-565

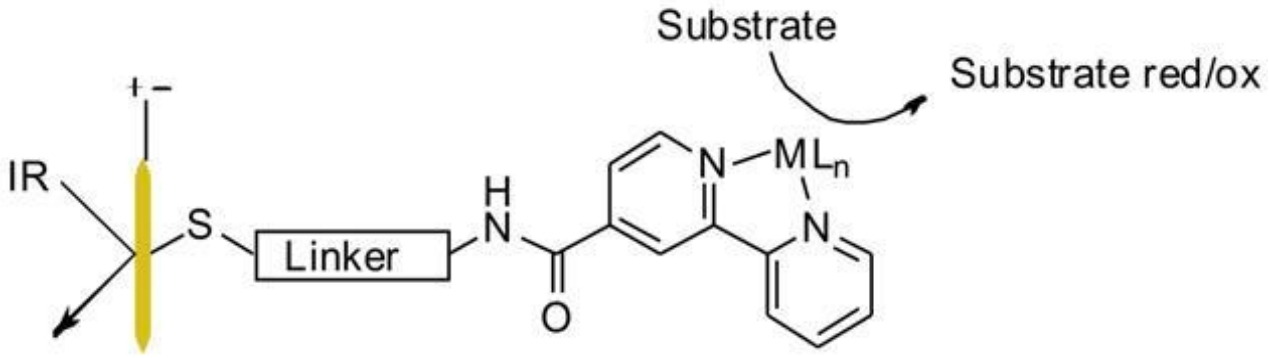
Bipyridine Complexes on Gold Electrodes - Synthesis, Immobilisation and Spectroelectrochemistry

Anja Sokolowski[1], Jacek Kozuch[2], C. Christoph Tzschucke[1]
[1]*Freie Universität Berlin, Berlin, Germany,* [2]*Technische Universität Berlin, Berlin, Germany*

Poster Session 2

Functionalisation of conductive surfaces by electrocatalytically active molecules makes it possible to convert electrical energy into chemical energy. A surface immobilisation facilitates electron transfer from electrode to the attached molecule and stabilises the catalyst.[1],[2],[3]
In our work, we investigate the viability of immobilisation of different catalysts on gold electrodes. Therefore, a modular route was designed wherein 2,2'-bipyridyl-4-carboxylic acid was covalently bound to 4-aminobenzenethiol or to cystamine by amide coupling. The resulting ligands were attached on gold surfaces and subsequently metalated. For monitoring complexation and catalytic activity a gold electrode is used as signal amplifier in attenuated total refection IR and as working electrode in an electrochemical setup. This methodology combines electrochemical and spectroscopic data from the same sample. Synthesis of the ligand, characterisation of the immobilised complexes and evaluation as catalysts will be presented.

References:
[1] S. A. Yao, R. E. Ruther, L. Zhang, R. A. Franking, R. J. Hamers, J. F. Berry, J. Am. Chem. Soc. 2012, 134, 15632-15635.
[2] J. D. Blakemore, A. Gupta, J. J. Warren, B. S. Brunschwig, H. B. Gray, J. Am. Chem. Soc. 2013, 135, 18288-18291.
[3] K. R. Brownell, C. C. L. McCrory, C. E. D. Chidsey, R. H. Perry, R. N. Zare, R. M. Waymouth, J. Am. Chem. Soc. 2013, 135, 14299-14305.



P-566

Synthesis, characterization and application of pyrene tagged chiral diphosphites for rhodium catalysed asymmetric hydroformylation

Anton Cunillera Martin[1], Dr. Cyril Godard[1], Prof. Aurora Ruiz[1]
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Poster Session 2

The immobilization of efficient homogeneous catalysts onto a solid support is currently an area of much interest to improve the sustainability of catalytic processes since it allows the recovery and reuse of the catalysts and usually maintain the level of selectivity compared to their homogeneous counterparts.[1] Among the strategies reported to immobilise metal catalysts, the use of non-covalent interactions provides interesting advantages since it usually does not requires additional synthetic efforts and maintain the structure of the ligand scaffold.[2]
In terms of support, carbon materials such as graphene, or carbon nanotubes emerged as promising supports because of their unique properties and large surface area.[3] Furthermore, they provide the possibility to immobilise catalysts via covalent or non-covalent interactions such as pi-pi stacking interactions, which allow the attachment of molecules containing large polyaromatic systems onto these carbon materials.[4]

In this work, we report the synthesis, characterization of chiral 1,3-diphosphite ligands derived from D-glucose bearing a pyrene moiety. Once coordinated to Rh, the system was immobilised onto carbon supports and used in the rhodium catalysed asymmetric hydroformylation of bicyclic alkene substrates. The results in terms of recycling and reuse of the catalysts will also be presented.

References:
[1] McMorn, P.; Hutchings, G.H. Chem. Soc. Rev. 2004, 33, 108.
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[3] Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. Chem. Rev. 2006, 106, 1105.
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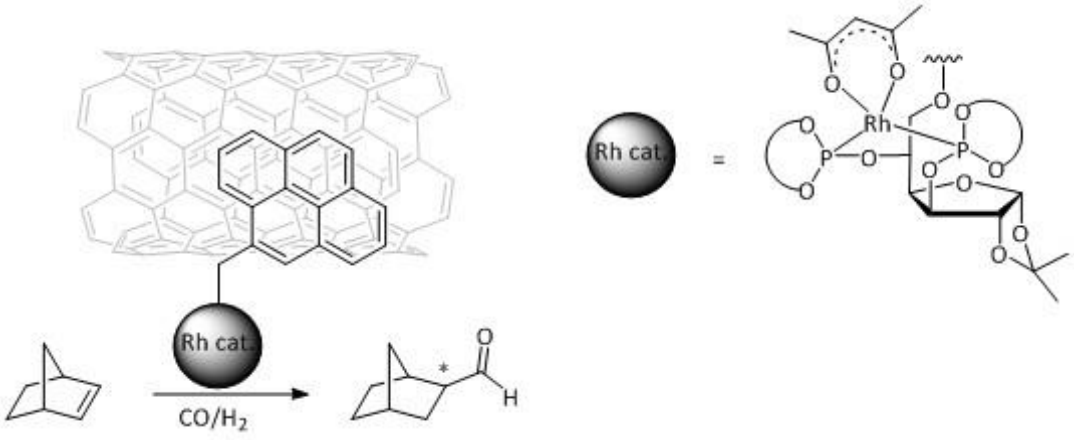

P-567

Understanding the control of the selectivity in oxygenation reactions

Paula Abril[1], Dr María Pilar del Río[1], Dr. José Antonio López[1], Prof. Dr Miguel Angel Ciriano[1], Dr. Cristina Tejel[1]

[1]*ISQCH (Instituto de Síntesis Química y Catálisis Homogénea), Zaragoza, Spain*

Poster Session 2

The synthesis of high valuable oxygenated compounds from crude and cheap raw chemicals is one of the most important transformations in current chemistry. In this context it is highly desirable to enable the use of oxygen as a primary oxidant because oxygen is inexpensive, abundant and environmentally benign. However, oxygenation of olefins with late transition metals produces 3-metalla-1,2-dioxolanes, whose evolution towards oxygenated products is not selective. The two sole exceptions to this behavior are a dianionic iridium complex leading to a 2-iridaoxetane,[1] and a rhodium triazenide complex,[2] both able to incorporate oxygen and transfer it to an olefin with an atomic economy of 100%.

In a completely different approach, Wacker type reactions are also a good alternative for the synthesis of high valuable chemicals, in which water and oxygen or hydrogen peroxide are the single subproducts. However most of the Wacker type reported oxidations involve the nucleophilic attack on a coordinated Pd(II) olefin, and only a few related examples with Rh(I) and Ir(I) complexes have been reported.[3]

In this communication we will show an iridium complex that promotes both type of olefin functionalization, i.e., the selective insertion of oxygen into olefinic bonds and the nucleophilic attack of a variety of nucleophiles such as alkoxides under controlled conditions. Some illustrative intermediates that show both reactions as the one depicted in the figure will be described.

References:

[1] V. W. Day, W. G. Klemperer, S. P. Lockledge, D. J. Main, J. Am. Chem. Soc. 1990, 112, 2031-2033.
[2] a) C. Tejel, M. A. Ciriano, E. Sola, M. P. del Río, G. Ríos-Moreno, F. J. Lahoz, L. A. Oro, Angew. Chem. Int. Ed. 2005, 44, 3267-3271.
[3] a) D. G. H. Hetterscheid, J.M. M. Smits, B. de Bruin, Organometallics 2004, 23, 4236-4246; b) J. S. Merola, R. T. Kacmarcik, Organometallics 1989, 8, 778-784.


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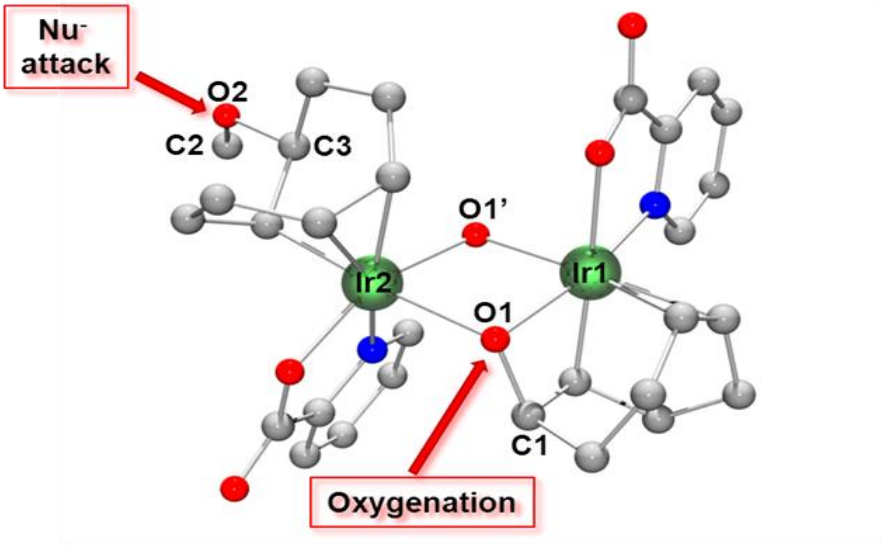
Nu⁻ attack
O2
C2
C3
O1'
Ir2
Ir1
O1
C1
Oxygenation

P-568

Directed functionalization of 2-ester substituted quinoxaline using LiTMP in the presence of Zinc Chloride.

Student Samuel R. A. Ferreira[1], Student Evelyn Mirella Pina Diniz[1], Student Simone Cavalcante Silva[1], Ph. D. Ricardo Vessecchi[1], Ph. D. Giuliano Cesar Clososki[1]
[1]*University of São Paulo, Ribeirão Preto, Brazil*

Poster Session 2

Nitrogen-containing heterocycles are privileged structures in organic chemistry [1,2,3]. Among them, quinoxaline derivatives are an important class of heterocyclic compounds widely used in industry and pharmaceutical formulation [4]. Over the last years, it has been reported a few studies describing the directed ortho metalation of quinoxalines. For example, Knochel and coworkers reported the use of $TMP_2MgCl.2LiCl$ for the deprotonation of quinoxalines under low temperatures but the methodology was not extended to unsubstituted substrates [5]. It is well know that the ortho metalation of quinoxalines is a difficult challenge due to very facile nucleophilic addition reactions due to low LUMOs energy levels of these substrates. Herein, we describe the deprotonation reaction of widely functionalized quinoxalines using a zinc-lithium amide mixture. Many problems have been found during the steps of metallation of these substrates when using $TMP_2Mg.2LiCl$ and TMPMgCl.LiCl (knochel bases). The use of TMPLi in the presence of zinc chloride has presente good results and completely avoided the undesired dimer formation, as reported by Knochel and coworkers in previous studies (Scheme 1). In addition, the palladium catalized cross coupling reaction of the corresponding organozinc intermediates with different aryl halides allowed the synthesis of a number of arylated derivatives (Figure 1).

Reference
1 - J. Org. Chem. 1995, 60, 2298-2301.
2 - J. AM. CHEM. SOC. 2007, 129, 12734-12738.
3 - Org. Lett. 2014, 16, 1232−1235.
4 – Eur. J. Med. Chem. 2014, 1-9.
5 - Chem. Eur. J. 2009, 15, 457-468


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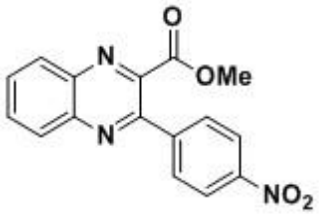
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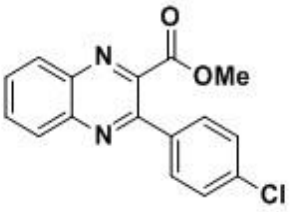
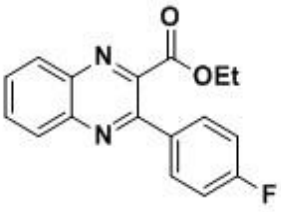
OMe
N
NO2

83%


O
N
OMe
N
Cl

71%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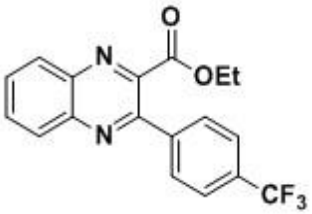
OEt
N
F

77%


O
N
OEt
N
CF3

65%

P-570

Synthesis of multi-heteroaromatic structures by metal catalyzed reaction of allenes with nucleophiles

Miss Lisa Cooper[1], Dr Maria Paz Muñoz[1]
[1]*University of East Anglia, Norwich, UK*

Poster Session 2

Nucleophilic addition to allenes have been previously studied using metal catalysis, in particular gold, where we have seen reports of hydroalkoxylation[1] [2], hydroamination[1] [2] [3] and hydroazidation[4] reactions which afford allylic ethers, allylic amines and allylic azides respectively via intermolecular addition.
In contrast, our group has published results for the di-hydroalkoxylation[5] and the bis-indolyation[6] of terminal allenes using platinum catalysis, where double intermolecular addition of the respective nucleophile to the terminal carbon is observed. Using results from the bis-indolyation reaction the research has been developed to give a broad investigation into the intermolecular addition of different nucleophiles to achieve a variety of complex structures.
Alongside the bis-indolyation, our group also published results involving the inter-intramolecular addition of nucleophiles to allenes[5]. This involved the addition of an external indole to allene bearing an indole moiety and this is being investigated to further optimize the selective formation of the desired product.

This poster will outline the results obtained from the study of double intermolecular and inter-intra molecular addition of nucleophiles to various allenes using platinum catalysis to obtain multi-heteroaromatic compounds, which can be developed to give biological and pharmacological properties.

References:
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2. Nishina, N.; Yamamoto, Y. Tetrahedron Letters. 2009, 65, 1799-1808.
3. Zhang, C.; Zhang, S. Q.; Cai, H. J.; Cui, D. M. Beilstein J. Org. Chem. 2013, 9, 1045-1050.
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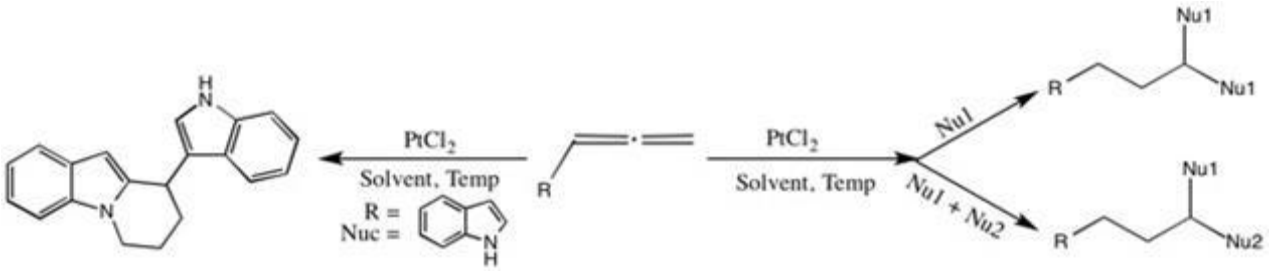

P-571

Immobilized Hybrid NHC-Au-(I) Complexes in Catalysis

Jeymy Sarmiento[1], Samuel Suárez-Pantiga[2], Teresa Varea[1], Gregorio Asensio[1]
[1]*Departamento de Quìmica Orgànica, Universitat de Valencia, Burjassot, Spain,* [2] *Department of Organic Chemistry, Stockholm university, Stockholm, Sweden*

Poster Session 2

A series of NHC-Au(I) complexes grafted on silica 1 have been prepared and characterized. The new hybrid materials have been tested as catalysts in several typical reactions promoted by gold(I) complexes. N,N'-disubstituted imidazolium carbenes were selected as supported ligands due to the stability of corresponding gold complexes and also to the easiness with which the steric and electronic properties can be tuned in these compounds.

The results obtained by using complexes[1] to promote the cycloisomerization[2] reaction of enines as a probe to test the catalytic activity of these hybrid materials will be reported. Compound 2 was selected as representative enine to compare our results with those obtained by Yu et al. with a phosphine/benzotriazole gold(I) complex supported on polystyrene.[3]
Complete conversions of the starting enine 2 into a 85:15 mixture of dienes 3 and 4 was obtained in CH_2Cl_2 at room temperature in a few minutes using 1 (1% mol.) as the catalyst for more than 10 cycles. The selectivity found in this case favoring the formation of the five- over the six-membered ring was the opposite of that reported[3] with supported phosphine gold complexes. Formation of alcohol 5[4] as side product also took place when traces of water were not excluded.

References:
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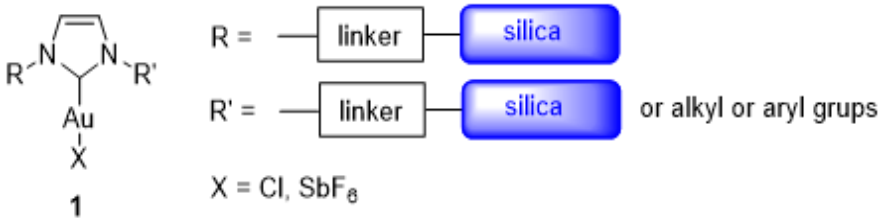


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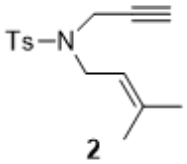
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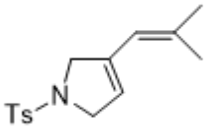
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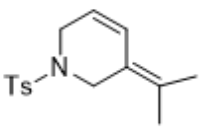
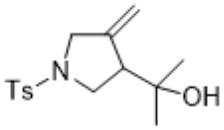
N

3


Ts
N

4


Ts
N
OH

5

P-572

Palladium-catalysed aminocarbonylation of n-(hetero)aromatic iodides

Dr. Attila Takacs[1], Gyöngyi Szőke[2], László Kollár[1,2]

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Poster Session 2

Heterocycles are important moieties in many pharmaceuticals [1]. Transition metal catalysis plays a key role in a selective functionalization of heteroaromatic systems [2]. Amides represent a ubiquitous functional group in pharmaceutically relevant compounds and are frequently attached to a heteroaryl core [3]. The three-component Pd-catalysed coupling of a hetero(aryl) halide with an amine and CO is an appealing approach to a selective amide synthesis [4].

In the present work, the palladium-catalysed aminocarbonylation of some iodo-N-heteroaromatic substrates will be presented. The palladium-catalysed carbonylation of 3,6-diiodopyridazine and 7-iodoindole with various N-nucleophiles was carried out under different carbon monoxide pressure (1-40 bar). Depending on the heteroaromatic iodide substrate, two types of carbonylated compounds, namely, carboxamides and 2-ketocarboxamides, are expected. The systematic investigation of 3,6-diiodopyridazine in the aminocarbonylation revealed that the corresponding 3,6-bis-carboxamido-pyridazine derivatives can be obtained in chemoselective reaction (Scheme 1).

Due to double carbon monoxide insertion, 7-glyoxylamido-indoles as major products were synthesised in high-yielding palladium-catalysed aminocarbonylation of 7-iodoindole with various primary and secondary amines (except aniline) under 40 carbon monoxide pressure (Scheme 2).

The high chemoselectivity, the easy work-up of the reaction mixtures and the moderate to high isolated yields of the corresponding carboxamides and 2-ketocarboxamides make these reactions of synthetic importance.

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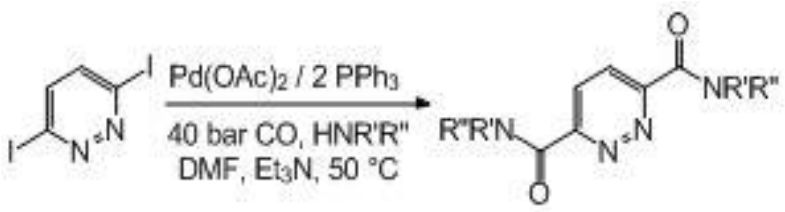


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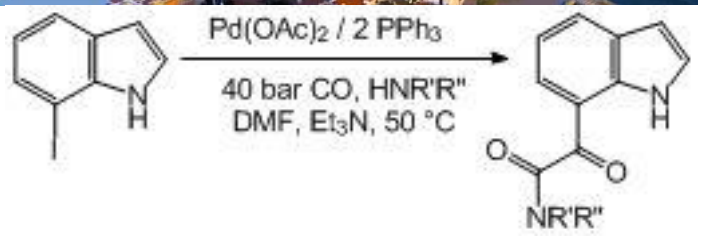
Pd(OAc)2 / 2 PPh3
40 bar CO, HNR'R"
DMF, Et3N, 50 °C
N
H
O
O
NR'R"

P-573

Studies on the asymmetric oxa-Heck-Matsuda reaction of styrenes

Dr. Nelson Martins[1], Mr Allan da Silva[1], Prof. Carlos Roque[1]
[1]*State University of Campinas (UNICAMP), Campinas, Brazil*

Poster Session 2

The Heck-Mizoroki reaction is a powerful and one of the most important synthetic tools for C-C bond formation. In this context, Correia et al have done extensive research of a variant of the Heck reaction using aryldiazonium salts, the Heck-Matsuda reaction. Amongst several successfully applications of this method, it has also been applied to the palladium-catalysed arylation of styrenes,1 and also the first examples of its enantioselective version.2

While working with o-hydroxy aryldiazonium salt, we have observed that styrenes can undergo oxy-arylation leading to substituted 1,2-diarylethyl derivatives and/or to 2-aryl-2,3-dihydrobenzofurans, depending on the reaction conditions and substrates. Indeed, both types of compounds had been identified previously in the literature, sometimes as unexpected products of Heck reactions.3,4,5 However, from a synthetic point of view dihydrobenzofurans are more interesting, because such scaffold is present in many important biologically active compounds, as for example isoflavonoids.

Therefore, we set as our goal to investigate the oxa-Heck-Matsuda reaction of styrenes, aiming at obtaining the oxa-Heck products preferably in an enantioselective fashion.

Accordingly, electron-donating groups on the para position of the styrene aromatic ring favour the ring closing step, with the formation of dihydrobenzofurans, whereas electron-withdrawing groups favour the “open” products. More substituted styrenes lead exclusively to the oxa-Heck products in good yields in a stereo and enantioselective fashion.

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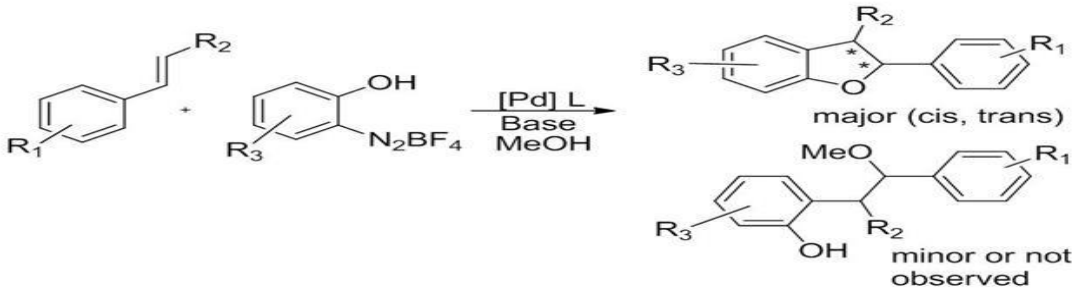
R2
R1
OH
R3
N2BF4
[Pd] L
Base
MeOH
R2
R3
R1
O
major (cis, trans)
MeO
R1
R3
R2
OH
minor or not
observed

P-575

Novel nickel and palladium allyl complexes stabilised by dialkyl terphenyl phosphines

Mr Mario Marin[1], Mr Carlos Navarro[2], Prof. Dr. M. Carmen Nicasio[1], Prof. Dr. Ernesto Carmona[2]
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Poster Session 2

Palladium-based catalysts have proved to be highly active in the formation of C-C and C-heteroatom bonds via cross-coupling reactions.[1] The most successful ligands to accomplish these transformations are electron-rich bulky phosphines and N-heterocyclic carbenes (NHCs).[sup]2,3[/sup]
Herein, we report the use of tertiary phosphines with the general formula PR_2Ar'' (Ar'' = terphenyl-type group), recently prepared in Carmona's group, as auxiliary ligands in the synthesis of nickel and palladium complexes. These phosphines are structurally related to Buchwald's phosphines.[2] A variety of neutral and cationic allyl complexes of palladium and also nickel stabilised by these phosphines (Figure 1) have been synthesised and characterised. The study of their catalytic activities in different cross-coupling reactions will be discussed.

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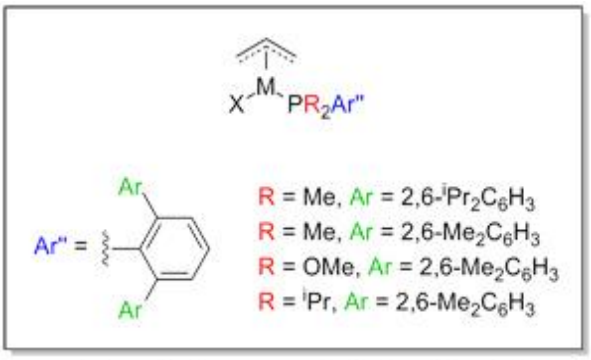

Figure 1: Complexes studied in this work

P-576

Iridium-Catalyzed Asymmetric Mono-Hydrogenation of Conjugated Dienes

Dr. Jean Palmes[1], Annina Verena Wehrle[1], Dr. Andreas Schumacher[1], Dr. Maurizio Bernasconi[1], Prof. Dr. Andreas Pfaltz[1]

[1]*Department of Chemistry, Organic Chemistry, University of Basel, Basel, Switzerland*

Poster Session 2

Acyclic deoxypolyketide fragments can be found in a variety of natural products. They can be synthesized using diastereoselective reactions utilizing chiral auxiliaries or catalytic methods. Among the catalytic reactions, asymmetric hydrogenation is attractive because of high atom economy. In this way, the deoxypolyketide fragment can be accessed by either iterative or full asymmetric hydrogenation of conjugated dienes. These processes are complicated by double bond migrations that can lead to poor diastereoselectivities.

In our study of the asymmetric hydrogenation of conjugated dienes, we found a highly regio- and enantioselective catalytic asymmetric hydrogenation of substituted α, γ-dienol acetates to allylic acetates using an Iridium pyridine-phosphinite complex. The chiral δ-substituted allylic acetates were obtained in excellent conversion and up to 99% ee. This method again exemplifies the unique catalytic activity of Iridium P,N-complexes in preferentially hydrogenating an unfunctionalized C=C bond in the presence of a C=C bond with an adjacent coordinating group.

P-577

STEREOSELECTIVE SYNTHESIS OF THE DIAZONAMIDE A MACROCYCLIC CORE

Mr Toms Kalnins[1], Ms Ilga Mutule[1], Ms Zane Medne[1], Prof Edwin Vedejs[1,2], Prof Edgars Suna[1]
[1]*Latvian Institute of Organic Synthesis, Riga, Latvia,* [2]*University of Michigan, Ann Arbor, USA*

Poster Session 2

Diazonamide A (1) is a marine natural product, which possesses unique anti-cancer activity in terms of efficiency, specificity and mechanism of action. Herein we report the stereoselective construction of the right-hand heteroaromatic macrocycle 2 en route to the total synthesis of compound 1.

The macrocycle 2 was assembled in a palladium-dioxygen complex-catalyzed Suzuki-Miyaura cross-coupling between tetracycle 5 and boronate 4 followed by atropodiastereoselective Dieckmann-type macrocyclization of biaryl 3 [1].

Authors are thankful to European Social Fund (1DP/1.1.1.2.0/13/APIA/VIAA/006) for financial support of the research and InnovaBalt project (REGPOT-CT-2013-316149) for travel grant for dissemination of the results.

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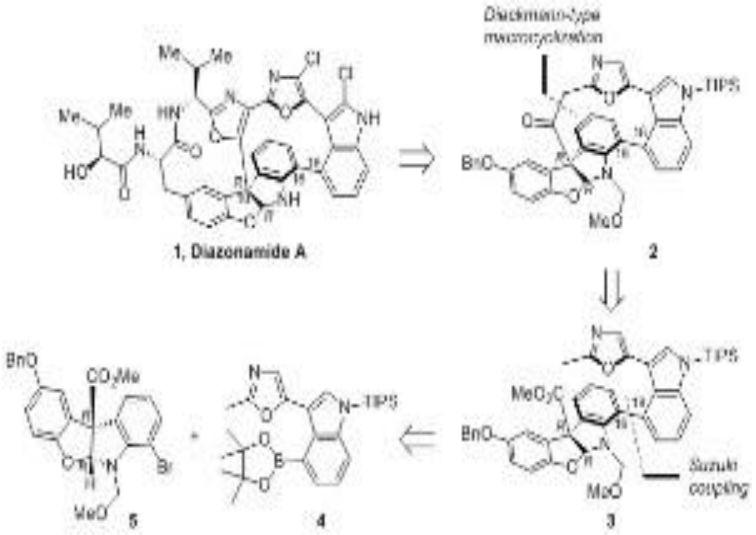

P-578

Rhodium-catalyzed [2+2+2] cycloaddition of cyano-yne-allene substrates: convenient access to 1,2-dihydro-2,6-naphthyridine scaffolds

Dr. Anna Roglans[1], Ms. Ewelina Haraburda[1], Dr. Agustí Lledó[1], Dr. Anna Pla-Quintana[1]
[1]*Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Girona, Spain*

Poster Session 2

One of the main goals of modern organic synthesis is to develop new reactions in which the molecular complexity is rapidly increased. The transition-metal-catalysed [2+2+2] cycloaddition reaction of three unsaturated partners [1], which allows for the formation of three new bonds, is a nice example of such a reaction type. Allenes, characterised by their two perpendicular π bonds, have been recognised as versatile substrates or intermediates in modern organic synthesis [2], and, due to the high density of unsaturation, have shown particular promise in the development of cycloaddition and cycloisomerisation reactions [2c].

Our interest in the construction of topologically new polycyclic structures, prompted us to explore the [2+2+2] cycloaddition reaction of linear cyano-yne-allene substrates leading to the construction of dihydronaphthyridine and pyranopyridine scaffolds. Starting from a series of cyano-yne-allene scaffolds with different tethers and number of methylenic units between the tether and the cyano group, the use of Wilkinson's catalyst allows the regioselective reaction of allenes through their external double bond to afford unsaturated pyridine-containing scaffolds after a dehydrogenative step.
[Figure]

Acknowledgments. We thank MICINN, Spain (project CTQ2011-23121 and Ramon y Cajal contract to A.LL.), Generalitat de Catalunya (2014-SGR-931) and UdG (grant to E.H.) for financial support.

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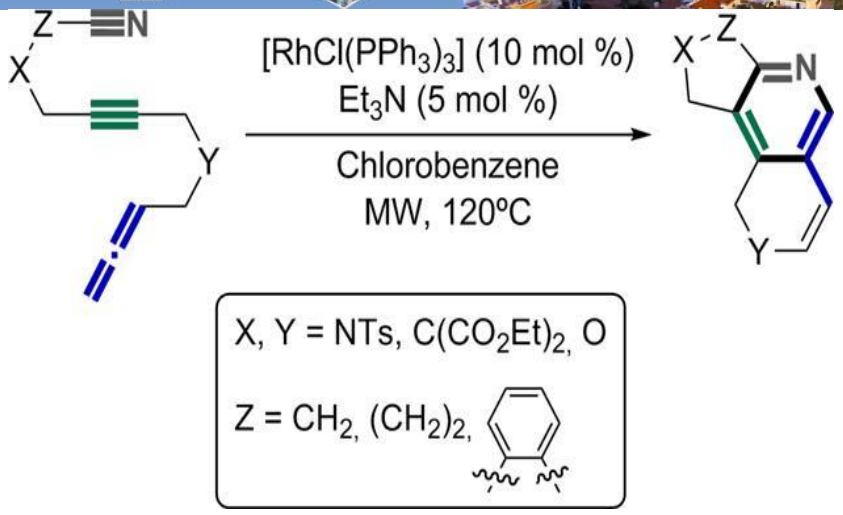

X, Y = NTs, $C(CO_2Et)_2$, O

Z = CH_2, $(CH_2)_2$,

P-579

Sustainable Three-Component Synthesis of Isothioureas from Isocyanides, Thiosulfonates, and Amines

Mr. Pieter Mampuys[1], Dr. Yanping Zhu[1], Dr. Tjøstil Vlaar[2], Dr. Eelco Ruijter[2], Prof. Dr. Romano V. A. Orru[2], Prof. Dr. Bert U. W. Maes[1]

[1]University of Antwerp - Organic Synthesis - Department of Chemistry, Antwerpen, Belgium [2]VU University Amsterdam, Department of Chemistry & Pharmaceutical Sciences and Amsterdam Institute for Molecules, Medicines and Systems (AIMMS) , Amsterdam, The Netherlands

Poster Session 2

Guanidines, R^1-N=C(NR^2R^3)(NR^4R^5), are important structural motives as they occur in various natural products, drugs and (agro)chemicals.[1] S-alkyl isothioureas are key intermediates for the synthesis of guanidines. Remarkably, only limited research effort has been devoted to their efficient and sustainable synthesis. The major disadvantages of the classical methods to S-alkyl isothioureas are the health risk, flammability and reactivity of the required reagents. Moreover, these procedures suffer from a poor atom and/or step efficiency, making them unattractive from a green chemistry point of view. We developed a new strategy based on a copper(I)-catalyzed three-component coupling of amines, thiosulfonates and isocyanides that overcomes these disadvantages and delivers the desired S-alkylisothioureas in a single step.[2] This new strategy can also be used to synthesize S-aryl isothioureas, which are very difficult to obtain by other methods.

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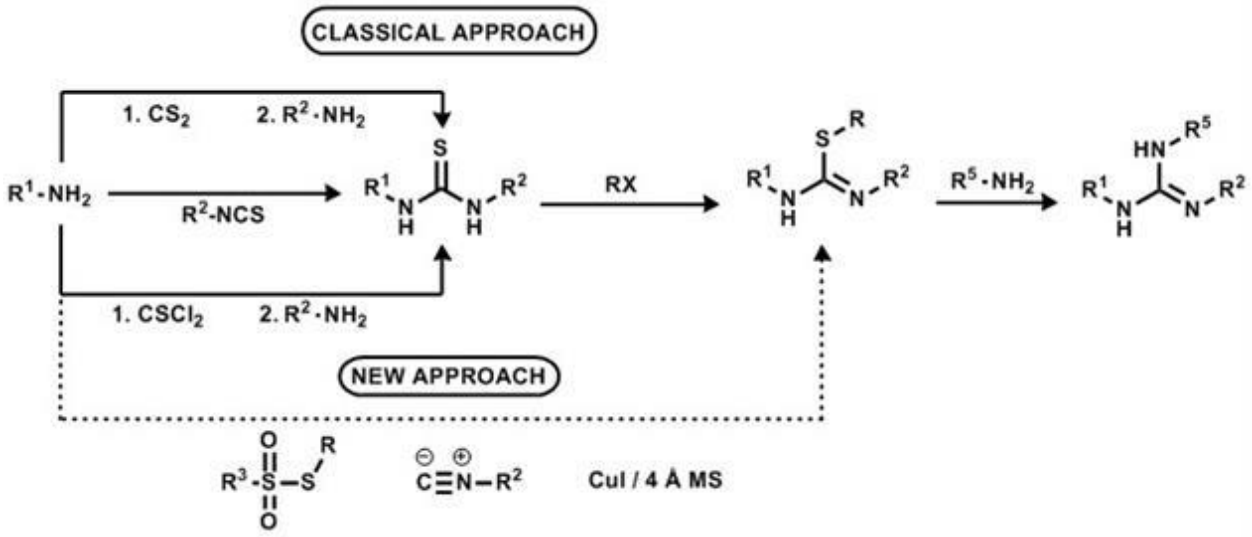

P-580

Mechanistic Investigations of Direct Arylation of Pyridine N-Oxides

Emma Svensson Akusjärvi[1], C. Christoph Tzschucke[1]
[1]*Freie Universität Berlin, Berlin, Germany*

Poster Session 2

Recently, we have developed a synthesis for asymmetrically substituted bi- and terpyridines by direct arylation of pyridine N-oxides using halopyridines.[1,2] However, the reaction gives lower yields than in the analogous reaction with bromobenzene.[3] According to the proposed mechanism, the aryl halide is not involved in the rate-determining C-H activation step.[4,5] Yet we observe that the arylation reaction is highly dependent on the nature of the aryl halide.
Since substrate and product could inhibit the reaction by coordination to palladium we performed kinetic measurements with potentially inhibiting additives. Although a slight decrease in product formation rate was observed, no significant decrease in yield was to be noted.
We have observed two side reaction pathways competing with the cross-coupling reaction. The homocoupling of aryl halide forming bipyridine and biphenyl respectively and the homocoupling of pyridine N-oxide substrate forming the N,N-dioxide have been observed. The extent of homocoupling is larger when electron-rich pyridine N-oxides and electron-poor aryl halides are employed. Herein, substrate consumption and product formation rates for differently substituted pyridine N-oxides as well as the quantification of side products will be presented.

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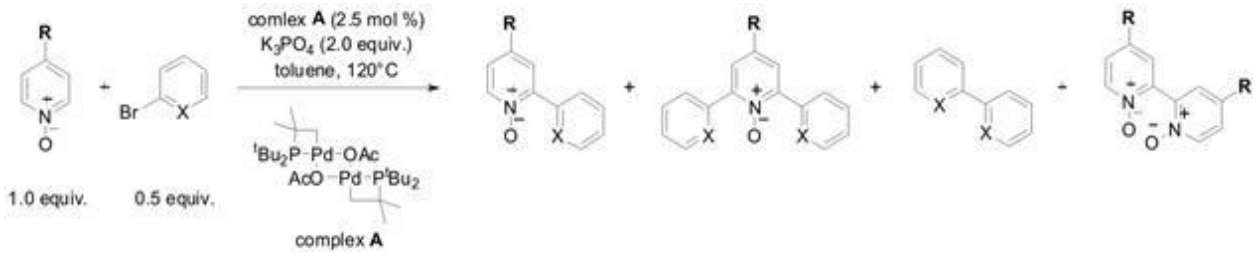

P-581

Synthesis, functionalization and applications of new NHC copper complexes in organic transformations

Dr Anna Szadkowska[1], Ewelina Zaorska[1], Sebastian Staszko[1]
[1]*University of Warsaw, Faculty of Chemistry, Warsaw, Poland*

Poster Session 2

The last decades has witnesses a number of synthetic routes and strategies using copper complexes to carry out C-H bond transformations. These methodologies aim at overcoming the deficiencies and drawbacks of common reactions. Among many copper complexes used in organic syntheses, catalytic systems based on N-heterocyclic carbenes (NHCs) are gaining more attention due to the opportunity to control of the nature of the catalytically substantial species in the different reaction media. Moreover, in a view of the fact, that NHCs complexes lead to more active and powerful catalytic systems, the examination of their potential selectivity in various transformations is continuously studied.
This contribution is focused on the direct synthesis of new NHC complexes, starting from commerically available compounds. In addition, several assays were carried out to study the effect of the ligand, solvent and additives on activity and selectivity in the fuctionalization of C-H bonds.

P-582

Easily accessible TADDOL derived bisphosphonite ligands: Synthesis and application in the asymmetric hydroformylation of vinyl arenes[1]

Dr. Simon Allmendinger[1]

[1] *Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

The asymmetric hydroformylation (AHF) of olefins remains a challenge in organic chemistry today.[2,3] This lies in the difficult task of controlling chemo-, regio- and enantioselectivity simultaneously while keeping high reaction rates. Despite the number of successful ligands developed so far, the design, synthesis and evaluation of novel, efficient and readily available ligands for this challenging transformation is still highly desirable.
With this goal in mind, we prepared a library of 14 bidentate phosphonite ligands based on the common TADDOL[4] motif. We herein report the synthesis and the results of their application in the asymmetric hydroformylation of styrene derivatives.

Starting from readily available building blocks, the desired bidentate phosphonite ligands have been synthesized in moderate to good yields. In addition, these ligands have shown to be remarkably stable towards air and moisture and could be stored for long periods (several months) without any significant degree of degradation.
Applied in the asymmetric hydroformylation of vinyl arenes this newly developed catalytic system showed high catalytic activity and selectivity. In general, excellent conversions of up to 99% and enantioselectivites of up to 95% were achieved.
Using High-pressure-NMR and -IR-techniques the coordination behavior was studied. Here these ligands revealed a highly selective binding behavior. Under the catalytic relevant reaction conditions one well-defined Rh-complex is formed.

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Easily accessible TADDOL derived bisphosphonite ligands: Synthesis and application in the asymmetric hydroformylation of vinyl arenes[1]

Simon Allmendinger, Bernhard Breit*
Institut für organische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, 79104 Freiburg, Germany; e-mail: Bernhard.Breit@chemie.uni-freiburg.de

The asymmetric hydroformylation (AHF) of olefins remains a challenge in organic chemistry today.[2,3] This lies in the difficult task of controlling chemo-, regio- and enantioselectivity simultaneously while keeping high reaction rates. Despite the number of successful ligands developed so far, the design, synthesis and evaluation of novel, efficient and *readily available* ligands for this challenging transformation is still highly desirable.

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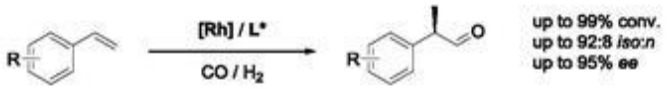

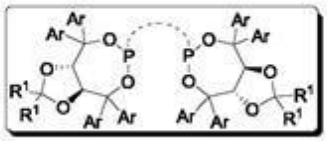

Starting from readily available building blocks, the desired bidentate phosphonite ligands have been synthesized in moderate to good yields. In addition, these ligands have shown to be remarkably stable towards air and moisture and could be stored for long periods (several months) without any significant degree of degradation.

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Using High-pressure-NMR and -IR-techniques the coordination behavior was studied. Here these ligands revealed a highly selective binding behavior. Under the catalytic relevant reaction conditions one well-defined Rh-complex is formed.

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P-583

Ni-catalyzed Hydrocarboxylation of Alkynes Employing Simple Alcohols as Hydrogen Donors

Dr. Masaki Nakajima[1], M.Sc. Xueqiang Wang[1], Prof. Ruben Martin[1,2]
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Poster Session 2

Metal-catalyzed carboxylation events employing CO_2 as a cheap and abundant C1-building block has gained increased attention in recent years. Recently, the groups of Ma and Tsuji reported a syn-selective Markovnikov-Hydrocarboxylation of alkynes utilizing stoichiometric amounts of pyrophoric Et_2Zn or silanes as reducing agents.[1] Unfortunately, however, such methods offered low regioselectivity profile in the presence of unsymmetrical substrates, invariably invoking a CO_2 fixation adjacent to an aromatic ring. As part of our interest in reductive carboxylation protocols,[2] we report herein a mild and user-friendly Ni-catalyzed divergent anti-Markovnikov-hydrocarboxylation strategy en route to a diverse set of acrylic acids using simple alcohols as hydrogen donors, offering a selectivity switch to that based on the utilization of Et_2Zn or R_3SiH.[3]

References:
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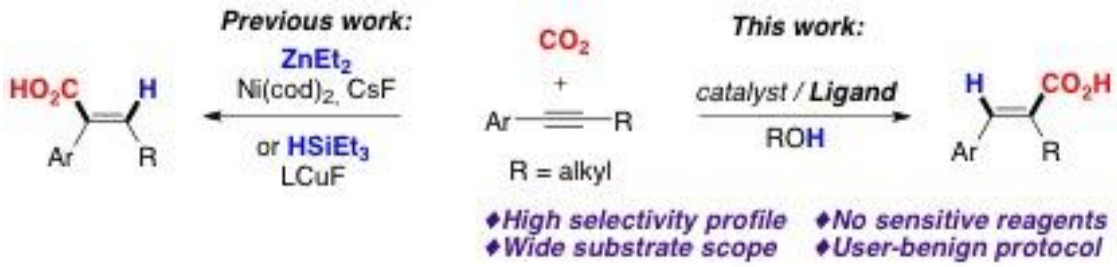
3) X. Wang, M. Nakajima, R. Martin. Manuscript in preparation



P-584

Copper Complexes bearing N-Anchored Tetradentate tris-Carbene Ligands (TIMENR) as Catalysts in ATRA Reactions

Dr Tomás R. Belderrain[1], Ana Pereira[1], Dr José M. Muñoz-Molina[1], Prof. Karsten Meyer[2], Prof. Pedro J. Pérez[1]

[1]*Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, Centro de Investigación en Química Sostenible (CIQSO) and Departamento de Química y Ciencias de los Materiales, Huelva, Spain* [2]*Department of Chemistry and Pharmacy, Inorganic Chemistry, Friedrich-Alexander University of Erlangen-Nürnberg, Erlangen, Germany*

Poster Session 2

The ATRA (Atom Transfer Radical Addition) reaction has become a powerful tool for the generation of carbon-carbon bonds in organic synthesis.[1] This process takes place by the addition of a polyhalogenated saturated hydrocarbon to an alkene in the presence of a radical catalyzed by a transition metal catalyst (Scheme 1).

Scheme 1

In these systems the metal undergoes a reversible oxidation/reduction process between two consecutive oxidation states. Therefore the choice of the metal complex becomes crucial. With this idea in mind, we have studied the catalytic capabilities of copper complexes bearing tripodal N-heterocyclic carbene ligands (TIMEN) (Figure 1) in ATRA reactions, since it was reported that complexes as, for instance, [(TIMENt-Bu)Cu](PF_6), exhibit reversible one-electron redox behaviour.[2] The results reported in this contribution TIMEN-copper catalysts display good activities in ATRA reactions in the presence of AIBN (azobisisobutyronitrile), specially in the case of unactivated olefin as 1-hexene.

Figure 1. Structure of the complex [TIMENt-BuCu](PF_6)

References:
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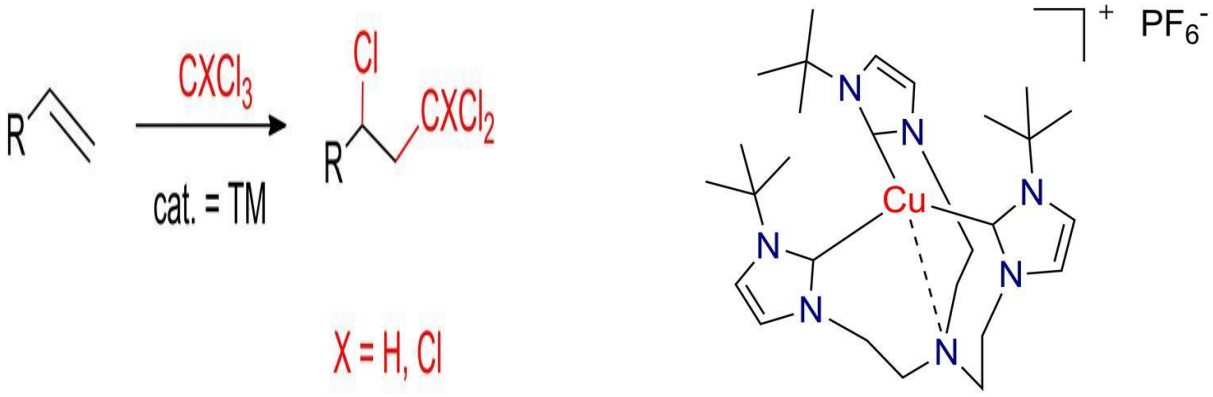


P-585

Base- and metal-free c-h direct arylation of unbiased arenes with diaryliodonium salts

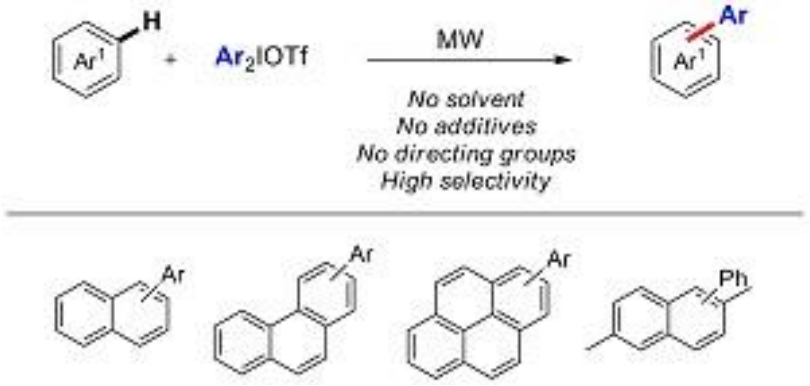
Miss Susana Castro[1], Dr. Rubén Vicente[1], Dr. Félix Rodríguez[1], Dr. Francisco Javier Fañanás[1]
[1]*Universidad De Oviedo, Oviedo, Spain*

Poster Session 2

Biaryl motif is a ubiquitous substructure that can be found in many relevant natural and pharmacological products. Moreover, it is important in the synthesis of complex polyaromatic systems with relevance in materials chemistry. These facts justify the need of developing new efficient methodologies to synthesize biaryls.

Traditionally, these compounds are prepared from prefunctionalized substrates employing transition metals as catalysts. However, recent studies focused on metal free C-H bond functionalization, which means cleaner and cheaper processes. In this context, we developed a new protocol that involves direct arylation of unbiased arenes using diaryliodonium salts, with no catalysts, additives or solvent.

Financial support from Industrial Química del Nalón S. A. is gratefully acknowledged.



P-586

Palladium-Catalyzed Carbonylative α-Arylation of 2-Oxindoles with (Hetero)aryl Bromides: Efficient and Complementary Approach to 3-Acyl-2-oxindoles

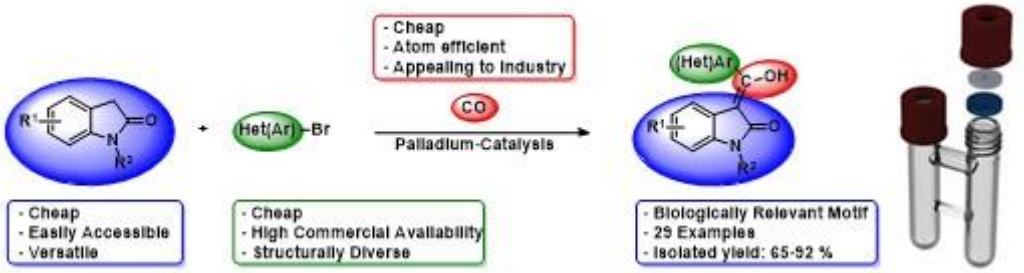
Mr. Zhong Lian[1,2,3], Dr. Stig, Friis, D.[1,2,3], Prof. Dr. Troels Skrydstrup[1,2,3]

[1]Carbon Dioxide Activation Centre (CADIAC), Aarhus C, Denmark, [2]Interdisciplinary Nanoscience Center (iNANO) , Aarhus C, Denmark, [3]Aarhus University, Aarhus C, Denmark

Poster Session 2

3-acyl-2-oxindoles constitute an exceptional class of structural motifs which have been found widely present in natural products and biologically active molecules such as GSK3 kinase inhibitos, influenza endonuclease inhibitor, and Tendidap which is a potent inhibitor of cyclooxygenase with excellent activity in rheumatoid arthritis and osteoarthritis clinical trials. Despite their versatile significance, only a limited number of synthetic routes for 3-acyl-2-oxindoles have been reported in the literature.

In this presentation, an efficient palladium-catalyzed carbonylative α-arylation of 2-oxindole with aryl and heteroaryl bromides for the one-step synthesis of 3-acyl-2-oxindoles is described. The transformation is complementary to known transition metal-catalyzed procedures, merely require mild base and provide good yields even with heteroaromatic substrates. Moreover, the methodology is extended to ^{13}C-acyl labeling, while the generality of the reaction is established through the synthesis of a biologically interesting compound.



P-587

Synthesis of bulky P-stereogenic ligands through SN2@P reactions

Ms Sílvia Orgué[1], Prof Antoni Riera[1,2], Prof Xavier Verdaguer[1,2]

[1]Institute for Research in Biomedicine (IRB Barcelona), Barcelona, Spain [2]Organic Department, University of Barcelona, Barcelona, Spain

Poster Session 2

Trivalent phosphorous compounds play an important role in homogeneous catalysis as ligands for metal catalysts. In the 1970's, P-stereogenic (P*) ligand DIPAMP, was successfully applied in the synthesis of L-DOPA. Since then, the use of P-stereogenic phosphorous compounds has been broadly extended.[1] In such compounds, the stereoselective construction of phosphorous chiral centers is a critical issue.[2]

Our group has worked on the synthesis of bulky P-stereogenic compounds over the last five years. We recently described the synthesis of optically pure borane-protected amino-phosphane 1 as a valuable P*-building block for ligand synthesis[3][4]. In the present work we have studied the substitution reactions at the P-center which have led to an efficient process for the synthesis of a large array of optically pure aminophosphanes. In order to demonstrate the utility of this process for the synthesis of new ligands for coordination chemistry and catalysis, P-ligand 9 was deprotected and coordinated to iridium.

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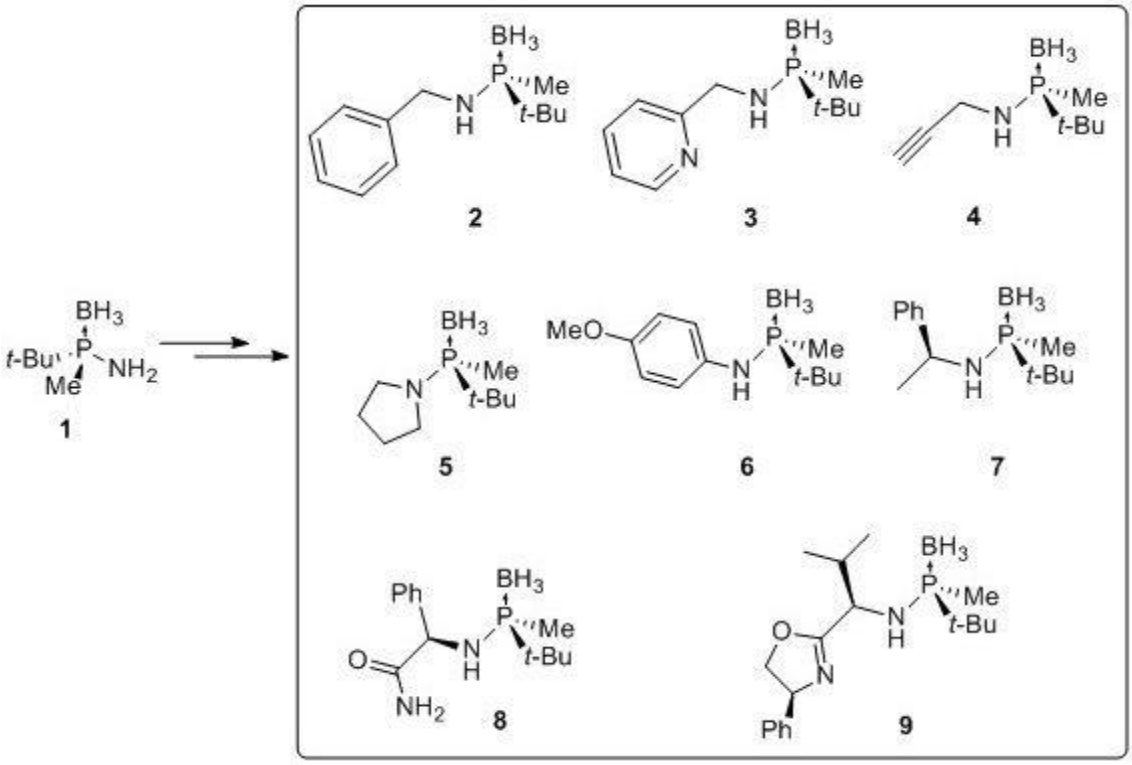
BH3
P
Me
t-Bu
t-Bu
Me
NH2
1
N
H
2
3
4
5
MeO
6
Ph
7
O
NH2
8
9

P-588

Quinolone synthesis adopting a different reaction pathway

Ing. Ondrej Pisa[1,2], Stanislav Rádl[1]
[1]*Zentiva, A Sanofi Company, Prague, Czech Republic* , [2]*UCT Prague, Prague, Czech Republic*

Poster Session 2

1,4-Dihydro-4-oxoquinoline derivatives are well known structures used mainly as antibacterial therapeutics (termed as antibacterial quinolones). However, in the last 20 years, the quinolone moiety has been successfully incorporated into molecules of other potential drugs from which the most prominent are HIV integrase inhibitor elvitegravir (launched in 2012) and anticancer TOPO II inhibitor voreloxin (phase III clinical development).

Reaction pathway leading to most of these compounds includes an aromatic nucleophilic cyclization step with F, Cl, and NO_2 as leaving groups (LG) mediated by bases like potassium carbonate.[1]

Problems with the use of potassium carbonate in the elvitegravir synthesis led to replacement with BSA (N,O-bis(trimethylsilyl)acetamide) which provided very good results with methoxy group as LG.[sup]2,3[/sup]

There are only few references reporting the utilization of methoxy group in this cyclization and the most common conditions include potassium carbonate in DMF furnishing low to good yields.[4] Furthermore, the increasing steric hindrance of R substituent (Scheme I; R = tert-butyl) prevents the cyclization to occur due to the decreasing availability of the NH proton for base (especially in case of R = tert-butyl).

All these facts have inspired us to investigate the background of the reaction with BSA on related substrates. It probably adopts a different mechanism incorporating silylated enolates as the reaction intermediates, which could prove as complementary to the action of a base. This presentation summarizes synthetic studies regarding the synthesis of precursors, the results of their cyclization, comparison of the reagent with potassium carbonate as well as the plausible mechanism.

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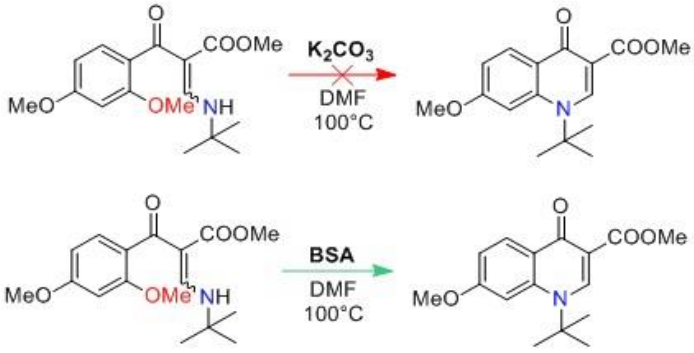
COOMe
MeO
OMe
NH
K2CO3
DMF
100°C
N
BSA

Scheme I

P-589

Synthesis of tetrathia[7]helicenes promoted by Pd-catalysed cross coupling reactions

Dr. Silvia Cauteruccio[1], Dr. Susan Sammak[2], Dr. Davide Dova[1], Prof. Emanuela Licandro[1]
[1]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, I-20133, Milano, Italy, Milano, Italy, [2]Società Consorzio Interdisciplinare Studi biomolecolari e applicazioni Industriali (CISI scrl), Via Fantoli 16/15, 20138, Milano, Italy, Milano, Italy

Poster Session 2

Tetrathia[7]helicenes (7-TH), formed by thiophene and benzene rings ortho-fused in an alternating fashion, are emerging as one of the most popular class of chiral helical-shaped molecules [1], thanks to their unique electronic and optical properties suitable for applications in optoelectronics [2], biomolecular recognition [3], and asymmetric catalysis [4]. Despite all these potential advantages, most of the synthetic methodologies to prepare 7-TH systems involve oxidative photochemical cyclization processes, which require specific equipment, highly diluted solutions, and can limit the scale-up of the synthesis of these derivatives. In our ongoing studies on the preparation of 7-TH derivatives, we have set up an innovative and non-photochemical synthesis of 7,8-diaryl substituted 7-TH compounds, exploiting Suzuki-type reactions and Pd-catalysed annulation with diaryl alkynes.

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[3] Cauteruccio, S.; Bartoli, C.; Carrara, C.; Dova, D.; Errico, C.; Ciampi, G.; Dinucci, D.; Licandro, E.; Chiellini, F. Chem. Plus. Chem. 2015, 80, 490.
[4] Cauteruccio, S.; Dova, D.; Benaglia, M.; Genoni, A.; Orlandi, M.; Licandro, E. Eur. J. Org. Chem. 2014, 2694.


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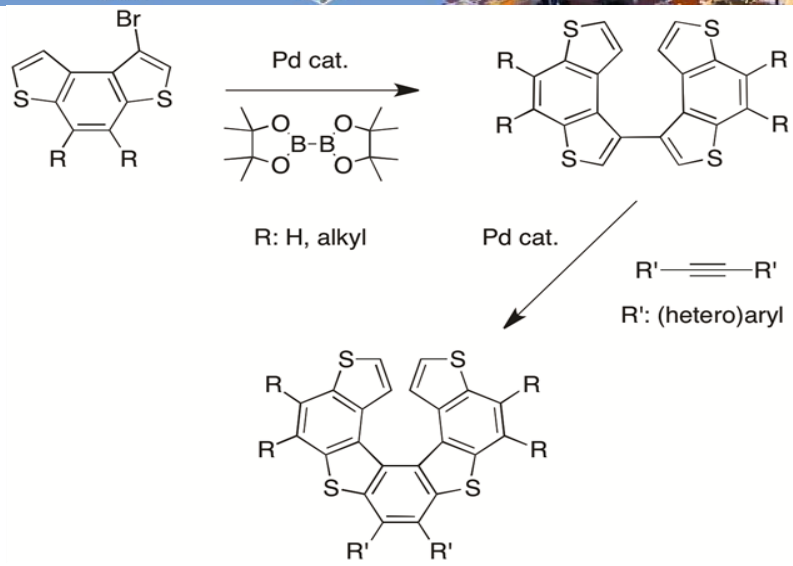

Br
S
S
R
R
Pd cat.
O
B-B
O
O
O
R: H, alkyl
S
S
R
R
R
R
S
S
Pd cat.
R'—≡—R'
R': (hetero)aryl
S
S
R
R
R
R
S
S
R'
R'

P-590

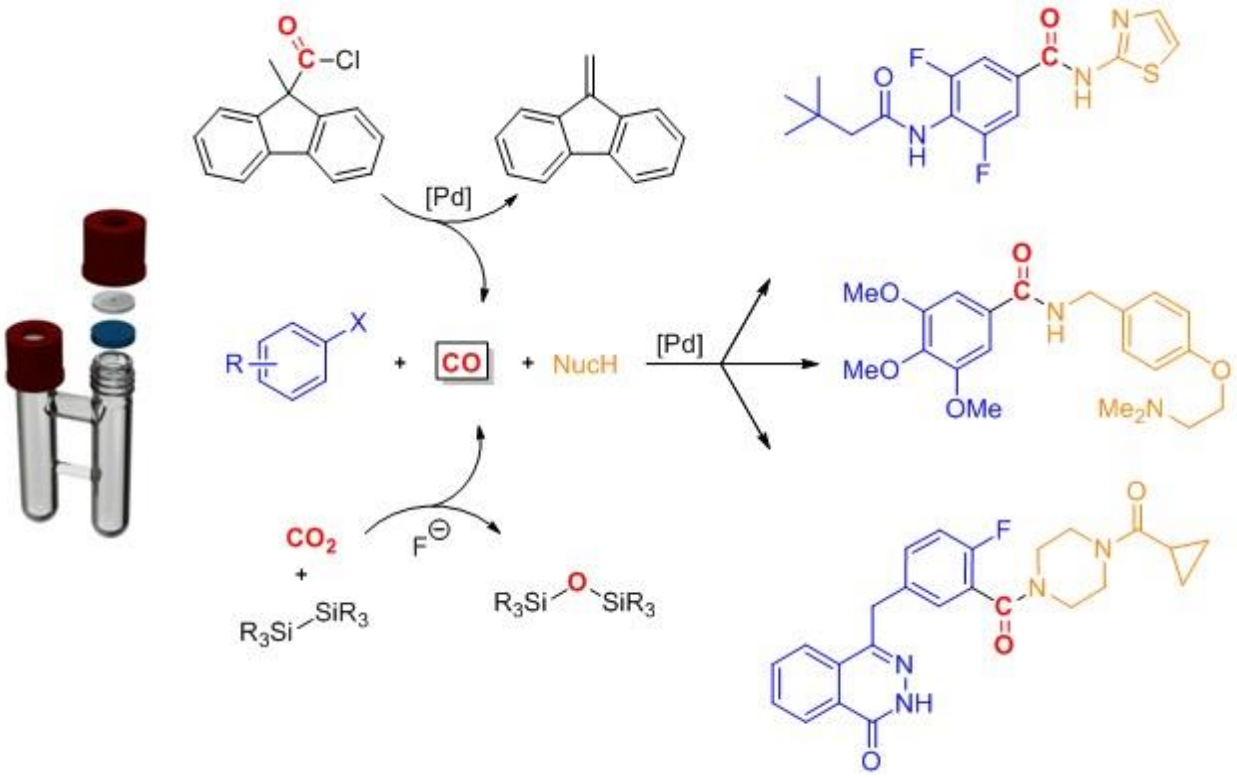
Palladium-Catalyzed Carbonylations Using Ex Situ Generated Carbon Monoxide

Mr Dennis Ulsøe Nielsen[1]
[1]*Aarhus University, iNANO, Aarhus, Denmark*

Poster Session 2

Carbon monoxide is a useful C1-building block for the installment of a number of carbonyl functionalities. However, its use is not without drawbacks. Specialized equipment needs to be employed due to the high toxicity and flammability of this diatomic gas. Therefore, research towards safer handling of carbon monoxide will increase the applicability of this reagent. In this presentation, two distinct paths are presented for the ex situ generation of carbon monoxide from an appropriate precursor applying a two-chamber system.

The first approach utilizes an acid chloride (COgen), which readily decarbonylates to produce carbon monoxide when treated with a specific Pd-catalyst. This methodology has been applied by our group in the synthesis of a variety of carbonyl containing functional groups. Examples of this technique will be presented. The second approach generates carbon monoxide via a fluoride-mediated reduction of CO_2 in the presence of a disilane. Notably, this reduction occurs at room temperature and does not require the assistance of a transition metal catalyst. Only a catalytic amount of fluoride is required to activate the disilane for the reduction and quantitative conversion of CO_2 into CO.



P-591

$Co_2(CO)_6$-alkyne complexes as stable precursors for the synthesis of enediyne macrocyclic systems fused to a benzothiophene core

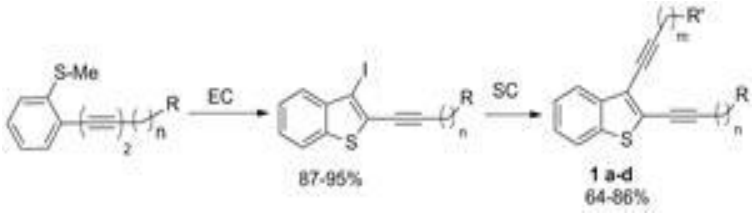
Dr Anna Lyapunova[1], Dr Natalia Danilkina[1], Prof. Irina Balova[1]
[1]*SPbSU, Saint Petersburg, Petrodvorets, Russian Federation*

Poster Session 2

Naturally-occuring macrocyclic enediyne antibiotics are well known as potent anticancer agents. Their biological activity is determined by the ability to undergo Bergman cyclization (BC). A broad range of synthetic analogs of these compounds have been synthesized and investigated. In search for highly active synthetic analogs of enediyne antibiotics we decided to develop a general synthetic approach towards heterocycle-fused macrocyclic enediyne systems using Nicholas reaction (NR) as a macrocyclization technique. In this way 9-, 10- (2, 3) and 11-membered (4) enediynes fused to a benzothiophene core were chosen as target model compounds.

Using the electrophilic cyclization (EC) and the Sonogashira coupling (SC) on the initial steps allowed us to synthesize substrates (1a-d) for the intramolecular macrocyclization (figure 1). NR was utilized on the key cyclization step which proceeded smoothly affording desired 10- and 11-membered Co-protected macrocycles (figure 2). 9-Membered macrocycle wasn't synthesized and corresponding dimer was separated. Subsequent mild decomplexation led to the desired oxaenediynes (2-4) in moderate and good yields. The activity in BC of compounds synthesized was estimated by Differential Scanning Calorimetry (DSC). It was found that 10-membered enediyne (2) is the most active and BC starts at 76°C.

Therefore, it was shown that our approach based on the subsequent use of EC, SC and NR is applicable to the synthesis of oxaenediynes fused to benzothiophene core. Our further research in this field is under the investigation.

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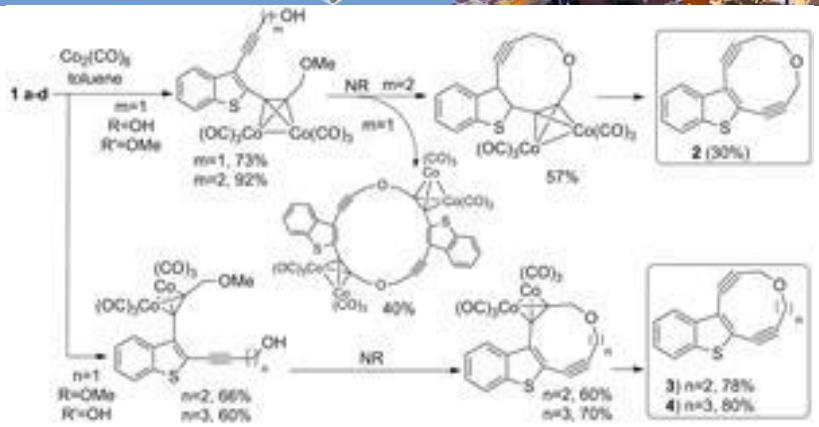
1 a-d
toluene
m=1
R=OH
R'=OMe
m=1, 73%
m=2, 92%
NR m=2
57%
2 (30%)
40%
n=1
R=OMe
R'=OH
n=2, 66%
n=3, 60%
NR
n=2, 60%
n=3, 70%
3 n=2, 78%
4 n=3, 80%

P-593

Tandem C-C bond formations initiated by Asymmetric Allylic Alkylation (AAA) Reactions

Miss Nisha Mistry[1], Dr Stephen Fletcher[1]
[1]*University of Oxford, Oxford, UK*

Poster Session 2

Asymmetric catalysis is an important strategy that allows the transformation of racemic or prochiral starting materials into single enantiomer products. Asymmetric allylic alkylations (AAA) that have been previously developed by our group[1] have shown to be a powerful C-C bond forming technique. These copper-catalysed AAAs of alkyl zirconium reagents give zirconium salts as by-products. The zirconium species generated in the course of the reaction might promote further reactivity. Hydroxylated alkenes have previously been described by Hoveyda[2] to undergo zirconium catalysed reactions. After the initial AA reaction, these alkenes should undergo a tandem reaction with the zirconium salts on the addition on Grignard reagents.

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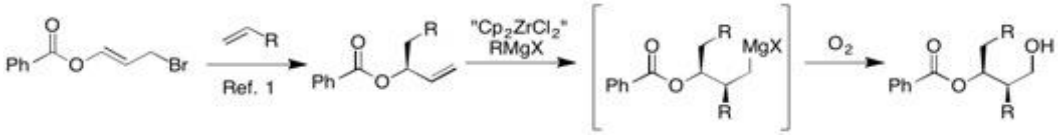

P-594

Palladium-Catalyzed Cross-Coupling Reactions in Natural Product Synthesis

Jokin Carrillo[1], Laura Mola[1], Jesus San José[1], Jaume Vilarrasa[1], Anna Maria Costa[1]
[1]*Universitat de Barcelona, Barcelona, Spain*

Poster Session 2

Cross-coupling reactions catalyzed by Pd(0) are a very useful tool in modern organic synthesis, which solves the challenge of C–C bond formation in the synthesis of many complex natural products. However, the application of these reactions to multifunctional molecules often requires a careful fine tuning of the procedures.

Our group is focused on the total synthesis of various cytotoxic macrolides such as Amphidinolide B_2,[1,2] Amphidinolide E,[1,2,3] and Palmerolide A.[4,5] In these syntheses, Negishi and Suzuki reactions have been used for the formation of Csp2-Csp2 and Csp3-Csp2 bonds. After many months of effort, we have developed new protocols that afforded the desired fragments in high yields and diastereoselectivities.

References:
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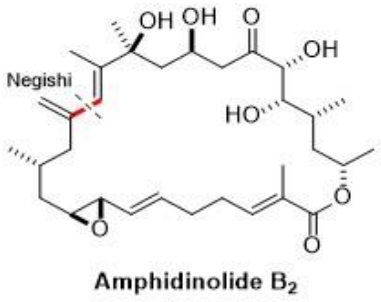
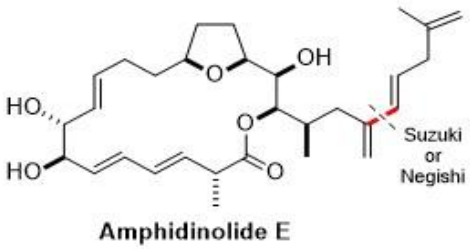
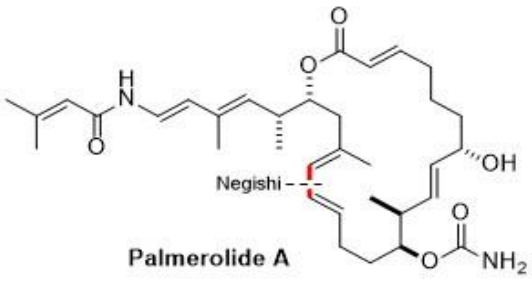
(5) Diyabalanage, T.; Amsler, C. D.; McClintock, J. B.; Baker, B. J. J. Am. Chem. Soc. 2006, 128, 5630.



Amphidinolide B_2



Amphidinolide E



Palmerolide A

P-596

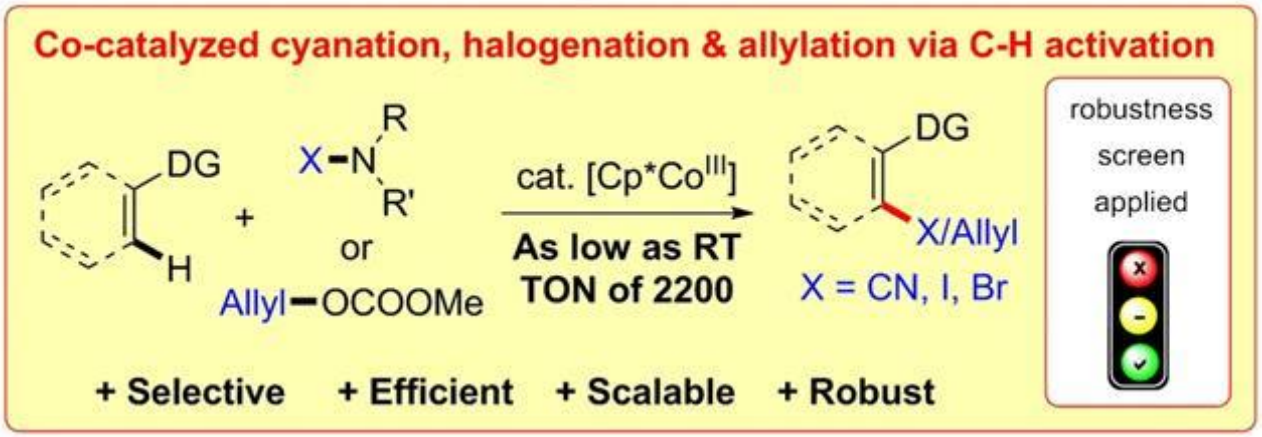
Co(III)-Catalyzed C–H Activation/Formal SN−Type Reactions: Selective and Efficient Cyanation, Halogenation, and Allylation

Dr. Xiaoming Wang[1], Dr. Da-Gang Yu, Mr. Tobias Gensch, Mr. Francisco de Azambuja, Ms. Suhelen Vásquez-Céspedes, Prof. Frank Glorius

[1]*WestfälischeWilhelms-Universität Münster, Münster, Germany*

Poster Session 2

Driven by the desire to further streamline the synthesis of complex molecules and valuable building blocks, transition metal-catalyzed C-H bond activation has evolved as an important field in catalysis research. Compared to noble metals, first-row transition metals are more earth-abundant, easily available, and inexpensive. As such, their use as catalysts attracts increasing attention, especially for C–H activation reactions. Herein, we developed the first cobalt-catalyzed C–H cyanation, halogenation, and allylation reactions. Various arenes, heteroarenes, and alkenes directly undergo such regio and chemoselective formal SN-type reactions with good functional group tolerance. Alkenyl substrates and amides were successfully utilized in Cp*Co(III)-catalyzed C–H activation for the first time. This C–H activation occurred efficiently at room temperature using 0.01–0.5 mol% of a bench-stable Co(III) catalyst. A TON of 2200 was obtained. Valuable organo nitriles, iodides, and bromides as well as allylated indoles were generated from easily available starting materials. The coordination of oxygen in the leaving group toward Co is proposed to play a vital role in ensuring selectivity and reactivity in these transformations.



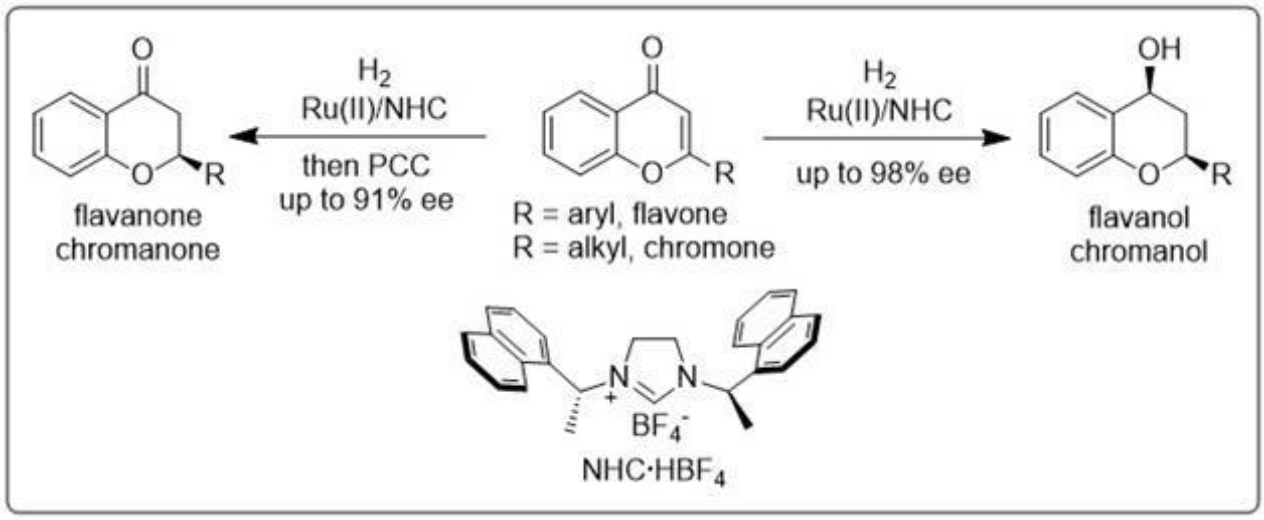
P-597

Ru(II)–NHC-Catalyzed Asymmetric Hydrogenation of Flavones and Chromones

Dr. Wei Li[1], Dr. Dongbing Zhao[1], Dr. Bernhard Beiring[1], Prof. Frank Glorius[1]
[1]*Westfälische Wilhelms-Universität Münster, Muenster, Germany*

Poster Session 2

Flavanoids and chromanoids including flavanones, flavanols, chromanones, and chromanols are a large family of well-known natural products .We have developed the asymmetric hydrogenation of 2-substituted flavones and chromones leading to the formation of enantiomerically enriched flavanones, flavanols, chromanones, and chromanols using a chiral ruthenium(II)–NHC complex.



P-598

Rapid access of the Taxol core

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Poster Session 2

Taxol is a billion dollar drug used in the clinical treatment of several cancers. Many synthetic efforts over the past four decades have produced less than 30 mg of Taxol derived. The highest reported overall yield is 0.4%[1] [2] [3].Taxadiene has been called the parent taxane and it has been proposed that an efficient access to Taxol and derivatives could be achieved through the synthesis of its core followed by oxidative C-H activation methods[4].
Our group recently reported a method to construct all-carbon quaternary centres by Cu-catalyzed asymmetric conjugate addition of organozirconocenes prepared in situ by hydrozirconation of terminal alkenes with the Schwartz reagent[5]. We reasoned that we could apply this methodology to introduce the quaternary centre in taxadiene. Herein we present the optimisation of this step using different alkenes as nucleophile precursors. Further transformations would involve an α-position ketone functionalization to give taxaenone (1), and presumably, (1) can be converted into taxadiene in a few steps.

This work was supported by the European Union's Seventh Framework Programme for research, technological development and demonstration (reg. No. 316955).

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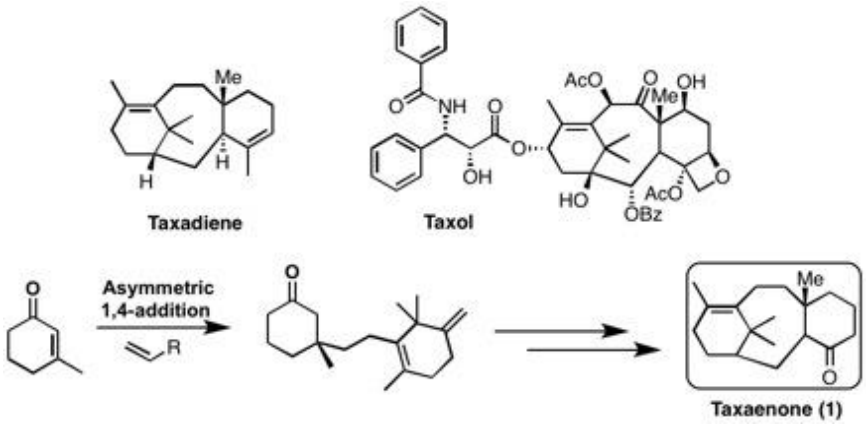

P-599

Functionalization of the tricyclic core structure of anticancer natural products

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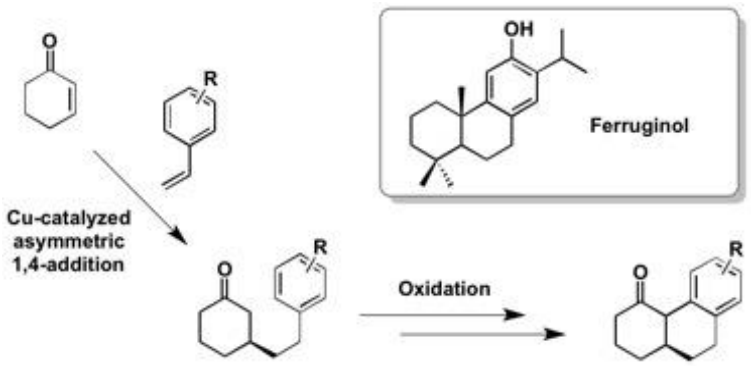
Poster Session 2

Natural products and their synthetic derivatives which show anticancer activity contain very often an identical core structure together with specific functional moieties. Synthetic routes to steroid like cores require in some cases a lot of steps together with protection and deprotection steps respectively. Hence, a development of easy pathways to basic core motifs is necessary. In this work initial steps were made to get access to the tricylic core structure present in several anticancer active molecules, e.g. ferruginol or TBE-31.
The introduction of the chiral centre is realized by a copper catalyzed asymmetric 1,4-addition of alkenes to α,β-unsaturated ketones. Tolerating a variety of functional groups provides a good starting point for various structures. The second step involves oxidative coupling reaction of the α-position of the ketone to the aromatic ring.
This method offers a general route to form natural product derivatives which can be analyzed at a later stage in terms of anticancer activity.



P-600

Oxidative radical cyclization reaction catalyzed by calcium iodide under visible light irradiation

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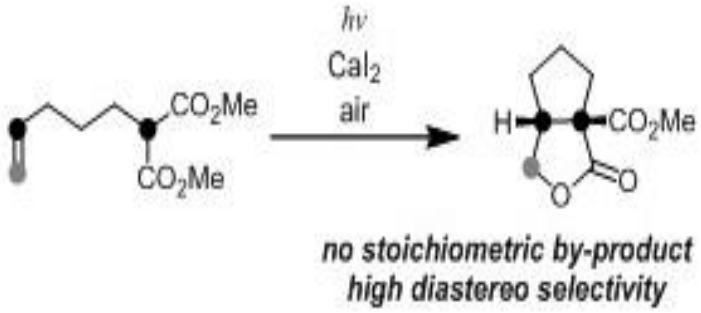
Poster Session 2

Substituted lactones form the core of many biologically important natural products. A lot of methodologies have been developed to provide these privileged structures such as stereoselective radical cyclizations most frequently using the 'Manganese(III) acetate' method for radical generation. We became interested in developing rare-metal-free oxidative radical cyclizations leading to biologically active substituted lactones.

We recently reported the use of calcium iodide for the photo oxidative tandem oxidation/rearrangement reaction of beta-Ketoesters to Tartronic Esters. And we also found that beta-ketoester is transformed to methylene radical species through abstraction of most acidic hydrogen by the iodo radical, which is formed from iodide in situ. We envisioned that the use of photo-chemically formed radical intermediate mentioned above for the intramolecular radical cyclization reaction, which would make it possible to avoid highly toxic heavy metals.

So, we developed efficient catalytic oxidative radical cyclization reaction leading to substituted lactones catalyzed by calcium iodide under aerobic photo-oxidation conditions. This reaction does not require stoichiometric or catalytic amount of inorganic reagent.



P-601

Iron Fluoride/NHC-Catalyzed Cross Coupling between Deactivated Aryl Chlorides and Alkyl Grignard Reagents with or without β-hydrogens

Ryosuke Agata[1,2], Takahiro Iwamoto[1,2,3], Naohisa Nakagawa[1,2], Katsuhiro Isozaki[1,2], Takuji Hatakeyama[1,4], Hikaru Takaya[1,2], Masaharu Nakamura[1,2]

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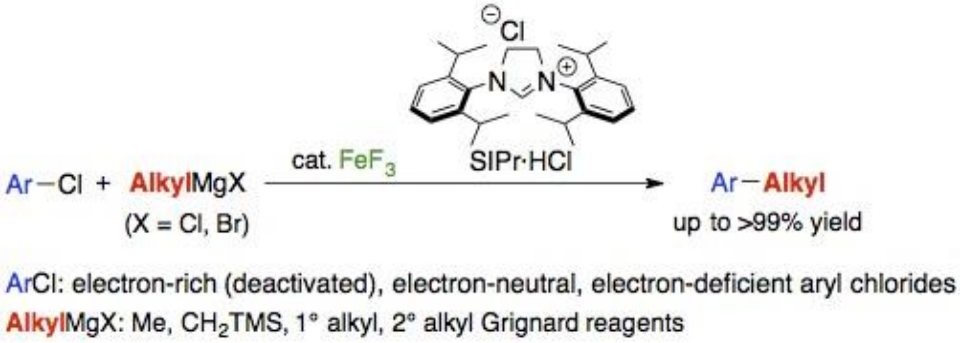
Poster Session 2

Iron catalysts have recently attracted considerable attention in cross-coupling chemistry due to their environmentally friendly and ecological advantages and more importantly their unique reactivity and selectivity which are not easily attained by the conventional cross-coupling catalysts. In the aryl–alkyl coupling reactions of aryl electrophiles with alkyl Grignard reagents, iron catalysts have been widely studied to achieve the higher catalytic efficiency compared with Ni or Pd catalysts. However there still remain significant limitation in substrate-scope, where the reaction of electron-rich (deactivated) aryl chlorides with alkyl Grignard reagents without β-hydrogens cannot be achieved under iron catalysis.

Herein we describe the first aryl–alkyl coupling reactions of deactivated aryl chlorides with alkyl Grignard reagents without β-hydrogens by using FeF_3/SIPr (1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) catalysts. Various aryl chlorides possessing electron-withdrawing or donating groups, as well as electronically neutral aryl chlorides react with methylmagnesium bromide to give the corresponding methylated products in high yields. In particular, even a more challenging substrate, 1-chloro-3,5-dimethoxybenzene, is efficiently converted into the desired methylated product. Furthermore this catalytic system exhibits a broad substrate scope regarding alkyl Grignard reagents. For example, (trimethylsilyl)methylmagnesium chloride and primary, and secondary alkyl Grignard reagents also participate in the reaction to afford a variety of alkylated aromatic compounds. We propose that the unprecedented catalytic activity would emerge from cooperative effects of SIPr and fluoride ligands, which coordinate to the iron center of reactive intermediates. A detailed mechanistic discussion will be provided in the presentation.



P-456

Towards the formation of planar-chiral ferrocene ligands via first-row transition metal catalyzed enantioselective C-H activation

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Poster Session 2

Chiral ferrocenes have been widely used as powerful ligands in asymmetric catalysis, including 1,2-disubstituted ferrocene derivatives exhibiting solely planar chirality.[1] For the synthesis of planar-chiral ferrocenes, enantioselective ortho-lithiation and subsequent reaction with an electrophile is a common pathway. An emerging synthetic alternative is the metal-catalyzed enantioselective C-H activation and until now, this could be achieved with Iridium[2] and especially Palladium[3] as metal catalyst. The challenge is the application of beneficial first-row transition metals as they are less expensive and often less toxic.
Promising results were obtained using Co[4] and Fe[5] as catalyst. Both nucleophilic Grignard reagents as well as electrophilic alkyl halides are suitable reaction partners depending on the catalytic system. Several ortho-directing groups were tested, showing that 2-ferrocenylpyridine (1) and N-(Quinolin-8-yl)-ferrocene-1-carboxamide (2) work best. First enantioselective reactions gave promising results.

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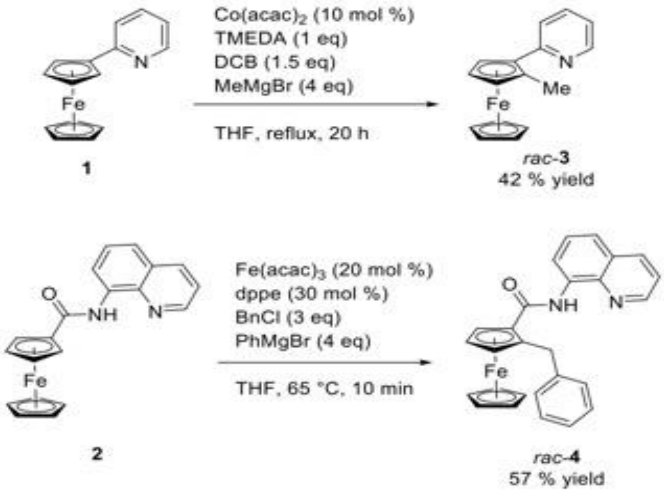

P-602

Synthesis of chiral Ruthenium-cyclopentadienyl complexes and application to formal [4+2] cyclizations of yne-enones

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Poster Session 2

Ruthenium catalyzed cycloisomerizations offer a rapid access to complex molecular frameworks in an atom economical fashion [1]. Therefore the cationic [CpRu(MeCN)3]PF6 complex found widespread application in organic synthesis. The endeavor to conduct these transformations in an enantio-selective manner led to several ligand design approaches, albeit resulting in mediocre selectivities. Recently our group pioneered in the development of highly efficient chiral Cp ligands for late transition metal catalysis [2] and we intend to explore their potential in combination with various metals.

Ruthenium (II) complexes derived from a 3,3 disubstituted R-Binol backbone proved to catalyze the formal [4+2] cyclization of yne-enones to the corresponding pyrans in high enantioselectivity [3]. This particular transformation delivers a sensitive framework in a mild way from easily accessible starting materials. Moreover, these products provide valuable building blocks for follow up functionalizations.

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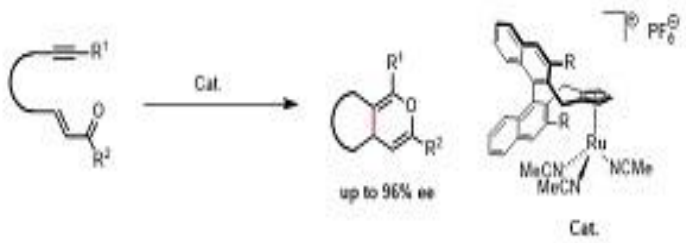

P-603

Chiral Cyclopentadienyl-Iridium Complexes as Catalysts for Cycloisomerizations of N-tethered 1,6-Enynes

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[1]*Laboratory of Asymmetric Catalysis and Synthesis, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*

Poster Session 2

Cyclopentadienyl (Cp) ligands represent an ubiquitous motif in organometallic chemistry. However, for several decades the lack of efficient chiral Cp-versions has limited the design of novel catalysts for asymmetric transformations. Recently, our group developed chiral disubstituted Cp-ligands drawing their chirality from a 3,3'-substituted Binol-backbone. [1]
We present new members of this ligand family and report the synthesis of the corresponding iridium-(III)-complexes. To demonstrate the value of these new complexes as efficient catalysts, enantio-selective cycloisomerizations were investigated. [2]
In detail, N-tethered 1,6-enynes were cycloisomerized under mild conditions via a 6-endo-dig-pathway to 3-azabicyclo[4.1.0]heptenes as single cyclopropane diastereomers and in high enantioselectivities up to 93% ee.

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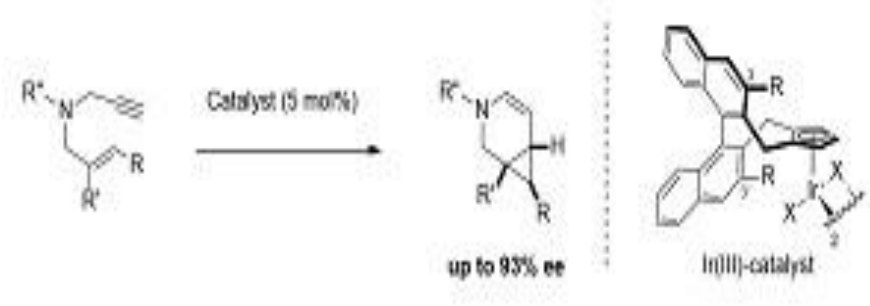

P-604

Synergistic catalysis: intermolecular reaction of aldehydes with allenamides

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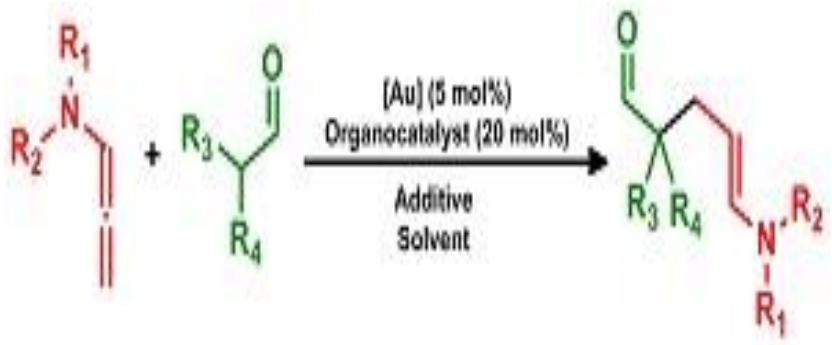
Poster Session 2

In the last few years asymmetric organocatalysis has proved to be a powerful tool to afford a variety of chemical transformations in good yield and enantioselectivity. Transition metal catalysis is well established as a method to activate different types of chemical bonds. The merging of these two methods allows new chemical transformations. Synergistic catalysis consists on the simultaneous activation of the electrophile and the nucleophile by two separate and distinct catalysts to afford a single chemical transformation. In this work a new synergistic catalytic system is tested.

Proline and Proline-derived organocatalysts work synergistically with cationic gold complexes to allow the intermolecular reaction between allenamides and aldehydes. The aldehyde is activated by the organocatalyst via an enamine intermediate, while the allenamide is activated by the gold complex. Specific additives are required to adjust the selectivity and avoid undesired side reactions. Thus, a new synergistic catalytic system that combines organocatalysis with cationic gold complexes allows the elusive reaction of aldehydes and allenamides to occur; as depicted in the scheme below.



P-606

Enantioselecetive Synthesis of Cyclohexanes by an Asymmetric Diels-Alder Reaction Followed by Diastereoselective Hydrogenation

Robin Scheil[1], Dr. Jaroslav Padevet[1], Prof. Dr. Andreas Pfaltz[1]
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Poster Session 2

The cyclohexane structure is a moiety which is found in many natural and synthetic products and can be formed by many ways. One possibility to stereoselectively synthesize chiral cyclohexanes is a two step procedure starting with an asymmetric Diels-Alder reaction to form a cyclohexene which is then reduced in an diastereoselective manner by hydrogenation (Figure 1).
There are many examples in literature of enantioselective Diels-Alder reactions which give cyclohexenes with excellent ee and exo/endo ratios[1]. In our group we showed that substituted olefins can be reduced using iridium catalysts with face selectivities higher than 90%[2]. Therefore we tested this strategy for the formation of several cyclohexanes.

Figure 1: Synthesis of cyclohexanes

We synthesized different cyclohexenes using literature known methods and obtained the products with perfect exo/endo selectivities and ee's higher than 90%. In the second step we used a pyridyl phosphinite ligand for the iridium catalyzed hydrogenation with high selectivities. Furthermore both diastereomeres could be obtained depending on which enantiomer of the catalyst was used showing that the selectivity is mainly catalyst controlled.

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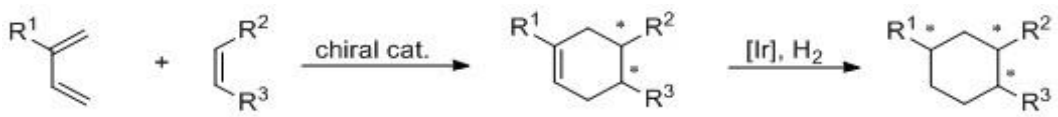


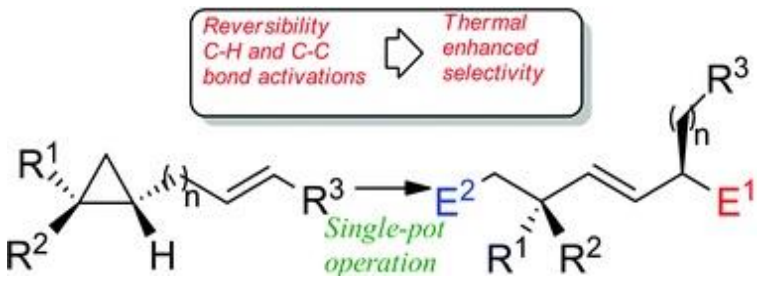
P-607

Remote Functionalization of Hydrocarbons with Reversibility Enhanced Stereocontrol.

Dr. Alexandre Vasseur[1], Prof. Dr. Ilan Marek[1]
[1]*Technion - Israel Istitute of Technology, Haifa, Israel*

Poster Session 2

Manipulation of functionality at a specific position of a hydrocarbon that would generate a reaction at a different location represents a major challenge in synthetic organic chemistry. The difficulty of such remote functionalization is even more pronounced for acyclic systems where flexible alkyl chains are present between the initiating and the final reactive centers. In this context, reaction of a metal complex with a functionality that would generate an unidirectional "walking-process" over an alkyl chain of an hydrocarbon producing a chemical reaction at a defined terminus position is a promising approach to functionalize molecules. We have reported the transformation of unsaturated fatty alcohols derivatives as a source of substituted allylmetal species and the stereoselective preparation of conjugated dienyl metal complexes from non-conjugated enol ethers. Such reactions could be triggered by initiating allylic C-H bond activations from the terminal double bond followed by an elimination reaction to generate the terminus remote functionalization. To further extend our approach, we became interested to investigate the case of ω-ene cyclopropanes. Its remote functionalization could be achieved through successive zirconocene-mediated allylic C-H bond activations followed by a selective C-C bond cleavage (Scheme 1). Importantly, in this study, the reaction proceeds through a very high 1,4-stereocontrol and turns out to be an efficient way for the diasteroselective synthesis of acyclic fragments possessing an all-carbon quaternary stereogenic center. Determination of the reaction mechanism by density functional theory calculations shows that the high diastereoselectivty observed in this process results from a large number of energetically accessible equilibria feeding a preferred reactive channel that leads to the major product. A paradoxal consequence of this pattern is that stereoselectivity is enhanced upon heating.



P-608

Novel P*,N-Ligands for the Iridium Catalysed Asymmetric Hydrogenation of Challenging Substrates

Mr. Ernest Salomó Prat[1], Ms. Sílvia Orgué Gassol[1], Prof. Antoni Riera Escalé[1,2], Prof. Xavier Verdaguer Espaulella[1,2]

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Poster Session 2

Asymmetric hydrogenation of alkenes using transition metal catalysts has come a long way and it is still a vital tool in organic synthesis.[1] Iridium-Crabtree type catalysts are very efficient in the hydrogenation of non-functionalized alkenes.[2] In 1997, Pfaltz and co-workers prepared the first chiral mimic of Crabtree's catalyst. Since then, important achievements have been reported in this field so far. We herein present a novel family of P*,N iridium catalysts.

Our group has developed a novel method for the stereoselective synthesis of P-stereogenic bulky aminophosphines[3][4] through Sn2@P reactions. By these means, a new family of phosphine-oxazoline ligands were synthesized. These ligands bear three independent chiral centers. Thus, by varying the absolute configuration of these centers and the groups at the R1 and R2 positions, a small library of ligands has been prepared. These were then successfully coordinated to Ir and tested in the hydrogenation of several challenging substrates. To our satisfaction, complete conversions as well as very high ee's were achieved.

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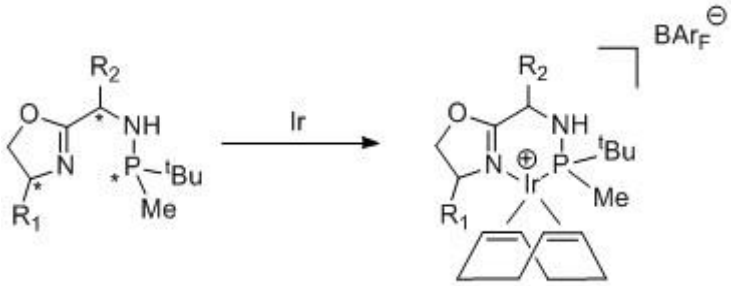

P-609

Towards a Cobalt-Mediated Nitration Strategy of C-H Bonds

Dr Christopher Whiteoak[1], Mr Oriol Planas[1], Dr Anna Company[1], Dr Xavi Ribas[1]
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Poster Session 2

Aromatic nitro compounds are important chemical intermediates and are also prevalent in dyes, pharmaceuticals, perfumes and explosives.[1] Classically, nitration of aromatic compounds has been carried out using a mixture of HNO_3 and H_2SO_4, whereby regioselective control and functional group tolerance under these harsh conditions is often challenging. As a result, the development of new milder regioselective nitration strategies continues to attract interest.[2] The regioselective functionalization of C-H bonds is a rapidly developing area of research, in particular the use of chelate directing groups to overcome regioselectivity issues. One approach, pioneered by Daugulis and co-workers, utilizes the 8-aminoquinoline moiety as directing group and since these seminal reports this substrate has attracted significant attention as a way of demonstrating the feasibility of a number of regioselective C-H functionalization's using a variety of transition metals.[3] Stahl and co-workers have recently shown that in this substrate that functionalization via a Single Electron Transfer (SET) pathway gives distinct products to an organometallic pathway.[4] Whilst developing new cobalt-catalyzed C-H activation protocols using the 8-aminoquinolone directing group, we have recently discovered a new cobalt-mediated nitration strategy and here we report our results to date on the development of this protocol.

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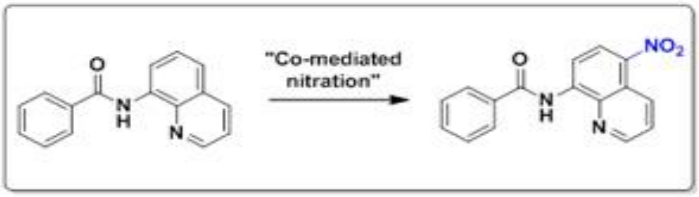

P-610

Mechanistic and synthetic studies of arene functionalization mediated by Cu(I)-catalyzed 1,3-halogen migration.

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Poster Session 2

The high cost and toxicity associated with many rare-earth metals has stimulated great interest in employing earth-abundant metals to transform readily accessible hydrocarbons into useful synthetic building blocks. We have recently identified new reactivity promoted by Cu(I) that 'recycles' the halide group of 2-halostyrenes through an unprecedented 1,3-halogen migration. The bromine is transferred from a sp^2 carbon to a sp^3 carbon, with concomitant borylation of the Ar-Br bond to yield useful benzyl boronic ester products. In the presence of (S,S)-Ph-BPE as a chiral ligand, a rare enantioselective halogenation results to produce benzyl bromides in good to excellent er. Displacement of the bromine with a variety of nucleophiles yields highly functionalized boronic esters with minimal erosion in the er. These intermediates can be readily engaged in further C-C and carbon-heteroatom bond formations to prepare drug-like molecules, including benzofused heterocycles and carbocycles. Mechanistic insight into the 1,3-halogen migration reaction supports formation of an intermediate ArCu(I) species, opening the door for future studies of this underexplored chemistry for C-C and C-heteroatom bond formation.

More recently, we have developed new Cu catalysts supported by NHC ligands for 1,3-chlorine transfer and 1,5-halogen migration. The utility of these catalysts for 'recycling' of oxygen- and nitrogen-based activating groups, as well as their performance in a variety of Cu-catalyzed tandem reactions, will also be described.

P-612

Iridium-Catalyzed Asymmetric Hydrogenation of Dialkylketimines

Dr. Thomas Debnar[1], Prof. Andreas Pfaltz[1]
[1]*Univerity of Basel, Basel, Switzerland*

Poster Session 2

Iridium-catalyzed asymmetric hydrogenation is a powerful method to convert prochiral imines into the corresponding chiral amines.[1] Dialkylketimines are among the most challenging substrates for hydrogenation since they often suffer from low reactivity and/or selectivity. Accordingly, only few effective catalyst systems have been reported for these types of substrates.[2] We found that neutral iridium(I) complexes carrying a chiral monodentate phosphoramidite ligand are highly active catalysts for the hydrogenation of N-phenyl dialkylketimines (Figure 1 a). A screening of various phosphoramidite ligands revealed that a combination of a BINOL-backbone and 2,6-dimethylpiperidine as the amine part are promising lead structures (L1, Figure 1 b). Ongoing studies aim to investigate other phosphoramidites with chiral backbones such as the spirobiindane system developed by Zhou and coworkers (L2, Figure 1 b).[3]
The synthesis of the phosphoramidites as well as the corresponding iridium complexes and the results of our hydrogenation experiments will be presented.

Figure 1: a) Hydrogenation of N-phenyl dialkylketimines with complexes of type 3. b) Promising phosphoramidite ligands in the hydrogenation of imines of type 1.

References:
[1] H. U. Blaser, F. Spindler, Comp. Org. Synth. 2014, 8, 274-299; (b) K. H. Hopmann, A. Bayer, Coord. Chem. Rev. 2014, 268, 59-82.
[2] Y. Schramm, F. Barrios-Landeros, A. Pfaltz, Chem. Sci. 2013, 4, 2760-2766.
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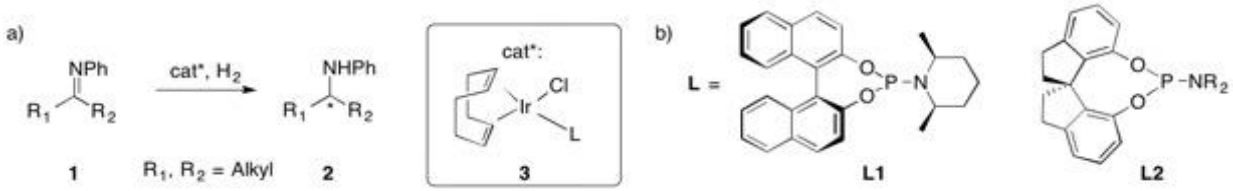


P-613

Trifluoromethylation of elecron-rich double bonds with CF_3H-derived $CuCF_3$ reagent

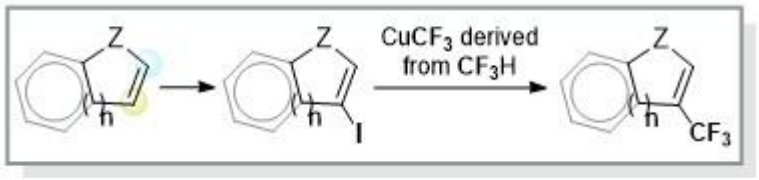
Jordi Mestre[1], Omar Boutureira[1], Sergio Castillón[1], Anton Lischynskyi[2], Vladimir Grushin[2]
[1]*Universitat Rovira I Virgili, Tarragona, Spain,* [2]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

Poster Session 2

Fluorine chemistry has focused the attention of drug discovery since the incorporation of fluorine or fluorinated groups drastically enhance the chemical, physical, and biological properties of the non-fluorinated parent molecules. Fluorinated carbohydrates are used as enzyme inhibitors and as tools for evaluating protein-carbohydrate interactions and recognition processes, serve as diagnostic agents and they are present in antiviral and antitumoural drugs.

A general method for accessing 2-trifluoromethylglycals and 3-trifluoromethylindoles by C(sp^2)-CF_3 bond formation was envisaged using valuable 2-iodoglycals , and easily accessible 3-iodoindoles as coupling partners with the trifluoromethylating $CuCF_3$ reagent prepared by direct cupration of CHF_3. This transition metal-mediated approach enables the challenging coupling between the nucleophilic positions in enol-ethers and enamines with the CF_3 moiety.

This trifluoromethylation procedure has been succesfully applied to a wide range of substrates under mild reaction conditions displaying broad functional group tolerance, complete regioselectivity and chemoselectivity.



- Metal-mediated trifluoromethylation
- Low-cost CF_3H as CF_3 source
- Regioselective trifluoromethylation

P-614

Co-Catalyzed C-H Bond Activation: Hydroarylative Cyclization of 1,6-Enynes with Aromatic Ketones, Aldehydes and Esters

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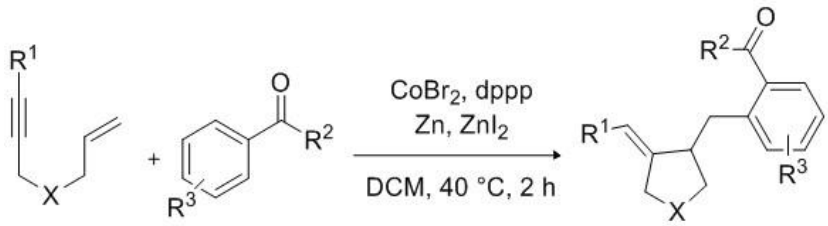
Poster Session 2

Cobalt complexes are known to catalyze intermolecular and intramolecular coupling of alkynes and alkenes. Very recently, Co-catalyzed C-H bond activation reactions also have attracted great attention. Our interest in both metal-catalyzed reductive coupling of alkynes and alkenes and C–H bond activation prompted us to explore the use of relatively inexpensive cobalt complexes as the catalysts for both coupling reaction and C–H bond activation in sequence. In this presentation, we report a hydroarylative 1,6-enyne cyclizations reactions catalyzed by a cobalt system as shown in the scheme. The reaction is highly chemo- and stereoselective. Aromatic ketones, or esters are all compatible with the reaction affording functionalized pyrrolidines and dihydrofurans. The catalytic reaction appears to proceed via a Co(III) metallacycle and carbonyl-directed ortho C–H activation . Furthermore, we successfully extend the reaction to include aromatic aldehydes by adjusting the catalytic conditions.



P-615

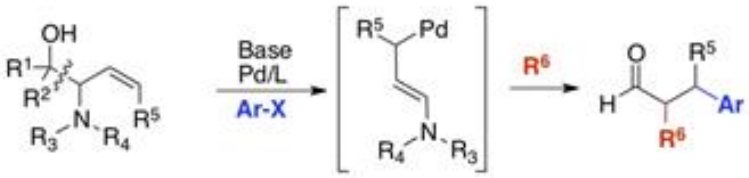
Pd-catalyzed Regioselective Arylation of 1,2-Amino Alcohols via C-C Bond-Cleavage

Chemistry Degree Míriam Sau[1], Prof. Miquel A Pericàs[1,2,3], Prof. Rubén Martín[1,3]
[1]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain* [2]*Univerity of Barcelona (UB), Barcelona, Spain* [3]*Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain*

Poster Session 2

In recent years, catalytic C-C bond functionalization has emerged as a new tool for molecular diversity from simple precursors. At present, most of these processes remain confined to the employment of strain molecules; [1] in sharp contrast, the development of catalytic functionalization of unstrained C-C bonds is still at its infancy, probably due to the remarkable activation energy required for effecting C-C bond-cleavage. [2] As part of our interest in this field of expertise, we describe herein a new catalytic arylation event via unconventional C-C bond-cleavage of unstrained amino alcohols, privileged synthons in organic synthesis. The protocol allows for the coupling of a wide variety of aryl halides, including challenging substrate combinations, thus resulting in a formal α,β-functionalization of aldehyde motifs from readily available amino alcohols.

References:
(1) Selected reviews; a) Seiser, T.; Cramer, N. Org. Biomol. Chem., 2009, 7, 2835.b) Murakami, M.; Matsuda, T. Chem. Commun. 2011, 47, 1100. c) Ziadi, A.; Martin, R. Org. Lett. 2012, 14, 1266-1269.
(2) a) Terao, Y.; Wakui, H.; Satoh, T.; Nomura, M.; Miura, M. J. Am. Chem. Soc., 2001, 123, 10407-10408. b) Iwasaki, I.; Hayashi, S.; Hirano, K.;Yorimitsu, K.; Oshima, K. J. Am. Chem. Soc., 2007, 129, 4463-4469 c) Xu, Y.; Wang, Yi.; Chiba, S. J. Am. Chem. Soc., 2009, 131, 12886-12887.



P-616

Structurally simple nickel(II) complexes for the catalytic and stereoselective construction of carbon-carbon bonds. Synthesis of C11–C19 fragment of peloruside A

Mr. Juan Manuel Romo[1], Mr Javier Fernández-Valparís[1], Dr Pedro Romea[1], Dr Fèlix Urpí[1]
[1]*Universitat De Barcelona, Barcelona, Spain*

Poster Session 2

Despite the tremendous accomplishments recently disclosed in the stereoselective construction of carbon-carbon bonds under catalytic premises, there is a lack of methods that take advantage of the nucleophilicity of nonactivated metal enolates in direct type reactions.

Aiming for simple and wide breadth methods, herein we describe a highly stereoselective addition of chiral N-acyl thiazolidinethiones to methyl orthoformate triggered by structurally simple nickel(II) complexes. As shown

below, the appropriate combination of a chiral scaffold, easy to handle $(R_3P)_2NiCl_2$ complexes, a Lewis acid (TESOTf), and 2,6-lutidine provide a single diastereomer of the corresponding acetal derived adduct in high yields under mild conditions. Likely, such an addition proceeds through a S_n1 type mechanism in which a putative oxocarbenium intermediate, the electrophile partner, approaches to the less hindered face of the enolate in a open transition state.

Therefore, the reported procedure is potentially amenable to parallel additions involving cationic intermediates.

As a proof of concept, the C11–C19 fragment of peloruside A has been stereoselectively synthesized by a combination of carbon-carbon bond forming processes from thiazolidinethione-derived enolates, which includes the abovementioned catalytic reaction and other additions of related titanium enolates.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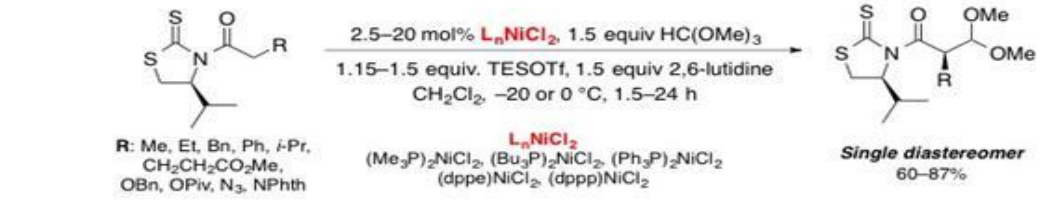
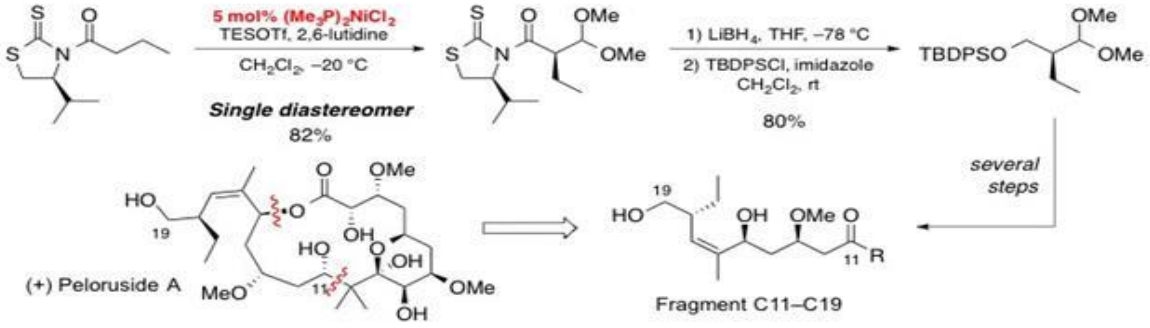

2.5–20 mol% LnNiCl2, 1.5 equiv HC(OMe)3
1.15–1.5 equiv. TESOTf, 1.5 equiv 2,6-lutidine
CH2Cl2, –20 or 0 °C, 1.5–24 h
R: Me, Et, Bn, Ph, i-Pr, CH2CH2CO2Me, OBn, OPiv, N3, NPhth
LnNiCl2
(Me3P)2NiCl2, (Bu3P)2NiCl2, (Ph3P)2NiCl2
(dppe)NiCl2, (dppp)NiCl2
Single diastereomer
60–87%


5 mol% (Me3P)2NiCl2
TESOTf, 2,6-lutidine
CH2Cl2, –20 °C
Single diastereomer
82%
1) LiBH4, THF, –78 °C
2) TBDPSCl, imidazole
CH2Cl2, rt
80%
several steps
(+) Peloruside A
Fragment C11–C19

P-617

Synthesis of allyl amines with an α-quaternary center by silver-catalyzed aziridination of dienols.

PhD Macarena Corro[1], Prof. Pedro J. Pérez[2], Dr. Yolanda Díaz[1], Prof. Sergio Castillón[1]

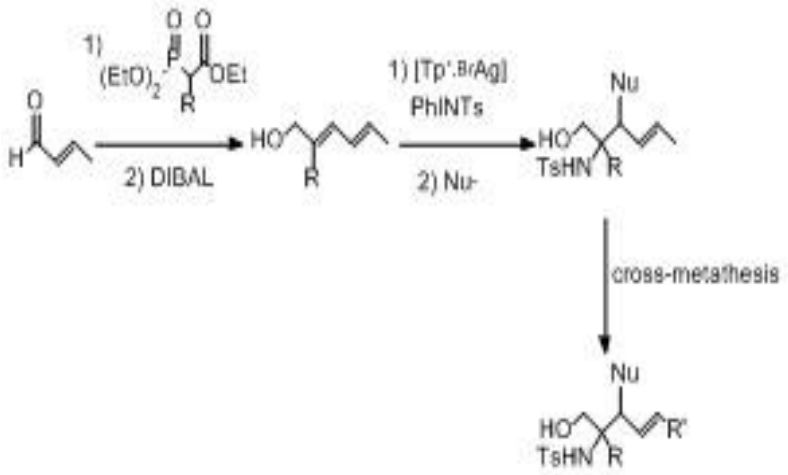
[1]Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Tarragona, Spain [2]Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible y Departamento de Química y Ciencia de los Materiales, Universidad de Huelva., Huelva, Spain

Poster Session 2

Sphigonsine derivatives such as FTY720, FTY720-OCH10$_3$ or CS-0777 are employed as inhibitors of sphingosine kinase in cancer therapies [1] . These compounds, which are characterized by containing a quartenary center in the α-position of the amino moiety, could be synthesized through an aziridination reaction. Recently, our research group has reported the intermolecular silver-catalyzed aziridination of dienols [2,3]. Following this study, we intend to extend this process with the purpose of obtaining FTY720 and CS0777 analogs using 2-alkyl substituted dienols as substrates for the aziridination reaction.

Here we describe the synthesis of these compounds following a common reaction sequence. Synthesis of 2-alkyl substituted 2,4-hexandien-1-ols can be accomplished from crotonaldehyde by a Wadsworth-Emmons olefination reaction followed by reduction of the ester intermediate. The dienols then can be submitted to silver-catalyzed aziridination followed by nucleophilic ring-opening process. Finally, metathesis with alkenes of different chain length could then give access to a library of the lipid analogues.

References:
[1] Plano, D.; Amin, S.; Sharma, A.K., J.Med.Chem 2014, 57, 5509-5524.
[2] Llaveria, J.; Beltrán, A.; Díaz-Requejo, M. M.; Matheu, M. I.; Castillón, S.; Pérez, P.J.; Angew. Chem. Int. Ed., 2010, 49, 709-7095.
[3] Llavería, J., Beltrán, A., Díaz-Requejo. M. M.; Matheu, M. I.; Castillón, S.; Pérez, P. J., J. Am. Chem. Soc., 2014, 136, 5342-5350.



P-618

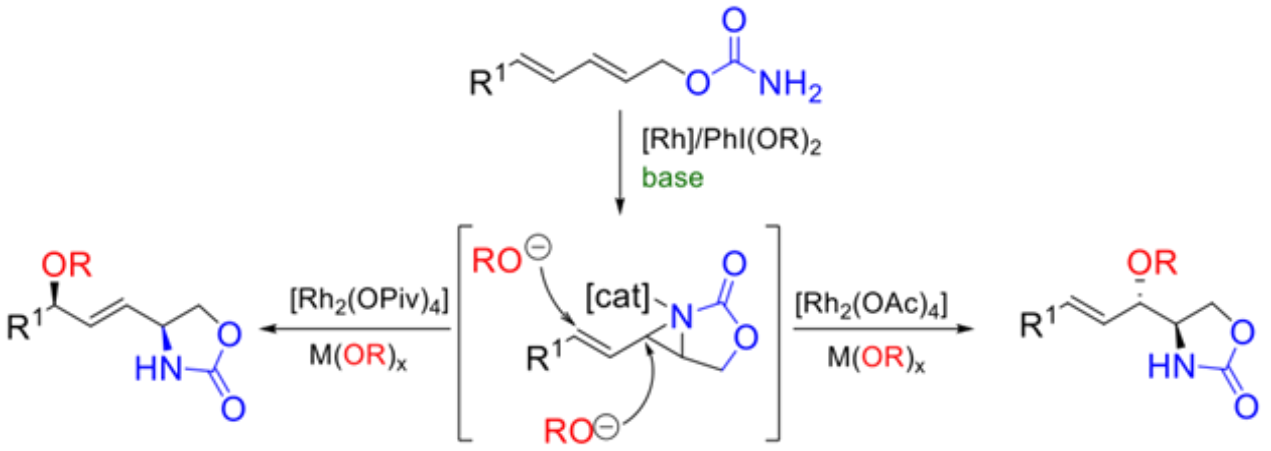
Rhodium-Catalyzed Regio– and Stereoselective Oxyamination of Dienes via Tandem Aziridination-Ring-opening of Dienyl Carbamates. Scope and Mechanism

Joan Guasch[1], Yolanda Díaz[1], Maria Isabel Matheu[1], Sergio Castillón[1]
[1]*Universitat Rovira I Virgili, Tarragona, Spain*

Poster Session 2

Vinylaziridines are versatile building blocks for the stereoselective synthesis of biologically and synthetically important compounds. They undergo regioselective ring-opening reactions via addition at either the vinyl terminus or directly at the aziridine depending on the reagents employed [1]. Ring-opening reactions of vinylaziridines with oxygen nucleophiles particularly constitute an extremely useful pathway for the stereoselective synthesis of unsaturated aminoalcohols [2].
In our work, the use of rhodium catalysts bearing different carboxylate ligands has allowed to control the regioselective oxyamination of dienes. The process is based on the stereoselective intramolecular aziridination of dienyl carbamates followed by a selective SN2 or SN2' ring-opening of the transient vinylaziridines governed by a combined effect between rhodium (II) catalyst and the nature of the counteraction of the base used. The scope and limitations of the tandem process will be analyzed. The role of the catalysts, iodinane reagents and bases in the selectivity will be discussed [3].

References:
[1]. a) Ohno, H. Chem. Rev. 2014, 114, 7784-7814. b) Aziridines and Epoxides in Organic Synthesis; Yudin, A. K., Ed.; Wiley-VCH: Weinheim, Germany, 2006.
[2]. a) Olofsson, B.; Khamrai, U.; Somfai, P. J. Org. Chem. 2000, 66, 4087-4089. b) Llaveria, J.; Beltrán, A.; Díaz-Requejo, M. M.; Matheu, M. I.; Castillón, S.; Pérez, P. J. Angew. Chem. Int. Ed. 2010, 49, 7092-7095.
[3]. Guasch, J.; Díaz, Y.; Matheu, M. I.; Castillón, S. Chem. Commun. 2014, 50, 7344-7347.



P-619

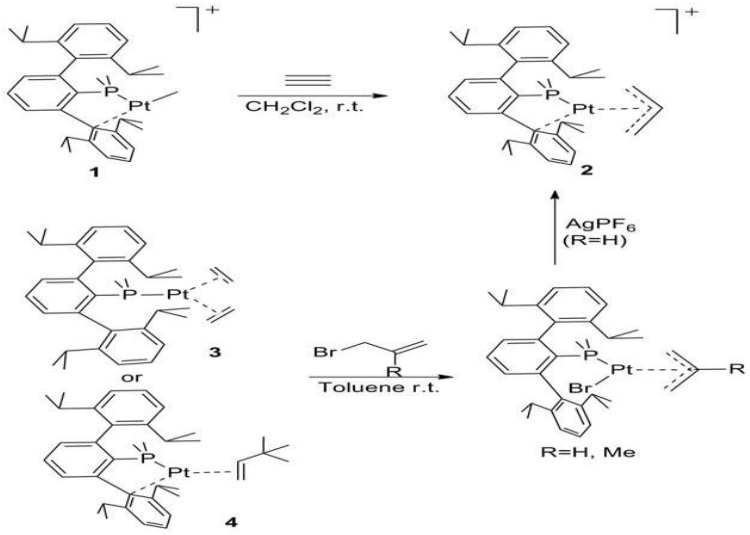
Low coordinated Pt(II) and Pt(0) complexes stabilized by terphenyl phoshines

Low Coordinated Pt(II) and Pt(0) Complexes Stabilized by Terphenyl Phoshines Laura Ortega Moreno[1], Dr Riccardo Peloso[1], Dr Celia Maya[1], Prof Ernesto Carmona[1]
[1]*Universidad de Sevilla, Sevilla, Spain*

Poster Session 2

Bulky phosphine ligands containing substituted terphenyl groups[1] have shown great ability to stabilize unsaturated 14 e[sup]-[/sup] Pt(II) species due to the formation of non-covalent C-Pt interactions. A variety of Pt(II) and Pt(0) complexes bearing the dimethyl aryl phosphines PMe_2(Ar[sup]Dipp[/sup]) and PMe_2(Ar[sup]Trip[/sup]) have been synthesized and characterized (Ar[sup]Dipp[/sup] = 2,6-bis(2,6-diisopropylphenyl)phenyl, Ar[sup]Trip[/sup] = 2,6-bis(2,4,6-triisopropylphenyl)phenyl).
Cationic Pt(II) methyl complex, 1, catalyses the dimerization of ethylene to form linear butenes and reacts with acetylene to form a Pt(II) allyl complex, 2. As suggested by deuteration experiments, an isomerization of the coordinated alkyne molecule into a vinylidene Pt(II) intermediate occurs before methyl insertion into the $Pt=CCH_2$ bond to form compound 2.
These ligands can also stabilize Pt(0) trigonal planar alkene complexes such as $Pt(PMe_2Ar[sup]Dipp[/sup])(C_2H_4)_2$, 3, and $Pt(PMe_2Ar[sup]Dipp[/sup])(CH_2CH[sup]t[/sup]Bu)$, 4, which can be converted into allyl halide complexes by oxidative addition of allylbromide and 3-bromo-2-methylpropene.
Complexes 1 and 4 have been also tested as catalysts for alkyne hydroamination and hydrosiliation, respectively.

Reference:
1. J. Campos, L. Ortega-Moreno, S. Conejero, R. Peloso, J. López-Serrano, C. Maya, E.Carmona, Chem. Europ. J., accepted.



Scheme 1

P-620

Tethered Cyclopentadienyl-Stannylene Ligands for C-H Activation

Dr Marta Roselló Merino[1], Dr Stephen M. Mansell[1]
[1]*Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, UK*

Poster Session 2

C-H activation chemistry offers huge potential in improving the way in which simple and inert hydrocarbons can be functionalized into more useful species as well as to simplify the synthesis of complex fine chemicals. However, the development of both selective and highly reactive catalysts for these transformations remains a challenge.

N-heterocyclic stannylenes are an interesting alternative to the ubiquitous N-heterocyclic carbene ligands that have been recently described [1] but that have not been explored as ligands in catalysis so far. We are investigating the use of unconventional tethered cyclopentadienyl-stannylene ligands in transition metal complexes for C-H activation as the electronic properties of the tin-containing ligand will open up novel modes of reactivity. In particular, the hemilability of the stannylene moiety could facilitate activation at the metal centre, and the bridging binding modes typically observed with stannylenes could bring together two metal fragments to promote unusual C-H activation modes. The tin donor atom can also act as both a Lewis acid or base which could facilitate transfer of ligands from/to the metal centre and the presence of a tether will provide additional stability while at the same time potentially increasing product selectivity.

Initial studies have focused on the synthesis of novel diamines, which contain indene and fluorene moieties, to form the backbone of our target stannylene ligands. The formation of the desired transition metal complexes has been tested by two main routes: initial reaction of the ligand backbone with a tin precursor followed by addition of the transition metal precursor or introduction of the transition metal before reaction with a tin source, and the reaction outcomes will be presented.

References:

[1] a) Inorg. Chem., 2008, 47, 11367; b) Inorg. Chem., 2011, 50, 2252.

P-621

Highly active ruthenium catalysts for the transfer hydrogenation of ketones: a study on the reactivity and mechanism

Mr. Jan Pechacek[1], Mr. Leoš Kořený[1], MSc. Petr Šot[1], MSc. Beáta Vilhanová[1], MSc. Jiří Vavřík[1], MSc. Jakub Januščák, Dr. Marek Kuzma[2], Assoc. Prof. Petr Kačer[1]

[1]*Department of Organic Technology, University of Chemistry and Technology in Prague, Prague, Czech Republic*
[2]*Laboratory of Molecular Structure Characterization, Institute of Microbiology, v.v.i., Academy of Sciences of the Czech Republic, Prague, Czech Republic*

Poster Session 2

Transfer hydrogenation of ketones is a well-established chemoselective technique for obtaining alcohols in high yields. Recent discoveries of highly active ruthenium complexes promise to mitigate the main disadvantages of the transfer hydrogenation, which include low reaction rates and, correspondingly, the necessity of high catalyst loading.

The presented work is focused on a highly active ruthenium complex described previously. The reactivity of this complex in the transfer hydrogenation of acetophenone was evaluated. Multiple catalytic bases were tested for their influence on the activity of the catalyst. During the testing of other ligands when the catalyst was formed in situ, a previously unreported induction period was observed. This phenomenon was examined by NMR spectrometry and is ascribed to reversible formation of an enolate.

Theoretical calculations were performed in order to elucidate the mechanism of the reaction. Multiple transition states were located, which enabled the reaction coordinates to be plotted. It was found out that the reaction is most likely to proceed in the inner coordination sphere of the ruthenium atom.

Acknowledgements: This work has been financially supported by the Grant Agency of the Czech Republic (Grant GACR 106/12/1276 and GACR 15-089925). Financial support from specific university research (MSMT No 20/2015).

P-623

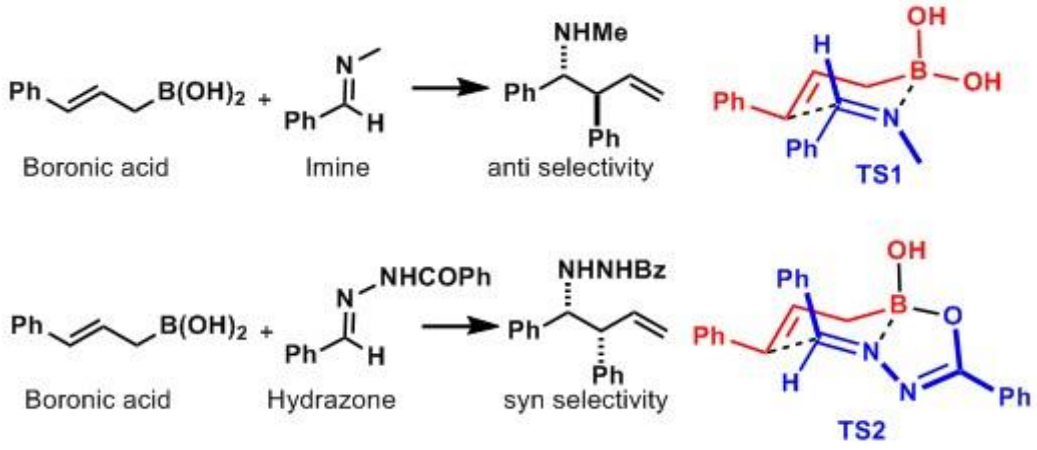
Stereoselective allylboration of imines and hydrazones using allylboronic acids

Rauful Alam[1], Arindam Das[1], Prof. Kálmán Szabó[1]
[1]*Stockholm Unviersity, Stockholm, Sweden*

Poster Session 2

Allylboronic acids are very useful building blocks in synthetic organic chemistry. Recently we have reported that allylboronic acids react with imines, indoles and hydrazones under mild conditions to afford high regio- and stereoselective homoallylic amines.[1,2] Our studies revealed that both E- and Z-aldimines react with allylboronic acids to give anti homoallylic amines selectively. Whereas, allylboration of hydrazones gives syn homoallylic amines (Scheme 1).

References:
[1] Alam, R.; Das, A.; Huang, G.; Eriksson, L.; Himo, F.; Szabo, K. J. Chem. Sci. 2014, 5, 2732.
[2] Das, A.; Alam, R.; Eriksson, L.; Szabó, K. J. Org. Lett. 2014, 16, 3808.



Scheme 1. Allylboration of imines and hydrazones

P-624

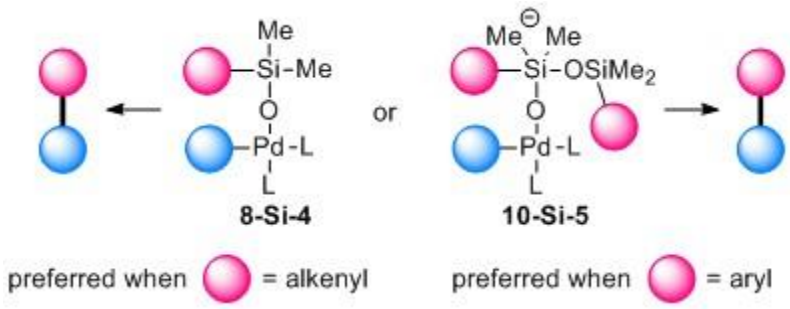
The Mechanistic Significance of the Si-O-Pd Bond in the Palladium-Catalyzed Cross-Coupling of Alkenyl- and Arylsilanolates

Andrea Ambrosi[1], Dr Steven A. Tymonko[1], Dr Russel C. Smith[1], Dr Michael H. Ober[1], Dr Hao Wang[1], Prof Scott E. Denmark[1]

[1]*University of Illinois at Urbana-Champaign, Urbana, USA*

Poster Session 2

Through the combination of reaction kinetics (both catalytic and stoichiometric), along with solution and solid state characterization of organopalladium(II) silanolates, and computational analysis, the intermediacy of covalent adducts containing Si-O-Pd linkages in the cross-coupling reactions of organosilanolates has been unambiguously established. Two mechanistically distinct pathways have been demonstrated: (1) transmetalation via a neutral 8-Si-4 intermediate; and (2) transmetalation via an anionic 10-Si-5 intermediate. In general, potassium salts of alkenylsilanolates react via neutral (8-Si-4) intermediates, whereas the enhanced nucleophilicity of the cesium alkenylsilanolates allows for the reaction to access the 10-Si-5 intermediate and proceed via the anionically activated pathway. However, if the direct transmetalation is slower, as in the case of arylsilanolates (which require interruption of aromaticity), then anionic activation via the 10-Si-5 intermediate becomes predominant. These conclusions mandate a revision of the reigning paradigm that organosilicon compounds must be anionically activated to engage in transmetalation processes (Hiyama-Hatanaka paradigm). Thanks to these studies, the mechanistic formulation for the cross-coupling of alkenyl- and arylsilanolates with aryl halides is now substantially understood.



P-625

Solvent-free synthesis of new chiral ferroceneamines

Prof. Guadalupe Hernández[1], Student Daniela Gutiérrez[1], Dra. Gloria E. Moreno[1], Student Claudia Herrera[1], Dra. Manju Sharma[2], Dr. Pankaj Sharma[3], Dr. Oscar Portillo[1], Dr. René Gutiérrez[1]

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Poster Session 2

In the past few years, chiral ferrocene derivatives have attracted a great interest due to their successful applications in asymmetric catalysis as chiral ligands of transition metal complexes, modular units in material science, e.g. in non-linear optics and structural unit of products with biological or biochemical activities.

On the other hand, recently, one of the major goals of synthetic organic chemistry lies in the research, discovery and exploitation of environmentally friendly methods. Consequently, several newer strategies have appeared such as, for example, solvent-free reactions.

In line with our research program in solvent-free synthesis, herein we would like to report an efficient procedure for the preparation of chiral ferrocenecarboxyamines derivatives 1 and 2 through a two step reactions under solvent-free conditons.

X-Ray structure of compound 1

X-Ray structure of compound 2

P-626

Novel Sugar-incorporated N-heterocyclic Carbenes and their Metal Complexes

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Poster Session 2

N-heterocyclic carbenes are established ligands for many transition metal complexes including Ag, Ru, Au, Pt, Pd, which are mainly used in homogenous catalysis. Recently, there have been several biological activity studies of NHC complexes containing gold, silver and platinum.[1] Modification of the organic residues bound to the NHC backbone influence the properties of the compounds. For biological applications, water soluble complexes are of special interest. Therefore, the polar sugar moiety in particular the acetyl (Ac) or benzoyl protected derivatives, were attached to the imidazolium nitrogen atom. □-D-Glucose was per-O-acetylated, brominated at C1 and then reacted with 1-methylimidazole (MeImi) to yield the corresponding imidazolium bromide in good yield.[2] After addition of silver oxide, the silver NHC complex 3 was isolated and used as transmetalating agent to prepare a variety of transition metal carbine complexes of the type [(OAcGlcMeImi)MXn(Y)] (M = Au, Pt, Ru, Rh; X = Cl; Y = p-cymol, cp*, cod) (compounds 4-9 Figure 1). Deprotection of the imidazolium bromide 2 followed by reaction with Ag2O afforded the glucose-substituted silver carbene complex 9. Transmetalation reactions of this compound as well as attempts to remove the acetyl groups of complexes 3-8 are currently in progress.

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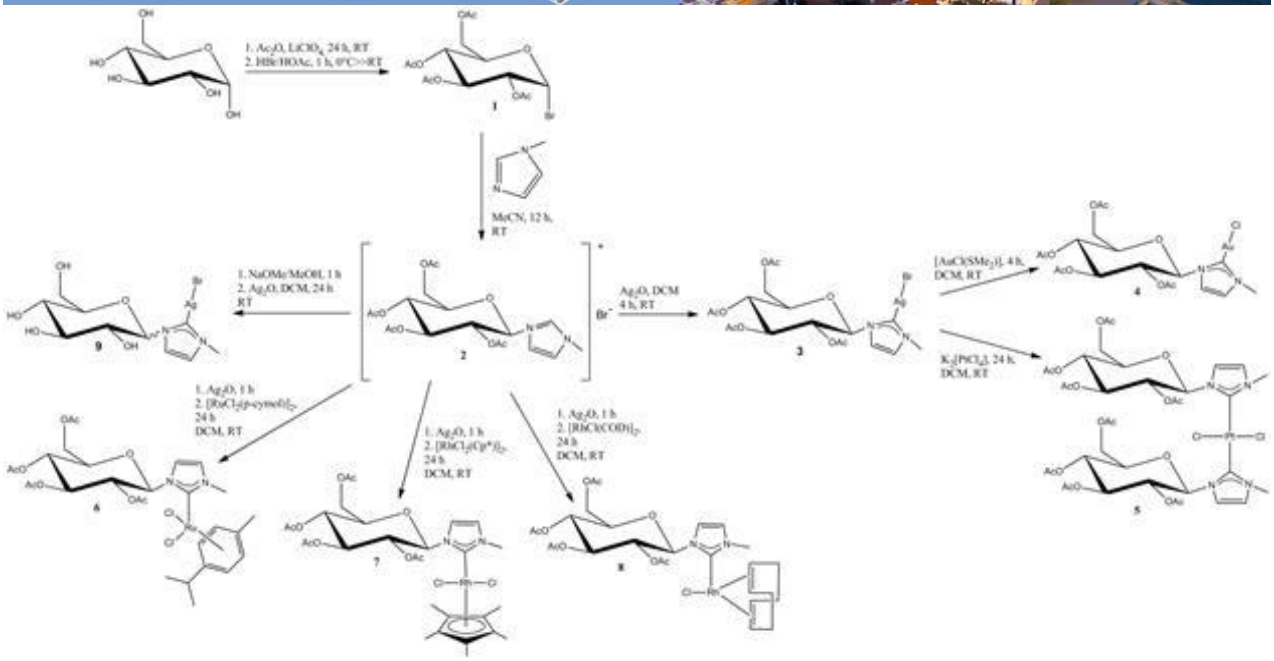

P-627

Synthesis of a new Pd(II) complex derived from a chiral macrocyclic hexaimine.

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Poster Session 2

Organopalladium chemistry has made remarkable progress in the last decades, and numerous novel reactions involving Pd-complexes acting either as catalysts or reagents have been discovered. The utility of such compounds ranges from potential new applications in organic chemistry and the usual efforts in understanding fundamental chemistry and physical properties. So far, most attention on this subject has also been aimed at synthesizing novel complexes derived from a wide-ranging assortment of functionalized ligands and as a part of an ongoing project centered into the bioactivity of Pd-complexes, we are currently focusing our efforts on the synthesis of chiral complexes derived from enantiopure imines. On this line, a chiral macrocyclic hexaimine ligand yields an unexpected new mononuclear palladium complex. The crystal and molecular structure for such complex has been fully confirmed by single-crystal X-ray studies.

Key words: Cyclopalladation, chiral ligand

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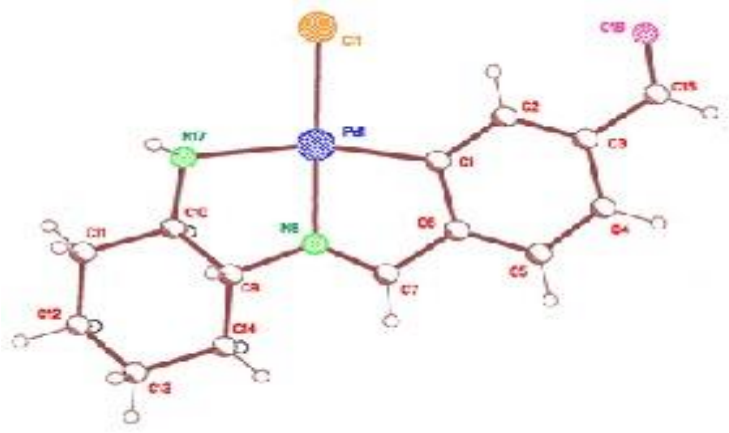

P-630

Iridium-Catalyzed Regioselective C-H Silylation Controlled by Lewis Acid-Base Interaction

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Poster Session 2

π-Conjugated molecules with a Lewis acid-base interaction have recently attracted attention due to the special properties of such molecules compared with π-conjugated molecules bearing only covalent bonds. We recently reported synthesis of silafluorene equivalents with a Lewis acid-base interaction. The silafluorene equivalent showed a higher fluorescent quantum yield than the corresponding silafluorene derivative (Figure 1).[1]

It is considered that such molecules could be synthesized more effectively and easily by Lewis acid-base interaction-controlled[2] C-H silylation. A silicon atom with electron-withdrawing group(s), such as a fluorine atom, can take a pentacoordinated structure and shows a Lewis acidic character. Here we present ortho-selective C-H silylation, which was controlled by a Lewis acid-base interaction. Treatment of 2-phenylpyridine with fluorodiphenylsilane in the presence of Ir(acac)(cod) and 2-norbornene gave an ortho-selective fluorosilylated product in excellent yield (eq 1).[3] The reaction exhibited a wide substrate scope, and a variety of π-conjugated molecules were synthesized in good to excellent yields, even in gram scale.

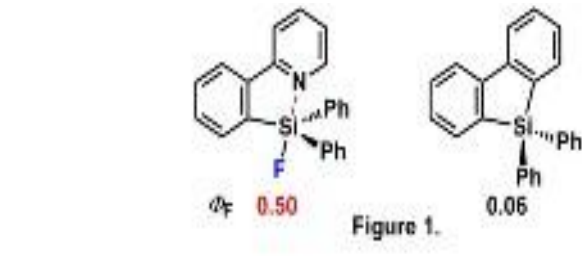
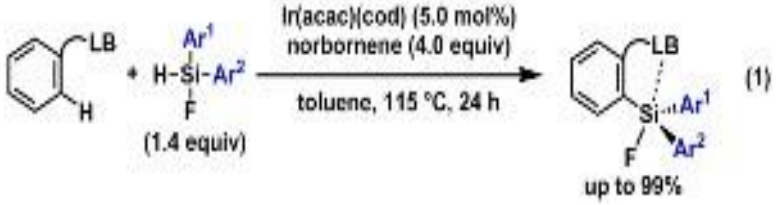


Figure 1.



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P-631

Latent ruthenium catalyst for metathesis of tetrasubstituted olefins

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Poster Session 2

Olefin metathesis reaction is a very important and wide spread C-C bond formation reaction, which was the subject of 2005 noble prize in chemistry. In this area, the metathesis of tetrasubstituted olefins is considered as a challenge task. A successful advance, in this regard was obtained by replacing the customary mesitylenes (Mes) rings in the ruthenium catalysts by ortho Tolyl rings (oTol).1 Another significant aspect of this area is the ability to control the initiation of the catalyst for applications related to the preparation of thermosets etc. In this regard, latent precatalyst consist of sulfur ligand, which their activation can be fully control constitute an advantage.2 In the current research, we combined the increased reactivity of the oTol-complexes, together with the latency of the sulfur chelated ligand, to create a latent precatalyst which can be dormant in the reaction mixture at ambient condition for a long period of time and efficiently active for tetra substituted olefins after activation by UV irradiation or heat.
Figure 1. Activation of tolyl ruthenium catalyst

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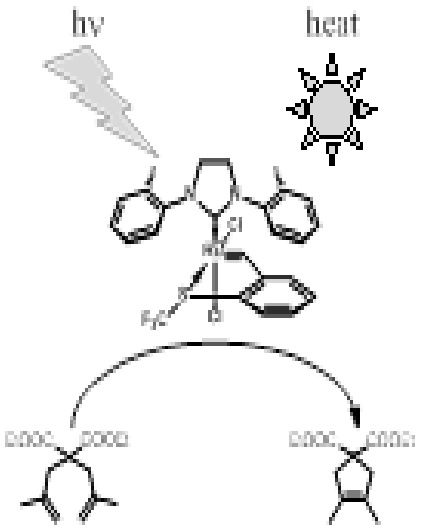

P-595

Zinc-catalyzed synthesis of 2-alkenylfurans via cross-coupling of enynones and diazo compounds

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Poster Session 2

The catalytic generation of zinc carbenes from enynones has been reported to be a powerful tool in cyclopropanation and Si-H bond insertion reactions, leading to a variety of furans derivatives.[1] In this work, we have described the ability of these furyl-zinc carbenes intermediates to achieve selective cross-coupling reactions with diazo compounds. This reactivity pattern has no precedent within the zinc carbenoid chemistry, and affords the synthesis of a vast array of 2-alkenylfurans in good yields.[2]

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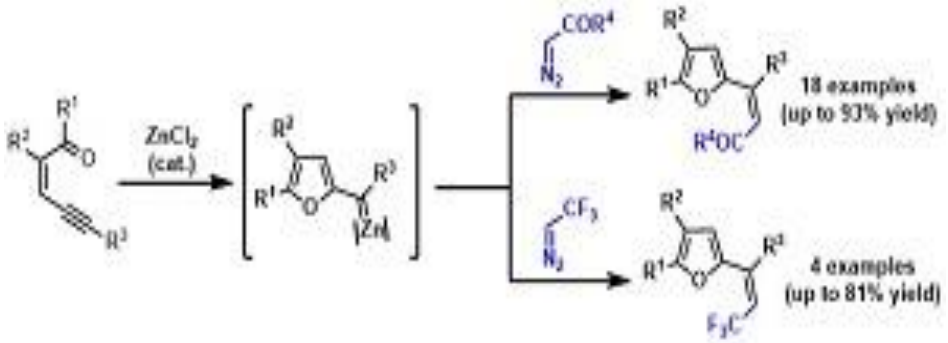

P-632

Selective C-H Bond Fluorination of Phenols with a Removable Directing Group: Late-Stage Fluorination of 2-Phenoxyl Nicotinate Derivatives

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Poster Session 2

With the great effort made in the past few years, several directing groups, e.g. aryl-N-heterocycles, amides and oximes assisted selective ortho-fluorination of aromatic C-H bonds have been developed.1 Given the broad application of fluorinated compounds in pharmaceuticals, agrochemicals and materials, more directing groups especially removable directing groups are required to be developed for directed C-H bond fluorination protocols. Benzyl alcohols are ubiquitous substructures found in pharmaceuticals and materials. C-H bond functionalization of benzyl alcohols are of great important due to the useful scaffold. Despite the great advance in C-H bond functionalization in the past decade, benzyl alcohol motifs are less studied as the substrates. Encouraged by our previous nitrate-promoted C-H fluorination of ketone oximes,2 we envisioned that the benzylalcohol-based O-benzyl oximes could be employed as the effective substrates due to their similar coordinating ability to transition metals.3

Propan-2-one O-benzyl oximes can readily be prepared by the derivation of benzyl alcohols. However, dislike the endo-palladation in our previous report, an exo-palladacycle is formed in case of O-benzyl oximes substrates, which remains challenging and less developed.4 Gratefully, by simply adjusting our previous C-H fluorination condition, mono-fluorinated products were obtained in moderate to good yields. Removal of the oximly directing group will finally furnish the ortho-fluorinated benzyl alcohols.

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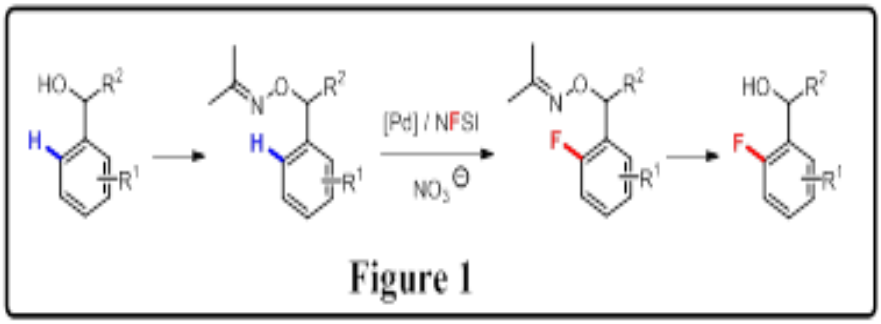

Figure 1

P-633

Organocatalytic Domino Michael-Hemiaminalization-Oxidation Reaction For the Synthesis of Optically Active 3,4-Disubstituted Dihydro-2(1H)-quinolinones

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Poster Session 2

Functionalized 3,4-dihydro-2(1H)-quinolinones are privileged scaffolds that can be found in a large number of clinical pharmaceuticals and natural products possessing various biological activities. Considering the medicinal significance of this structural core, these compounds have drawn great attention from synthetic chemists and those in the medicinal field.1 A number of catalyzed reactions such as transition metal-catalyzed, photochemical, radical-mediated, and other reactions have been carried out for the synthesis of 3,4-dihydro-2(1H)-quinolinones. However, only a few examples involve the asymmetric synthetic approach to construct functionalized 3,4-dihydro-2(1H)-quinolinone systems.2 And in most cases, stoichiometric chiral reagents are required. So the exploration of efficient catalytic asymmetric methods of generating this architecture is still highly desired, particularly those using simple and readily available starting materials under mild organocatalytic conditions. Then a novel method is developed for the enantioselective synthesis of highly functionalized 3,4-disubstituted dihydro-2(1H)-quinolinones bearing two trans contiguous stereogenic centers with excellent diastereoselectivities and high to excellent enantioselectivities in our lab. The process combines an enantioselective organocatalytic Michael¨Chemiaminalization reaction and a highly efficient oxidation reaction sequence with good yields and stereoselectivity. And the operation can also be performed successfully on gram-scale with the same diastereoselectivity and enantioselectivity under modified conditions.

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P-635

Fast and Selective Dehydrogenative C-H/C-H Arylation of Anilides in a Ball Mill

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Poster Session 2

Biaryl motifs are widely found in pharmaceuticals and agrochemicals. Despite the classic coupling reactions e.g. Suzuki reaction, dehydrogenative C-H / C-H activation arylation has emerged as the most efficient way to access biaryl scaffold.1 However, there remain several challenges need to be overcame. First, regio-selective cross-coupling between substituted arenes and substrates. Second, large excess amount of coupling partner (usually, simple arenes were used as solvents). Third, the reactions required a long period of time and were less efficient for the electron-deficient arenes.

Ball milling as a mechanochemical technique in synthetic chemistry has been received great attention due to their environmentally friendly and solvent-free synthesis approaches, which remarkably enhance the efficiency of the reactions.2 However, application of mechanochemical technique in C-H bond functionalization is less studied. Encouraged by our previous asymmetric Michael addition in ball mill,3 we envisioned to develop a novel and efficient C-H/C-H arylation of anilides in ball mill.

The coupling reactions in ball mill proceeded smoothly between anilides and various arenes (both electron-rich and electron-deficient arenes). Meanwhile, the protocol required less coupling partners and reaction time and featured in highly regio-selectivity.

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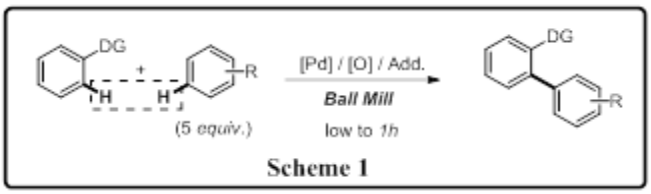

Scheme 1

P-636

Highly Efficient and Practical Fe-Catalyzed Hydrogenation of Olefins

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Poster Session 2

Transition-metal-catalyzed hydrogenation of unsaturated compounds has been widely used for the production of value-added bulk and fine chemicals.[1] Homogeneous hydrogenation is generally carried out with catalysts derived from precious metals, such as Rh, Ru, Ir, and Os, some of which are highly toxic. The high cost, toxicity, and potential depletion of precious metals have forced chemists to develop green, sustainable catalysts for hydrogenation. Because iron Fe is abundant, cheap, and environmentally benign, Fe-catalyzed hydrogenation has recently drawn much attention nowadays, however, only limited progresses have been achieved.[2] We developed a new method for the hydrogenation of olefins by using an Fe catalyst generated in situ from bench-stable Fe(II) complexes and LiAlH4.[3] This method makes the hydrogenation of olefins very easy to handle and enables the development of new Fe catalysts for the hydrogenation more efficient through ligand screening. One of the Fe catalysts derived from Fe complex of phosphine-bipyridine ligand exhibited unprecedented activity for the hydrogenation of olefins, with turnover numbers up to 10,000 and turnover frequencies up to 37,740 h-1. The NMR studies of the active Fe catalyst showed that a Fe-hydride species stabilized by Al might be a real catalyst.

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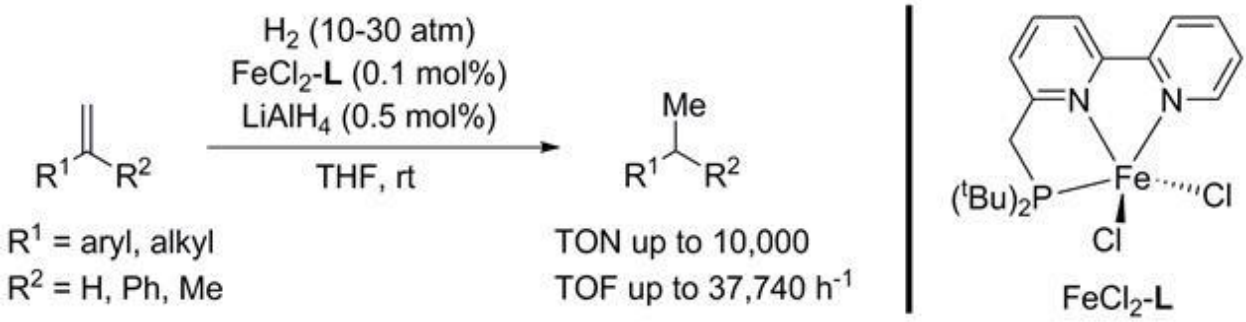

P-637

Palladium-Catalyzed Hydrocarboxylation of Alkynes with Formic Acid

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Poster Session 2

Acrylic acid, an important commodity chemical, is widely used as a base material for the production of paints, plastics, superabsorbent polymers, and rubbers. In industry, acrylic acid is prepared by partial oxidation of propene, which is refined from petroleum.[1] However, the growing demand for plastics and superabsorbent polymers, and the diminishing supply of petroleum have stimulated intense interest in sustainable processes for the production of acrylic acid. Catalytic hydrocarboxylation of acetylene with CO, is an atom-economical approach to acrylic acid.[2] However, this nonpetroleum-based process has a major drawback in that it uses high-pressure toxic CO gas. In contrast, formic acid is a nontoxic, renewable liquid and can be produced by catalytic hydrogenation of CO2 and oxidation of biomass. However, the catalytic hydrocarboxylation of acetylene with formic acid to form acrylic acid remains unexplored. Herein we report that the hydrocarboxylation of acetylene with formic acid can be achieved in the presence of palladium catalysts and a catalytic amount of benzoic anhydride. The conversion of acetylene into acrylic acid occurred with turnover numbers of up to 350 under mild reaction conditions. And this catalytic system could also be used for efficient hydrocarboxylation of other alkynes, thus providing α,β-unsaturated acids in up to 97 % yield.[3]

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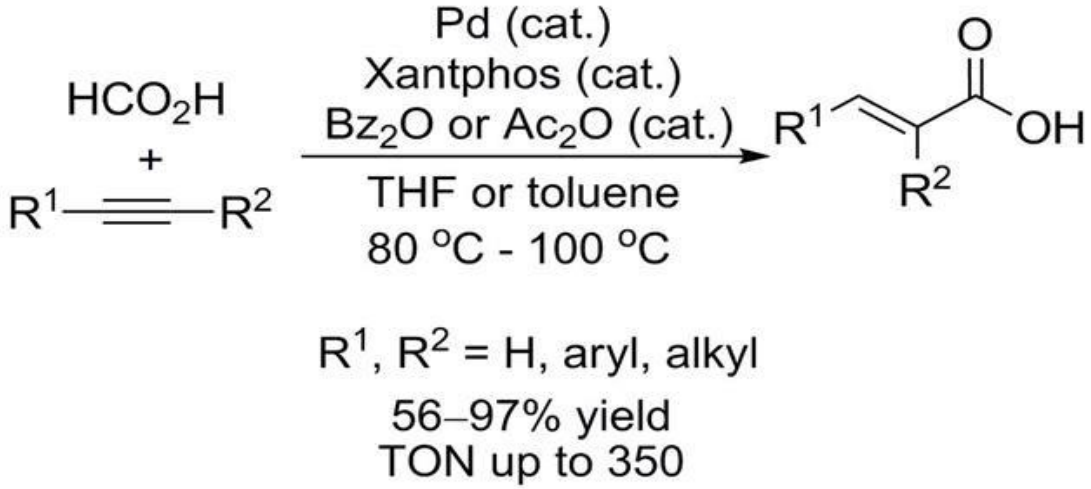

P-638

Nickel-Catalyzed Hydroacylation of Styrenes with Simple Aldehydes

Mr. Li-Jun Xiao[1], Prof. Jian-Hua Xie[1], Prof. Li-Xin Wang[1], Prof. Qi-Lin Zhou[1]

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Poster Session 2

Transition metal-catalyzed hydroacylation of alkenes with aldehydes is a useful and atom-economic method for the synthesis of ketones. This cross-coupling reaction involves a metal-catalyzed activation of a C-H bond and an addition of aldehyde to the alkene to form a new C-C bond. The intermolecular hydroacylation of alkenes with aldehydes was extensively studied by using rhodium catalysts. However, due to the acyl-rhodium intermediates formed in the reaction tend to undergo undesired decarbonylation during the processes, the successful substrates usually require an additional coordination groups. The intermolecular hydroacylation of alkenes with simple aldehydes without directing group remains a challenge. We here report a Ni-catalyzed hydroacylation of styrenes with simple aldehydes. This new reaction produces branched ketones in high yields (up to 99%) with excellent branch/linear selectivities (b/l up to 99:1).

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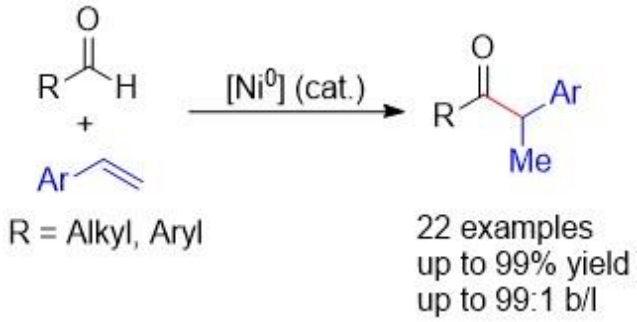

P-639

Iron-Catalyzed Asymmetric Intramolecular Cyclopropanation

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Poster Session 2

Iron, a readily available, inexpensive, and environmentally benign metal, is an ideal alternative to precious metals for the catyalysis. However, compared to other transition metals, iron is less developed as a catalyst for organic processes, particularly asymmetric reactions.[1] Iron catalysts usually exhibit lower enantioselectivity and narrower substrate scope than precious metal catalysts. Moreover, iron catalysts never show good enantioselectivity for a number of important reactions including the asymmetric cyclopropanation of olefins, which is widely used in organic synthesis.[2] We here report the first iron-catalyzed asymmetric intramolecular cyclopropanation.[3] Iron catalysts with a chiral spiro bisoxazoline ligand and a bulky, non-coordinative counter ion exhibited high yields and excellent enantioselectivities (up to 97% ee) in the intramolecular cyclopropanation of olefins. This new reaction provides a convenient method for the synthesis of versatile [3.1.0]bicycloalkanes.

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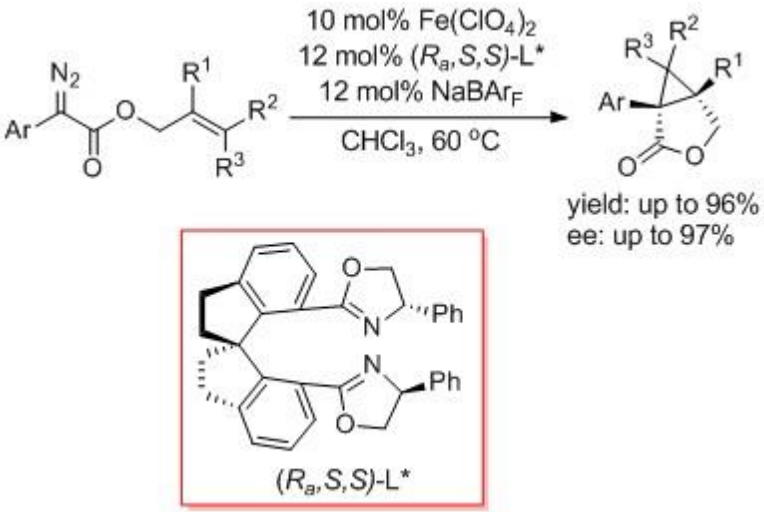

P-640

Hydrosilylation of Terminal Alkynes by Water Soluble Rh(III) Catalysts Based on Carboxylate-Functionalized Polydentate N-Heterocyclic Carbene Ligands

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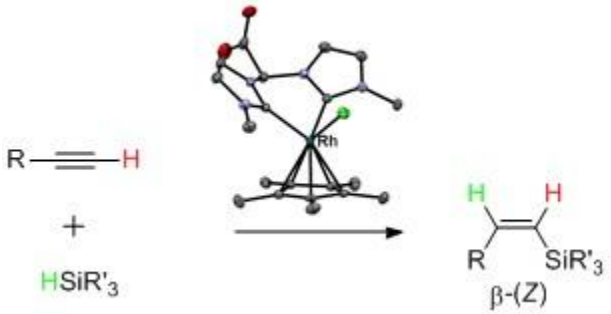
Poster Session 2

The optimization of a catalytic process has a relevant role in sustainable chemistry. In that sense, the use N-Heterocyclic (NHCs) carbene ligands has allowed the development of new catalysts with tunnable steric and electronic features leading in many cases to a substantial increase of the activity and selectivity of the processes.[sup]1 In general, polydentate functionalized NHC carbene ligands have been less studied than the mono- and bidentate NHCs, but its potential in catalysis is notorious.[sup]2 Our interest focuses on the synthesis of suitable precursors for polydentate NHCs ligands for the preparation of water-soluble catalysts, a much more sustainable reaction medium for catalytic processes of industrial interest.[sup]3

The hydrosilylation of C-C triple bonds is the most straightforward method for the preparation of vinylsilanes which are valuable building-blocks with important applications in organic synthesis. Metal-catalyzed hydrosilylation of terminal alkynes is an efficient and atom economical route to vinylsilanes. However, the control of the regio- and stereoselectivity of the reaction still remains an important challenge. Of the three possible isomers, the anti-Markovnikov anti-addition gives the least thermodynamically stable β-(Z)-vinylsilane isomer that have aroused great interest as an intermediate in organic synthesis. Thus, catalyst design is pivotal in order to overcome the stability of the β-(E) and α-vinylsilane isomers in favor of the less stable β-(Z).

In this work, we have synthesized rhodium(III) and iridium(III) complexes containing the functionalized NHC-based ligand 2,2-bis(3-methyl-imidazol-1-il-2-ylidene)acetate, which are efficient catalysts precursor for the hydrosilylation of terminal alkynes to β-(Z)-vinylsilane derivatives with excellent yields and selectivities (figure 1).



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P-641

Pyridine-hydrazones as Chiral N,N Ligands in Palladium Catalysis

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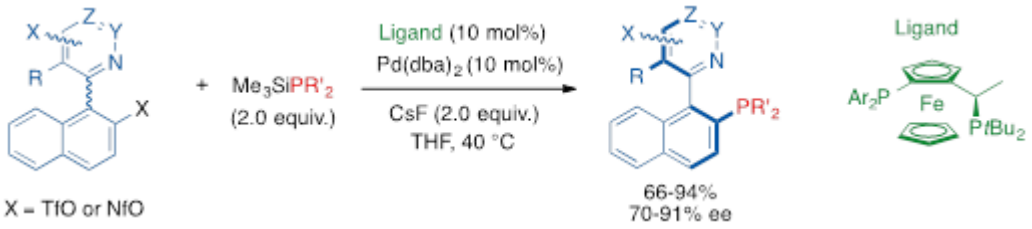
Poster Session 2

The design and synthesis of new families of chiral ligands has been one of the cornerstones for the formidable developments recently achieved in the field of asymmetric catalysis. Currently, there is a growing interest in nitrogen-based ligands1 (bipyridines, bisimines, bisoxazolines, pyridine-bisoxazolines, etc), which offer several distinct properties compared to the widespread phosphorous-based ligands. In this context, hydrazones appear as an interesting class of useful ligands (Scheme 1). Our results employing [Cu(OTf)2/I] catalysts in Diels-Alder reactions2 and [PdCl2/I] complexes as precatalysts in Suzuki-Miyaura reactions3 revealed that the use of C2–symmetric pyrrolidines as terminal dialkylamino groups, making rotations around N–N bonds inconsequential, is the key to achieve high enantioselectivities. In continuation of our research program on ligand design for asymmetric catalysis, herein we wish to present recent results collected by using pyridine-hydrazone complexes [PdX2/II] in Palladium catalysis. Inparticular, using boronic acis as substrates in all cases, good-to-excellent enantioselectivities have been observed in conjugate additions of to enones, 1,2-additions to cyclic sulfonylimines and Suzuki–Miyaura cross–couplngs with aryl bromides.



Scheme 1. Pyridinehydrazone catalyst design and applications in Palladium chemistry.

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P-642

Optimization of a photooxygenation flow reactor

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Poster Session 2

Microreactors are a promising tool in the field of synthetic organic chemistry, since even hazardous or explosive transformations can be carried out in a much safer manner. Dangerous photochemical procedures are nowadays manageable and parameters such as UV exposure time, flow-rate and reactor volume can be controlled very precisely.[1] Thus the photosensitized addition of $^1O_2$ to unsaturated compounds has also been investigated extensively.
The sensitized photooxygenation of α-pinene in different continuous flow reactors was compared by Lapkin and co-workers.[2] In their work, optimal performance was achieved with microstructured setups. Furthermore, the spectral properties of the emission source as well as elevated oxygen pressure were essential to obtain high conversions.
The ultimate goal of this project is to find a method for the efficient photooxygenation in a continuous flow microreactor. Thereby, cyclohexadiene 1 was chosen as model substrate and Rose Bengal (RB) was used as a sensitizer. The mixture was irradiated under flow conditions with a LED lamp at 560 nm (Table 1). The formed endoperoxide 2 was then directly reduced by thiourea.
The synthesis of diol 3 under flow conditions was successful, resulting in 25 % yield. At elevated oxygen pressure, only poor conversion was observed. Therefore, we tried to reduce the oxygen flow (48 µl/min) using a backpressure regulator. It became apparent that the chosen channel length of 8 cm was not appropriate. Hence a microreactor with a path length of 3 m was chosen for further experiments giving 88 % of diol 3.

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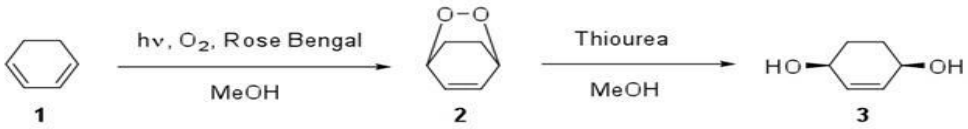
Table 1: Photooxygenation of cyclohexadiene 1



Procedure[a]	Light source	Yield [%][c]
Batch	Osram Ultra Vitalux lamp (14W)	11
Bubble reactor	Osram Ultra Vitalux lamp (14W)	73
Microreactor (HTM serie)[b]	LED (560 nm)	25
Microreactor (XXL serie)[b]	Osram Ultra Vitalux lamp (14W)	88

a) [**1**]=0.2 M, RB=0.02 eq. b) flow-rate=0.044ml/min, oxygen flow=48µl/min
c) Measured by ^{1}H-NMR, using DMF added as an internal standard

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METALAZIDES IN THE CONSTRUCTION OF MULTIMETAL STRUCTURES

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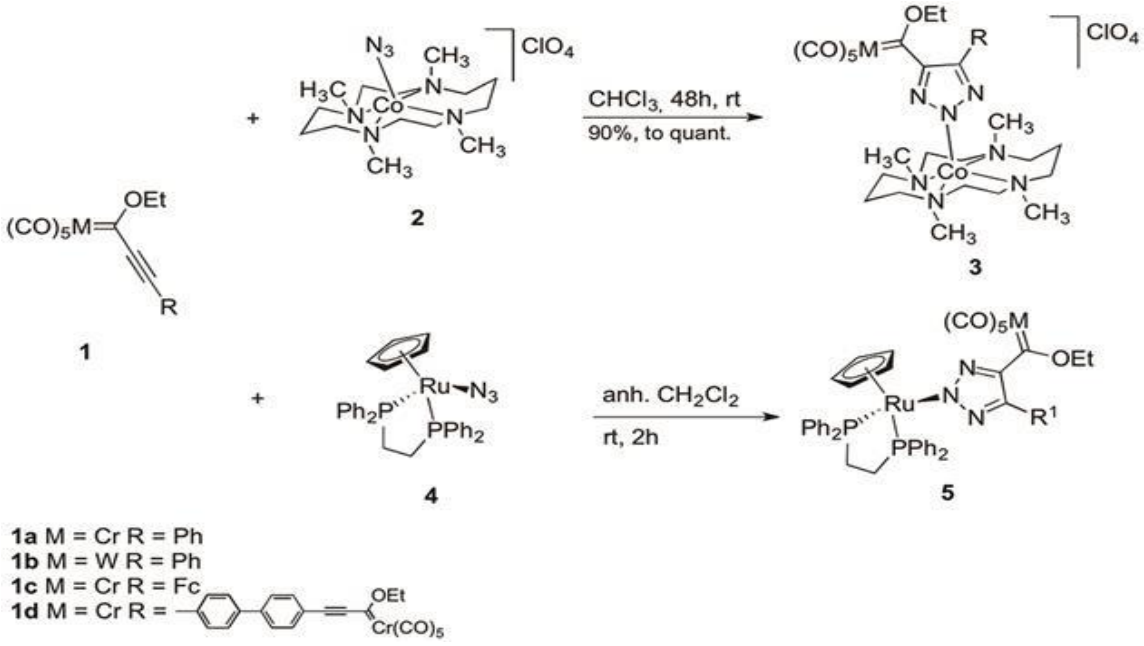
Poster Session 2

Although the Cu(I)-catalyzed 1,3-cycloaddition of azides and alkynes (CuAAC) is widely employed to assemble complex organic molecules through a 1,2,3-triazole tether, the use of metal azides is much more restricted.[1] Here we report the combination of metal azides and metal alkynes as a useful tool for the construction of polymetallic complexes. Thus, reaction of equimolar amounts of mono- and biscarbenes 1 and [(Me$_4$cyclam)Co[sup]II[/sup](N$_3$)]-ClO$_4$ (2) in CHCl$_3$ at RT for 48 h, leads to the quantitative formation of bi- and polymetallic triazolates 3 . The structure of the products was established by means of spectroscopic data and confirmed by X-Ray diffraction analysis of 3a. In a similar manner, the reaction of 1 and ruthenium-azide complexes 4 leads to quantitative formation of bi-and polymetallic complexes 5.



The electronic properties of the polymetallic systems prepared and the study of the interaction between the metal centers will be discussed.

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P-645

Gold(I)-Catalysed Allylic Etherification: Access to Enantioenriched Allylic Ethers

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Poster Session 2

Our group has recently reported a route to allylic ethers via a gold(I)-catalysed Sn2' reaction of allylic alcohols 1. It was proposed that the reaction proceeds via chair-like intermediates.

Further optimisation of our allylic etherification methodology has been carried out, and access to enantioenriched allylic ethers via chiral transfer from enantioenriched allylic alcohols has been demonstrated.

Synthetic and computational studies carried out in collaboration with Macgregor and co-workers will also be presented.

P-646

Base-Promoted Acyl Transfer Reaction of Pseudoephedrine Amides derived from alpha-Aminomalonic Acid

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Poster Session 2

Decarboxylative protonation [1] of substituted aminomalonates and derivatives is a synthetically convenient and straightforward route to synthesize a variety of unnatural alpha-amino acids, biologically important organic compounds which are used in chiral pool synthesis as enantiomerically pure building blocks. [3] Recently, our group has established a good approach to this decarboxylative protonation process, developing a novel base-promoted rearrangement reaction that converts N-substituted alpha-aminomalonates into N-alkoxycarbonyl alpha-amino acid derivatives under mild conditions. [2] Moreover, it should be emphasized that this methodology provides a wide range of alpha-alkylated products in good yields when the enolate intermediate is trapped by alkylation in a tandem sequence.

Herein we present the asymmetric version of this protocol in which (S,S)-pseudoephedrine amides derived from malonic acids have been studied as decarboxylative reactant for further alkylation with an external electrophile. The promising result obtained in terms of both yields and stereocontrol make this methodology an interesting alternative for the preparation of alpha-aminoacids in high enantioselection once the chiral auxiliary is cleaved.

Acknowledgments: The authors thank the UPV/EHU, MICINN (CTQ2011-22790), and EJ/GV (IT328-10) for financial support.

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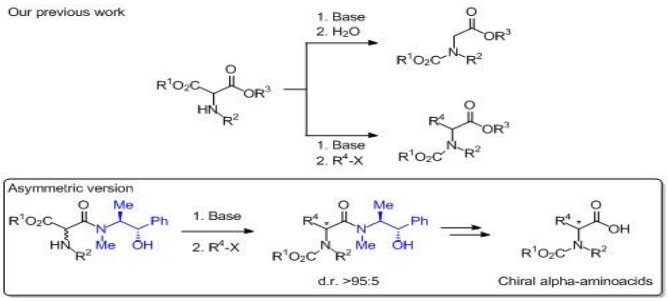

P-647

Azole-based Fluorophores via Regioselective Pd-catalyzed Direct C-H Arylation Reactions

Mrs Giulia Marianetti[1], Dr. Marco Lessi[2], Dr. Chiara Manzini[2], Prof Fabio Bellina[2], Mr Luca Perego[1], Dr. Andrea Pucci[2], Mr Pierpaolo Minei[1], Mr Cristofer Pezzetta[1]

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Poster Session 2

Push–pull organic fluorophores possessing electron-donor (D) and -acceptor (A) architectures exhibit interesting intramolecular charge-transfer (ICT) properties. These features make them suitable for applications in various fields, such as organic solar cells,[1] anion sensors,[2] nonlinear optics,[3] fluorescence imaging,[4] optically responsive polymers[5] and piezoelectric materials.[6] One of the most fascinating advantages concerning these materials consists in the possibility of tuning the π-conjugation, the band gap, and therefore the electro-optical properties by a judicious selection of D–A couples which can be easily inserted through scalable and efficient synthetic procedures.[6] It is current opinion that the employment of heteroaromatic backbones usually increases the polarizability, the stability and the thermal and chemical robustness required for the fabrication processes of the final device. Moreover, heteroatoms may act as auxiliary donors or acceptors, and further improve the overall polarizability of the fluorophore. In this communication we illustrate our efforts in the application of selective Pd-catalyzed direct C-H arylation protocols[7] to the synthesis of novel fluorophores featuring a 1,4-phenylene-linked bis azole scaffold.

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P-648

Synthesis and Reactivity of Zwitterionic Metal-Alkenyls from Chromium(0) and Tungsten(0) FischerCarbene-Complexes

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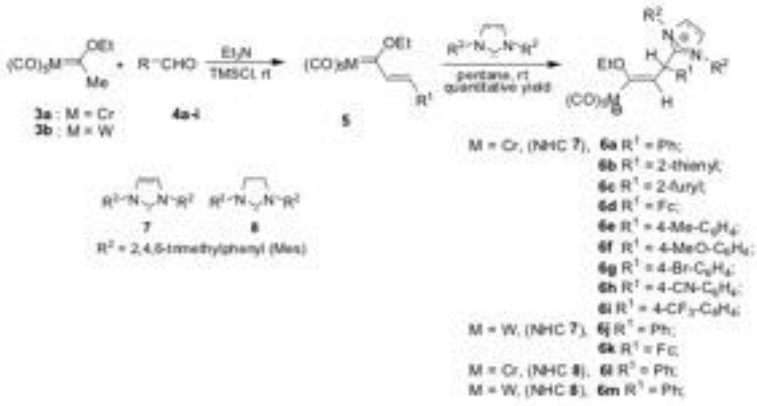
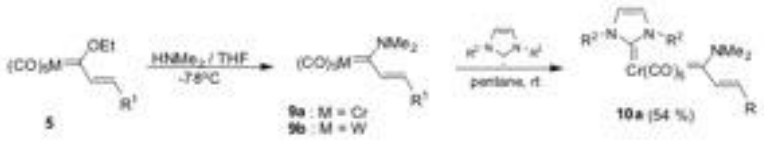
[1]*Universidad Complutense, Madrid, Spain,* [2]*Universidad Complutense, , Spain,* [3]*Universidad Complutense, , Spain*

Poster Session 2

Herein we report the reactivity of a series of differently substituted styrylchromium(0) and tungsten(0) Fischer carbene-complexes towards N-heterocyclic carbenes (NHCs). The obtained products result from the 1,4-addition to the alkoxycarbenes (Scheme 1), but from a ligand (CO) substitutionin the case of the aminocarbene derivatives (Scheme 2).



Scheme 1



Scheme 2

P-649

Hydrosilation induced by N→Si intramolecular coordination giving substituted 1-aza-2-silaindoles

Prof. Antonin Lycka[1], Dipl. Ing. Miroslav Novak[2], Assoc. Prof. Libor Dostal[2], Prof. Frank de Proft[3], Prof. Ales Ruzicka[2], Assoc. Prof. Roman Jambor[2]

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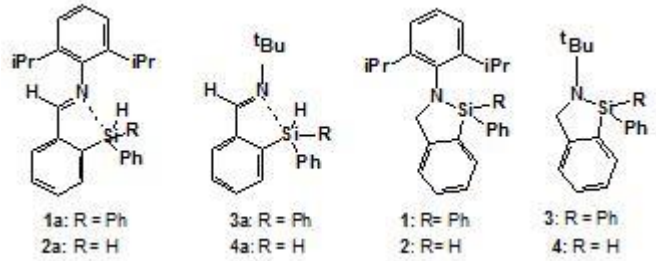
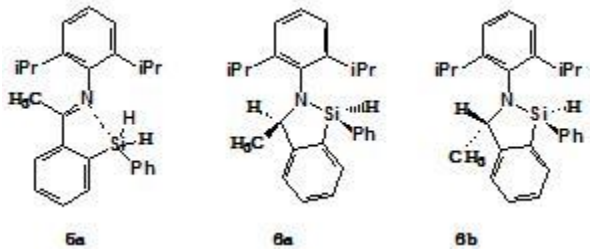
Poster Session 2

Our attempts to synthesize N→Si intramolecularly coordinated organosilanes 1a - 4a yielded 1-[2,6-bis(diisopropyl)phenyl]-2,2-diphenyl-1-aza-2-silaindol (1), 1-[2,6-bis(diisopropyl) phenyl]-2-phenyl-2-hydrido-1-aza-2-silaindol (2), 1-tert-butyl-2,2-diphenyl-1-aza-2-silaindol (3) and 1-tert-butyl-2-phenyl-2-hydrido-1-aza-2-silaindol (4), respectively. Isolated organosilicon compounds 1 - 4 are an outcome of the spontaneous hydrosilation of the CH=N imine moiety induced by N→Si intramolecular coordination.



Analogously, our attempt to synthesize compound 5a gave a mixture of diastereomeric 1-[2,6-bis(diisopropyl)phenyl]-2-phenyl-2-hydrido-1-aza-2-silaindols (6a,b),



Compounds 1 - 6 were characterized by 1H, 13C, 15N and 29Si NMR spectroscopy and X-ray diffraction analysis [1, 2].

Acknowledgement: The authors thank the Czech Science Foundation for financial support (Grant No: 15-07091S).

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P-650

Novel Zinc-catalyzed transformations through enynone activation

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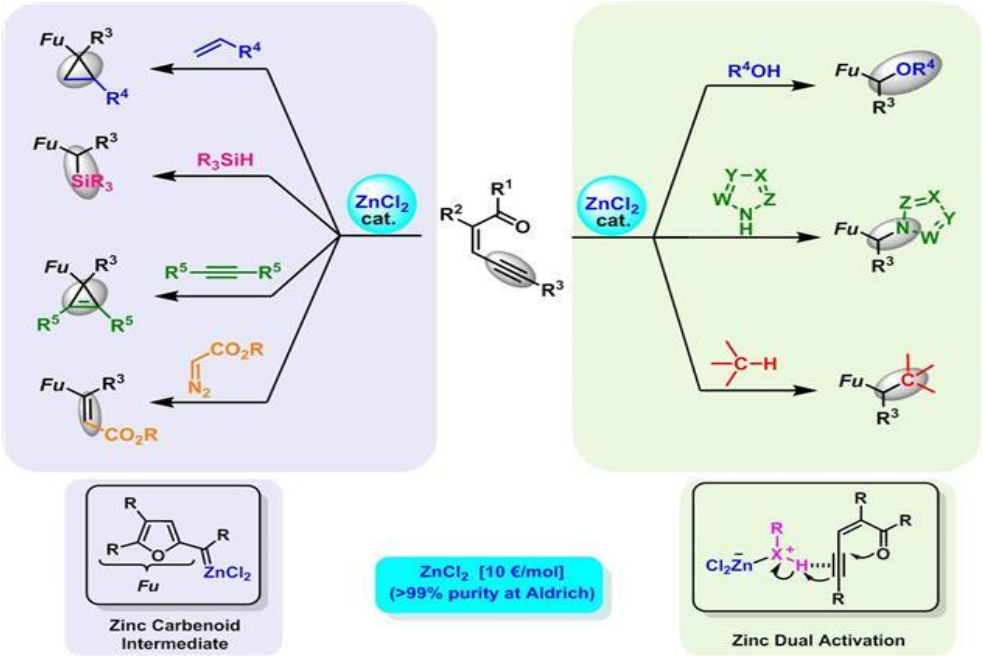
Poster Session 2

The alkyne functionality plays a relevant role in chemistry. In the recent years, novel and valuable transformations of alkynes involving transition metals have been developed. These processes are based on the carbophilic properties of some metals such as gold, platinum or rhodium, which activate the alkyne by a preferential coordination to the ?-system. Despite the relevance of these achievements, the cost of these catalysts constitutes an important drawback in terms of sustainability.

We have studied the feasibility of using inexpensive and low-toxic zinc salts for the alkyne activation, specifically for the catalytic generation of zinc carbenoids from alkynes and their applications in organic synthesis.

In this communication, we show the ability of simple ZnCl2 to activate enynones for the in-situ generation of zinc carbene intermediates. These intermediates can be trapped with alkenes (ACIE, 2012, 51, 8063), silanes (CEJ, 2015, 21, 8998), alkynes (OL, 2014, 16, 5780) or diazocompounds (CC, 2014, 8536) to access a variety of valuable furan derivatives. These processes constitute the first examples of catalytic transformations involving zinc carbenes. In addition, a new activation mode, namely dual-activation, was found in the reaction with alcohols and azoles. In these cases, coordination of zinc to X-H bonds triggers the enynone activation and enables the synthesis of furan derivatives with a concomitant formation of new C-O and C-N bonds (ACIE, 2013, 52, 5853).



P-651

Synthesis of Various 3,10-Dialkylpicenes via Ni-Catalyzed C–O Bond Alkynylation

Hiroki Mori[1], Yasuhiro Okuda[1], Shuhei Nishinaga[1], Jie Xu[1], Yasushi Nishihara[1,2], Xi-Chao Chen[1], Jia-Ji Zhao[1]
[2]*ACT-C, Japan Science and Technology Agency , Saitama, Japan*

Poster Session 2

In high performance organic semiconductors picene showed ?values as high as 1.1 cm2/Vs and robustness even in the presence of O2and H2O. However, the construction of highly-fused ?-system generally requires harsh reaction conditions and strong oxidants, thus derivatization of picene is still challenging. Previously, we reported the synthesis of 3,10-dimethoxypicene through Wittig reaction and the subsequent intramolecular palladium-catalyzed cyclization via C–H bond fuctionalzation.
1
In this presentation, we report a divergent synthesis of 3,10-dialkylpicenes by nickel-catalyzed C–OMe bond alkynylation as the key step, starting from 3,10-dimethoxypicene. Very recently, Tobisu and Chatani have reported nickel-catalyzed C–OMe bond alkynylation of anisoles.
2
Inspired by this new methodology, we carried out nickel-catalyzed C–OMe bond alkynylation of 3,10-dimethoxypicene. Over the screening of reaction conditions, we found that utilization of mesitylene in dilute solution (25 mM) is essential to proceed the desired C–OMe bond alkynylation. Consequently, the best result was obtained at 140 ºC for 72 h; the desired dialkynylated product was isolated in 76% yield. Dialkynylated product possesses high solubility and can easily be purified by column chromatography. Subsequently, desilylation is carried out by treating with TBAF, and desilylated 3,10-diethynylpicene was obtained in 91% yield. Finally, derivatization toward 3,10-alkylpicenes was succeeded in yields up to 71%. Further elucidation of physicochemical properties will also be discussed.

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(1) Nishihara, Y. et al. Org. Lett. 2013, 15, 3558.
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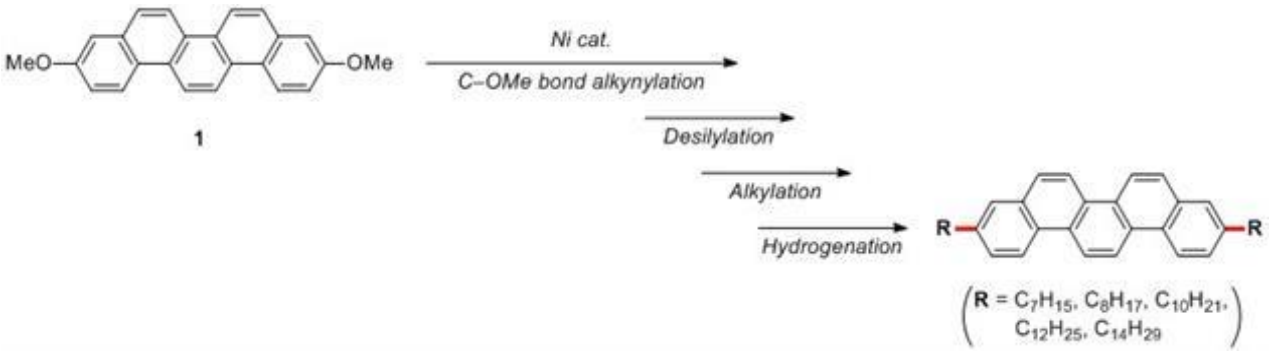

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Impact of Isomeric Structures on FET Performances in Phenanthrodithiophene (PDT) Derivatives: Selective Synthesis, Physicochemical Properties, and Application to Organic Field-Effect Transistors

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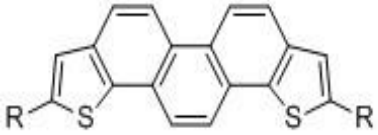
Poster Session 2

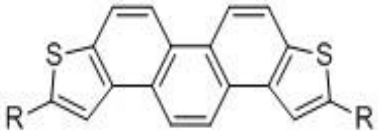
Organic field-effect transistors (OFETs) have attracted much attention as the key components for electronic devices because of their flexibility and light-weight. Previously, we have reported the synthesis of phenanthro[1,2-b:8,7-b']dithiophene (PDT-1) and phenanthro[2,1-b:7,8-b']dithiophene (PDT-2) through cross-coupling reaction of polyhalobenzene with (Z)-alkenylboron compounds and sequential double cyclization via C–H bond activation. However, this synthetic method was not suitable for a large-scale synthesis of PDTs due to a tedious isolation of stereoisomers as PDT precursors and low overall yields (3% in 9 steps for PDT-1, 0.5% in 9 steps for PDT-2).

Herein, we report an efficient synthetic procedure and OFET characteristics of PDTs and alkylated derivatives. First, PDT-1was synthesized through the palladium-catalyzed Suzuki–Miyaura or Negishi couplings of 2-thienylboronic acid or the corresponding zinc compound with 1,4-dibromobenzene, followed by epoxidation/Lewis-acid-catalyzed Friedel-Crafts-type intramolecular cycloaromatization in overall 50% yield in 3 steps. Moreover, PDT-2was also synthesized via the same synthetic method of PDT-1and overall yield was improved up to 33% in 3 steps. Furthermore, dibromination of PDTs and sequential Suzuki–Miyaura coupling with alkylboranes, derived from 9-BBN and 1-dodecene, gave C12-PDT-1and C12-PDT-2in 82% and 67% yields, respectively. Next, we fabricated OFET devices by using all four compounds on Si/SiO2substrate. As a result, the fabricated devices exhibited a typical p-channel FET behavior and C12-PDT-1-based OFET showed the highest hole mobility as high as 2.2 cm2/Vs.



PDT-1 (R = H)

C_{12}-PDT-1 (R = $C_{12}H_{25}$)



PDT-2 (R = H)

C_{12}-PDT-2 (R = $C_{12}H_{25}$)

A

B

C

D

E

F

G

H

I

J

K

L

M

N

O

P

Q

R

S

T

U

V

W

X

Y

Z