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Talks

Session 2

Organometallic Chemistry for Medicinal Applications

G. Gasser[1]

[1]Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, 75005 Paris, France;
gilles.gasser@chimieparistech.psl.eu

Inspired by the works of Jaouen, Brocard, Biot and co-workers,[1-3] our group has been working over the last years towards the development of novel organometallic drug candidates against different medical conditions, notably neglected tropical diseases[4] and fungal infections.[5] The latter represent a global problem, notably for immunocompromised, patients in hospital, covid-19 patient wards and care home settings. The ever-increasing emergence of multidrug resistant fungal strains is a sword of Damocles hanging over many healthcare systems. For example, we could demonstrate that a ferrocenyl derivative of fluconazole had an impressive activity on clinical isolates, where antimycotic potency up to 400 times higher than fluconazole was observed.[6] Also, this compound showed activity towards azole-resistant strains. This finding is very interesting since its primary target is the same as that of fluconazole, emphasizing the role played by the organometallic moiety. *In vivo* experiments in mice model of Candida infections revealed that this compound reduced the fungal growth and dissemination but also ameliorated immunopathology, a finding suggesting that this compound is active in vivo with added activity on the host innate immune response. During this talk, we will present our latest results, emphasizing the importance of the organometallic part in the bioactivity unveiled.

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Are Two better than One? A Journey in Bimetallic Organometallic Chemistry and Catalysis

D. Broere[1]

[1]Organic Chemistry and Catalysis, Institute for Sustainable and Circular Chemistry, Utrecht University Universiteitsweg 99, 3584 CG, Utrecht, The Netherlands. Email: d.l.j.broere@uu.nl

Various metalloenzyme active sites feature complex architectures that enable multiple metals and ligands to work together to facilitate bond activation processes that are essential to enzyme function.[1] Drawing inspiration from nature, various research groups have developed synthetic systems where metals and ligands cooperatively activate chemical bonds.[2] Another avenue in cooperative bond activation involves complexes wherein multiple metal centers are positioned in close proximity and work together to make/break chemical bonds.[3] However, whereas nature often uses both strategies simultaneously, synthetic chemists have some catching up to do. On the bright side, we can explore chemical space that is beyond the reach of nature.

In my group we have developed so called ‘expanded pincer’ ligands that bind two metals in close proximity and feature design elements for metal-ligand cooperativity.[4] In this presentation, I will highlight how combining metal-metal and metal-ligand cooperativity can flatten the potential energy surfaces of catalytic reactions. I will also share recent insights into a new organometallic pathway for C–H functionalization.

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Talks

Session 3A

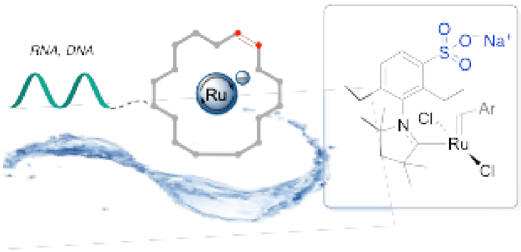
On-DNA and on-RNA olefin metathesis

D. Fogg[1,2], C. Blanco[1]*, C. Zhang[3]*, A. Brunschweiger[3]*

[1]Center for Catalysis Research & Innovation, and Department of Chemistry and Biomolecular Sciences, University of Ottawa, [2]Department of Chemistry, University of Bergen, [3]Institute of Pharmacy and Food Chemistry, Julius Maximilian University Würzburg

Macrocyclic drugs hold significant potential as novel antiviral, lipid-lowering, and oncology therapeutics [1,2]. Technologies that enable the synthesis and screening of diverse macrocyclic scaffolds en masse, such as mRNA display and DNA-encoded libraries (DEL), are opening new opportunities for lead discovery. Olefin metathesis is of particular interest for on-oligonucleotide macrocyclization given its unmatched versatility and flexible, biologically inert linkers. However, the need for ring-closing metathesis (RCM) in water is incompatible with the majority of metathesis catalysts.

Prior attempts at on-DNA olefin metathesis have revealed severe constraints arising from catalyst decomposition (resulting in challenges with degradation of DNA[3]), and from the need for high salt concentrations to stabilize the catalyst, which compromises DNA solubility. Here we address these limitations by employing a catalyst designed for water tolerance, water-solubility, and oligonucleotide compatibility[4,5]. RCM macrocyclization is achieved in bulk water on various oligonucleotides—including, for the first time, on RNA. These findings establish a framework for the metathetical elaboration of oligonucleotides, opening new opportunities at the frontiers of chemical biology and drug discovery.



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Synthesis of a Tin Carbonyl Complex and its Isomerisation to a Carbene-Stabilised Tin Atom

M. Dietz[1], S. Aldridge[1]*

[1]Department of Chemistry, Central Research Laboratories, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, UK.

Transition-metal (TM) carbonyl complexes play a key role in various catalytic processes and their coordination chemistry and reactivity patterns have been well studied. More recently, significant focus has shifted towards low-valent main-group compounds, which have been shown to mimic TM reactivity. Several examples for (non)classical carbonyl complexes of lighter *p*-block elements have been synthesized under ambient conditions.[1] However, only two silicon-based examples for group 14 carbonyl complexes have been reported and heavier congeners have not been achieved thus far.[2–3] Our group has previously reported the synthesis of bis(boryl)stannylene **1**,[4] which has been shown to readily activate E–H (E = N, O, B, Si) bonds, as well as dihydrogen, due to its unique electronic properties.[5] This can be attributed to the adjacent diazaborolyl substituents, which give rise to a high-lying HOMO and an energetically accessible LUMO. The coordination chemistry of this stannylene, however, has widely been unexplored.

In this work, we report the synthesis of the first tin carbonyl complex (**2**) and its isomerisation to an unprecedented stannavinylidene (**3**), in which a tin atom is stabilized by a single carbene ligand. By adjusting the reaction conditions, stannavinylidene **3** can further react to yield a CO coupling product *via* C–C bond formation. The formation and electronic structures of these novel compounds, as well as the CO homologation mechanism are studied by quantum chemical calculations, which are supported by further coordination and insertion chemistry with an isonitrile derivative. Additionally, single electron reduction of stannylene **1** allows for the isolation of a stable anionic tin-centred radical.

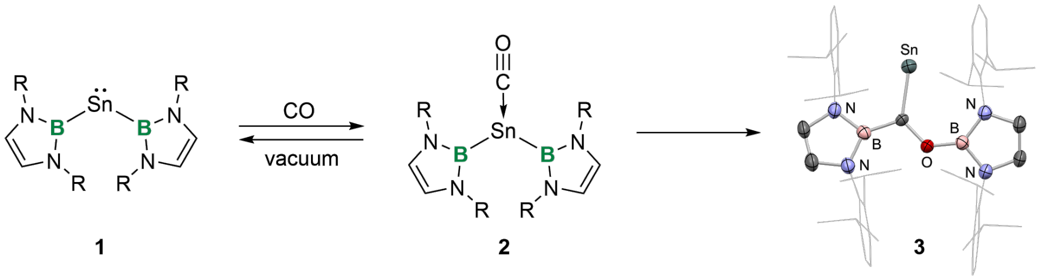

Figure 1. Synthesis of tin carbonyl complex **2** and isomerisation to stannavinylidene **3** (R = 2,6-Di*iso*propylphenyl).

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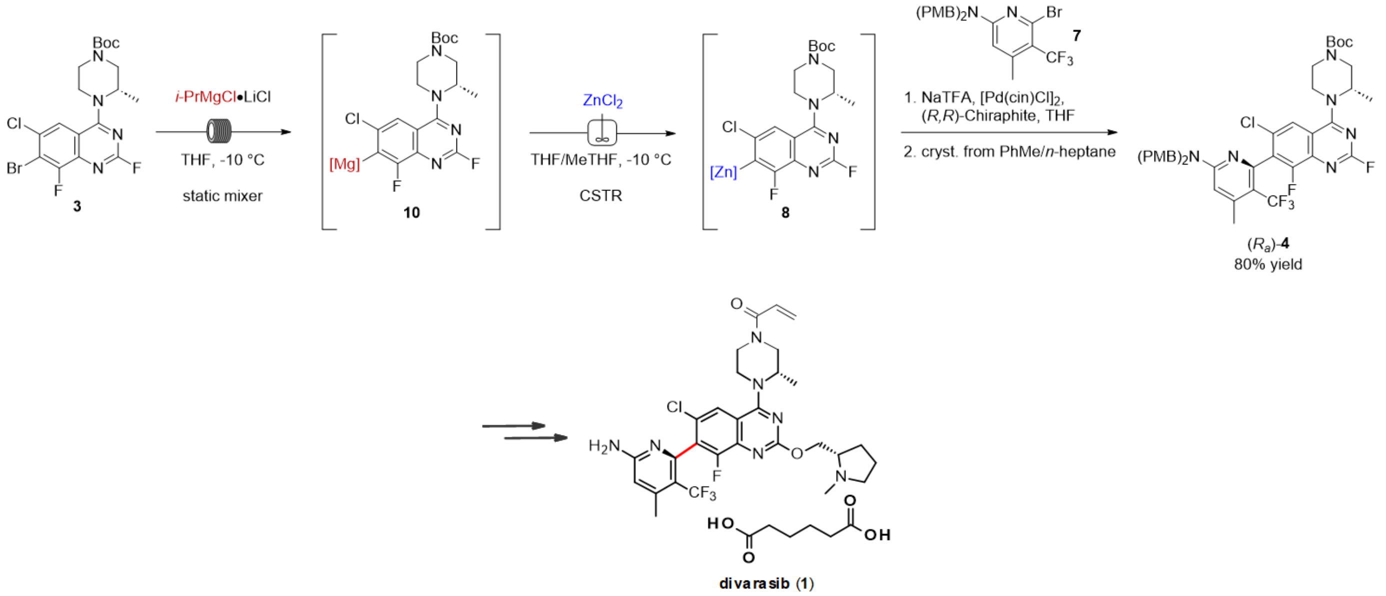
Organometallic Chemistry at Scale - A Highly Atroposelective Negishi Coupling Enables the Commercial Manufacturing Process of Divarasib

S. Bachmann[1], R. Bigler[1]*, D. Kaldre[1]*, D. Kummli[1]*, R. Lebl[1]*, D. Linder[1]*, C. Ochs[1]*, U. Orcel[1]*, I. Prévot[1]*, J. Sedelmeier[1]*, E. Trachsel[1]*, J. Xu[2]*, H. Zhang[2]*

[1]Synthetic Molecules Technical Development, F. Hoffmann-La Roche Ltd., Grenzacherstrasse 124, CH-4070 Basel, Switzerland, [2]Department of Small Molecule Process Chemistry, Genentech, Inc., 1 DNA Way, South San Francisco, California 94080, United States

The first example of a highly atroposelective Negishi coupling at manufacturing scale, allowing for the isolation of (R_a)-**4** as a single isomer without chromatography,[1] will be presented. The implementation of a continuous process for the metalation step of the Negishi coupling allowed for the elimination of the cryogenic reaction conditions from the manufacturing process of divarasib (**1**),[2] a highly potent KRAS G12C inhibitor currently undergoing Ph III clinical trials.[3]



More detailed investigations as to the identification and characterization of the best catalyst, the role of the additive and the reaction kinetics of the Negishi coupling will be presented.

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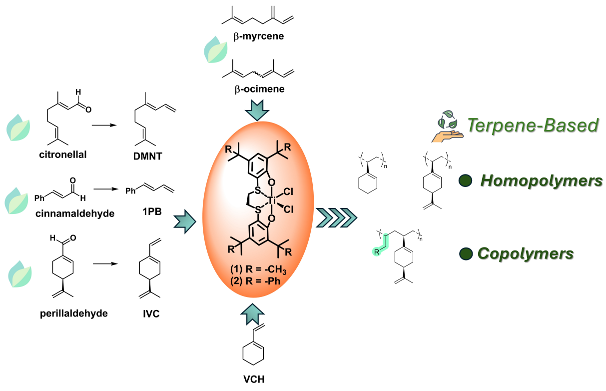
Stereoregular (Co)polymerization of Terpene-Based Monomers Mediated by Titanium [OSSO]-Catalysts

A. D'Amato[1], I. Grimaldi[1]*, M. C. Gambardella[1]*, A. Buonerba[1]*, R. Marzocccchi[2]*, F. Auriemma[2]*, C. Capacchione[1]*

[1]University of Salerno, Department of Chemistry and Biology "A. Zambelli", Via Giovanni Paolo II, 132, I-84084 Fisciano (SA) Italy, [2]University of Naples Federico II, Department of Chemical Sciences, Via Cintia, I-80126 Naples, Italy

Stereoregular polymerization of linear 1,3-dienes has advanced to achieve complete control of stereochemistry, determining the final polymeric material's properties. On the other hand, the growing interest in bio-based monomers has sparked a renewed impulse towards polymerizing natural occurring cyclic monomers with conjugated double bonds.[1] Particularly, terpenes and terpenoids, renewable monomers, can be directly polymerised or readily derivatised into polymerizable 1,3-dienes through their chemical transformation.[2] When activated by methylalumoxane (MAO), homogeneous [OSSO]-type titanium complexes have demonstrated exceptional activity and stereocontrol in the polymerisation of styrene and conjugated dienes, making them a promising candidate for the stereoselective (co)polymerisation of bio-based dienes.[3] In this contribution, catalysts **1-2** are showed to be promising activators for the isospecific polymerization of IVC (perillaldehyde derived), VHC, and its copolymerization with two linear terpenes, β-myrcene and β-ocimene (Scheme 1), with an in-depth insight on the mouldability of the final material's properties.[4] Further combination of IVC with 1PB and DMNT, obtained from cinnamaldehyde and citronellal, respectively, gain model polymers for the investigation of reversible and irreversible cross-linking processes owing of the functionalisable exocyclic double bond present in their structure.



Scheme 1. [OSSO]-Ti complexes **1-2** promote the isospecific (co)polymerisation of terpene-based monomers.

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Photodehydrogenation of Alcohols Catalysed by a Single NHC Based Ru(II) Complex

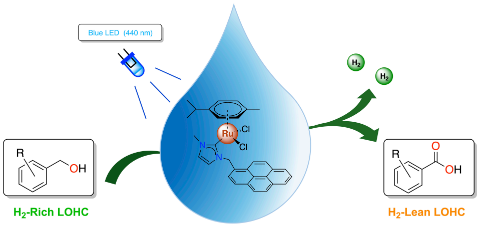
G. Guisado-Barrios[1], L. Ibañez-Ibañez[2]*, J. A. Mata[2]*

[1]Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), 50009, Zaragoza (Spain). , [2]Institute of Advanced Materials (INAM), Avda. Vicent Sos Baynat s/n, 12006, Castellón (Spain)

v>

The dehydrogenation of alcohols stands as a central transformation in organic reactions, allowing the synthesis of a wide variety of functionalized molecules with extensive applications in agrochemicals, pharmaceuticals, and material sciences. Specifically, acceptorless alcohol dehydrogenation (AAD) to carboxylic acids, catalyzed by transition metals, has gained attention for eliminating the need for stoichiometric oxidants and for its prospective use in alternative energy technologies, such as Liquid Organic Hydrogen Carriers (LOHCs) for hydrogen storage in liquid form. [1]

The (AAD) has been widely reported thermally using mainly ruthenium complexes, which stand out in terms of activity. [2] The incorporation of visible light has enabled alcohols oxidation to the corresponding of aldehydes or ketones using a ternary hybrid catalytic system. [3] Conversely, visible light-induced transition metal catalysis constitutes an emerging class of photocatalysis that relies on the use of transition metal complexes able to act simultaneously as (i) photosensitizer and as (ii) catalyst in conventional bond breaking/ forming processes. In this context, our group reported the visible light assisted acceptorless dehydrogenation of N-heterocycles and formation of H_2 catalysed by a mesoionic carbene (MIC) based Ir(III) metal complex [Cp*Ir(MIC)(CH_3CN)]OTf. [4a] In this contribution, an efficient ruthenium(II)-catalyzed hydrogen production from benzylic alcohols to benzyl carboxylates under visible light will be presented. Our photocatalytic system features a standalone N-heterocyclic carbene-based Ru(II) complex, which both harvests visible light and facilitates H2 generation under mild, aqueous conditions. [4b]



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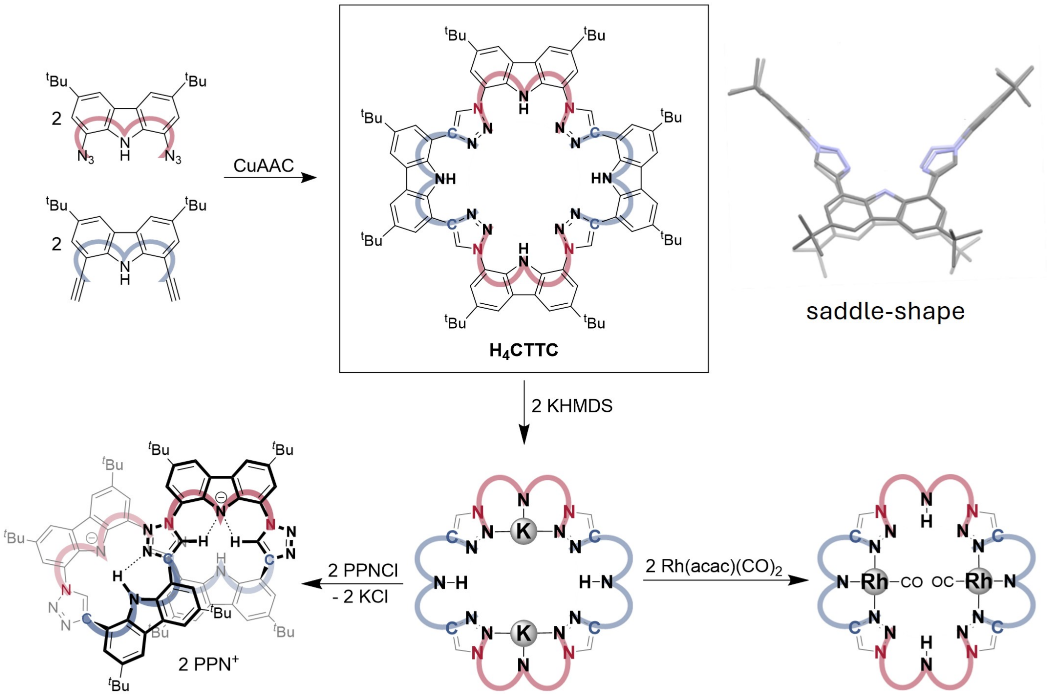
Conformational Changes of a Saddle-Shaped Macrocycle Upon Metalation

D. Kunz[1], V. Munzert[1]*, T. Maulbetsch[1]*

[1]Institut für Anorganische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Recently, we synthesized an expanded porphyrinoid macrocycle (*cyclo*-tetra-(triazolyl carbazole), H_4CTTC) in a copper-catalyzed click reaction[1]. Due to the connection of the carbazoles to the triazoles via either their C or N atoms, two different pairs of NNN-pincer pockets (N-pocket (red), C-pocket (blue)) are formed, which can be regarded as half a porphyrin each.[1]



Upon deprotonation of the carbazole-NH-units, the saddle-shaped quatrefoil CTTC ligand allows for complexation of up to four metal cations in close proximity. To investigate possible cooperative effects in multimetallic CTTC complexes, we monitored the metalation of the pincer-like pockets. Equilibria between different metalated isomers occur, but selectivity can be achieved. Li^+ and K^+ exhibit a clear preference to occupy the N-pocket, whereas after transmetalation the dirhodium complex isomerizes from the N- to the C-pockets. In the solid state, we observe fascinating structures of saddle-shaped stacked dimers as well as a figure-eight motif for the [H_2CTTC]-dianion with the weakly coordinating cation PPN^+ (bis(triphenylphosphine)iminium), which also will be presented and discussed.

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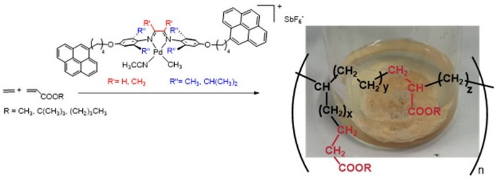
Pd-catalysis for functionalized polyolefin synthesis: the successful interplay between ligand and solvent

B. Milani[1], A. Dall'Anese[1]*, M. Souleymanou[2]*, C. Godard[2]*

[1]Università di Trieste, Department of Chemical and Pharmaceutical Sciences, Trieste, Italy, [2]Universitat Rovira i Virgili,
Department de Quimica Fisica i Inorganica, Tarragona, Spain

The introduction of polar functional groups into the otherwise apolar skeleton of polyolefins to yield, in a controlled manner, functionalized polyolefins is still considered as a "*holy grail*" in the field of polymer synthesis. Palladium and nickel complexes with a-diimine ligands are the most promising candidates to obtain efficient catalysts for the direct, controlled, copolymerization of ethylene with acrylic esters.[1] In the case of palladium-a-diimine catalysts the main issue deals with the incorporation of the polar vinyl monomer, which in most of the cases is found at the end of the branches as the result of the chain walking process. Recently, we have reported that revisiting Brookhart's catalysts by introducing a thiopheneimine in place of diethyl ether in the fourth coordination site of palladium and carrying out the ethylene/methyl acrylate (MA) copolymerization in 2,2,2-trifluoroethanol (TFE), the acrylic ester is inserted both in the main chain and at the end of the branches in a ratio that is modulated by the N-S ligand.[2] We have now investigated a new series of a-diimine ligands characterized by a pyrene pendant arm. The relevant cationic Pd(II) complexes, $[Pd(CH_3)(NCCH_3)(N\text{-}N)][SbF_6]$, generate very active catalysts for the ethylene/MA copolymerization. We have also discovered that, for these catalysts, the macromolecule microstructure is the result of an interplay between the a-diimine ligand and the solvent used as reaction medium. In particular, when N-N is the 2,6-diiso-propyl substituted a-diimine and the copolymerization is carried out in TFE, excellent catalyst performances are obtained: productivity up to 73 kg CP/mol Pd in the synthesis of ethylene/MA copolymer with M_n up to 165 kDa ($M_w/M_n = 1.55$) and having 0.8 mol % of inserted MA, and MA incorporated almost exclusively into the main chain (Figure). This catalytic behaviour is also valid for ethylene/n-butyl acrylate and ethylene/*tert*-butyl acrylate copolymerization.[3]



Acknowledgements

Claudio Pellecchia and his group are acknowledged for molecular weight measurements.

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Talks

Session 3B

Organometallic catalysts for chemical and electrochemical regeneration of NADH

A. Macchioni[1], G. Menendez Rodriguez[1]*

[1]Dipartimento di Chimica, Biologia e Biotecnologie and CIRCC, University of Perugia

NADH (Nicotinammide Adenine Dinucleotide) is an essential and ubiquitous coenzyme that plays a central role in several energy-conversion processes of living organisms and in a large variety of redox reactions, where it acts as an intracellular electron and hydrogen carrier [1]. It is also used in many biocatalytic processes for the large-scale production of biofuels, chemicals, and pharmaceuticals. Because of its high cost, the utilization of NADH for industrial applications is necessarily related to the possibility of its catalytic regeneration from the oxidized form, NAD^+. This can be achieved applying enzymatic, chemical, electrochemical, and photochemical methodologies.

In our research group, we are developing organoiridium catalysts, bearing pyridine and pyrazine-amidate ligands, for both chemical [2-3] and electrochemical [4-5] regeneration of NADH, designed through a rational approach based on the deep understanding of the reaction mechanism [6]. As for the chemical regeneration of NADH, the substitution of pyridine with pyrazine and the presence of carbohydrazide dangling group in the bidentate ancillary ligand led to catalysts with record performance comparable to that of enzymes, using phosphite as inexpensive hydrogen donor [7]. The pyrazine moiety has the double role of making the iridium center more acidic, being less σ-donating than pyridine, without weakening the Ir−N bond, being more π-accepting than pyridine. The second element of novelty, i.e., the carbohydrazide dandling group in close proximity of the Ir center, likely facilitates the shuttling of the hydride from the donor to the metal, and from the metal to NAD^+, and inhibits the formation of the detrimental, out-of-cycle Ir_NAD^+ adduct. As for the electrochemical regeneration of NADH, we report the first two progenitors of a class of redox mediators for indirect NADH regeneration, which exhibit TOF, production rate and faradaic efficiency comparable to those of classical rhodium complexes [4]. Furthermore, in the attempt of reducing the overpotential of NAD^+ to NADH reduction, we succeeded in developing a complex acting as a reversible catalyst for NAD^+/NADH interconversion [5]. All these results will be discussed in the present contribution.

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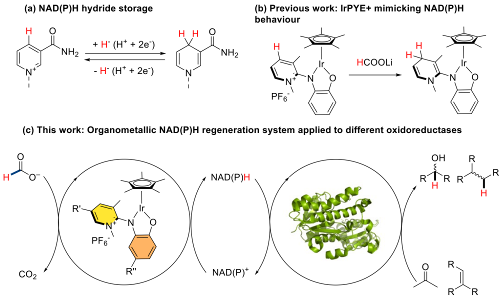
^{IR}PYE^{+} AS VERSATILE AND BIOCOMPATIBLE ORGANOMETALLIC NAD(P)H REGENERATION SYSTEM

L. Monte[1], R. Keller[1]*, F. Paradisi[1]*, M. Albrecht[1]*

[1]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern (Switzerland)

NADH is a crucial cofactor in many oxidoreduction enzymatic processes due to its ability to reversibly store hydrides on the nicotinamide moiety (Fig. 1a). Despite its importance, the use of NADH is limited by high cost, low stability, and stoichiometric utilization.[1] To overcome these limitations, several research groups have explored various cofactor regeneration systems aimed at reducing the costs associated with NADH-dependent reactions.[2,3] Among these, NAD(P)H regeneration using organometallic complexes has been extensively studied over the past decades, providing numerous metal-based catalysts. Nevertheless, integrating these catalysts into enzymatic biocatalytic systems presents significant challenges, primarily due to mutual inhibition between the enzyme and the metal catalyst and the difficulty of identifying biocompatible reaction conditions.[4] We recently developed an iridium complex bearing a pyridylidene-amine (PYE) ligand that exhibits unique functional ligand-type reactivity, storing the hydride on the heterocycle ring and mimicking NADH-type reactivity (Fig. 1b). This complex also catalyzes NAD(P)H reduction.[5] Herein, we focused on the application of our optimized ligand for efficient NAD(P)H regeneration under biocompatible conditions and explore ways to prevent the mutual inhibition between the two systems. We will discuss two solutions that successfully solve these issues.


(a) NAD(P)H hydride storage

(b) Previous work: IrPYE+ mimicking NAD(P)H behaviour

(c) This work: Organometallic NAD(P)H regeneration system applied to different oxidoreductases

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New Electrochemiluminescent Multinuclear Ruthenium Complexes for Diagnostics

L. Arnal[1], G. Facchetti[1]*, I. Isabella[1]*, L. De Cola[1,2]*

[1]Department of Pharmaceutical Science DISFARM Università degli Studi di Milano, Via Golgi, 19, Milan 20133, Italy., [2] Department of Biochemistry and Molecular Pharmacology, Istituto di Ricerche Farmacologiche Mario Negri IRCCS, Via Mario Negri 2, Milan 20156, Italy.

Electrochemiluminescence (ECL) – the production of molecular excited states without light excitation but through charges recombination – is a well-known process. This mechanism presents diverse advantages, vs the most used photoexcitation: i) due to the absence of light excitation the background is reduced; ii) is very sensitive and selective; iii) it finds application in diagnostics and in particular immunoassays reaching detection limit close to femtomolar.[1]

Ruthenium complexes are widely used as emitters for ECL-based detection methods and more recently also other metal complexes have been investigated.[2] In order to improve the detection limit the use of multinuclear compounds has emerged as strategy. However, the ECL signal is not linearly correlated with the number of emitters, due to the self-quenching of the (spatially-closed) compounds.

Here we show a class of water-soluble Ru complexes which have been chemically and spectroscopically characterized. In addition, to increase the signal the grafting of these complexes on different kind of silica nanoparticles was deeply studied. We have compared the single complexes to the formation of multinuclear species by the binding or encapsulation of the emitters on/in the silica nanostructures to assess how their proximity can affect the photophysical properties and ECL amplification.

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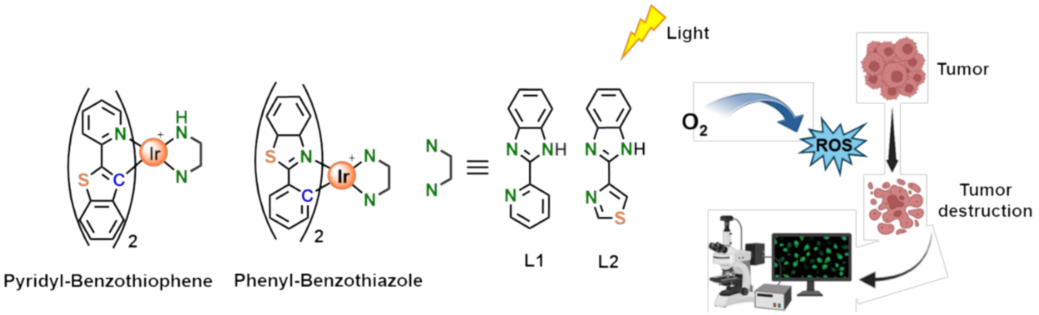
Towards Tailored Therapy: The Role of Cyclometalated Ligands in Ir(III) Complexes

V. Fernández-Moreira[1], E. Morales-Pioz[1]*, M. Redrado[2]*, A. Benedi[1]*, A. de Aquino[3]*, L. Rodríguez[3]*, M. Gimeno[1]*

[1]Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain, [2]Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, Paris, 75005 France, [3]Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

Photodynamic therapy (PDT) has emerged as a promising treatment for certain types of cancer. This innovative approach harnesses the power of light to activate a photosensitizer (PS), triggering the production of reactive oxygen species (ROS) and ultimately inducing cell death. PDT offers a localized treatment, providing several advantages over traditional chemotherapy and helping to reduce side effects.[1] Transition metal d^6 complexes have shown great potential as PS agents for PDT due to their intrinsic photophysical properties. These complexes often exhibit high photostability, and the efficient population of the excited triplet state facilitates ROS generation.[2]

Herein, we present the synthesis of Ir(III) complexes with the general formula $[Ir(C^\wedge N)_2(N^\wedge N)]^+$, using 2-(2-pyridyl)benzothiophene and 2-phenylbenzothiazole as cyclometalated ligands (C^N) and various N-donor bisimine ligands (N^N) (Figure 1). A comprehensive analysis was conducted to investigate the impact of the different C^N ligands on both luminescent properties and key biological activities, including cell proliferation inhibition, cell death mechanisms, cellular uptake, ROS generation and biodistribution studies. Our findings highlight the pivotal role of ligand design in tailoring the photophysical and biological behavior of Ir(III) complexes, paving the way for the development of more effective and personalized PDT agents.



Acknowledgments

The authors acknowledge the financial support from the Spanish State Research Agency (PID2022-136861NB-I00; CNS2023-143600, PID2022-137862NB-I00, PID2022-139296NB-I00), grant 2024ICT334 funded by CSIC and the Government of Aragón-Fondo Social Europeo (E07_23R). M.R. thanks the Fondation pour la Recherche Médicale (FRM) for their financial support (SPF202309017545)

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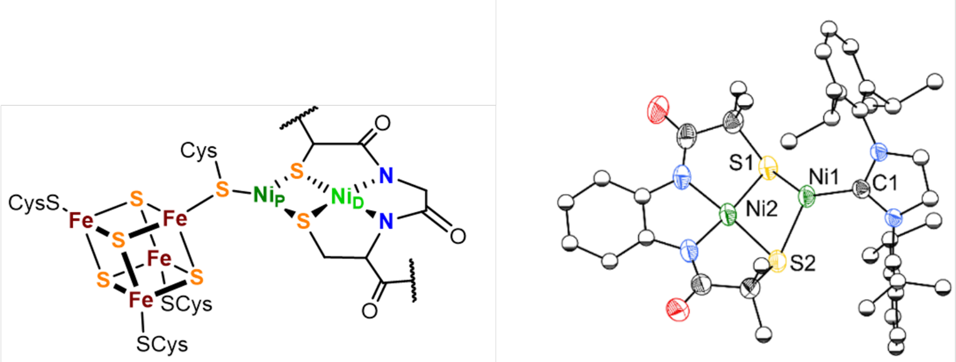
Mixed valence {$Ni^{2+}Ni^{1+}$} complexes as models of Acetyl Coenzyme A Synthase intermediates

N. T. Stephaniuk[1], D. W. Wilson[1]*, B. C. Thompson[1]*, A. Collauto[2]*, M. M. Roessler[2]*, R. A. Musgrave[1]*

[1]Department of Chemistry, 7 Trinity Street, London, UK, SE1 1DB, [2]Department of Chemistry and Centre for Pulse EPR Spectroscopy, Imperial College London, 82 Wood Lane, London, UK, W12 0BZ

Bacterial enzymes are known to utilize the Wood-Ljungdahl Pathway (WLP), which outlines the conversion of carbon dioxide into acetyl coenzyme A (acetyl-CoA), a key biological metabolite.[1,2] Central to the WLP is acetyl-CoA synthase (ACS), one of the few nickel-containing enzymes, which catalyzes the synthesis of acetyl-CoA from CO. The active site of ACS is known as the A-cluster, which consists of a {NiNi} cluster bridged to a $[Fe_4S_4]^{n+}$ cluster (Figure 1, left).



Many mechanisms have been proposed to describe the activity of ACS, including divergent diamagnetic (nickel (0/II)) and paramagnetic (nickel (I/III)) mechanisms, with extensive research conducted to understand, isolate, and quantify intermediates along both proposed pathways.[2,3] In an effort to probe the role of the two nickel centers (with varying oxidation states) of significance to the A-cluster, we report bimetallic models of two hypothesized intermediates on the paramagnetic pathway of ACS function, namely an anionic {$Ni^{2+}Ni^{1+}$} complex $[\mathbf{1}]^-$ (Figure 1, right) featuring a three-coordinate Ni-center with similarity to the A-cluster, which reacts with carbon monoxide to yield a {$Ni^{2+}Ni^{1+}$–CO} complex $[\mathbf{2}]^-$ analogous to the enzymatic CO-bound A-cluster. Synthesis of these bimetallic complexes, along with characterization by X-ray diffraction, NMR, UV-Vis, and electron paramagnetic resonance spectroscopies, will be discussed.[4]

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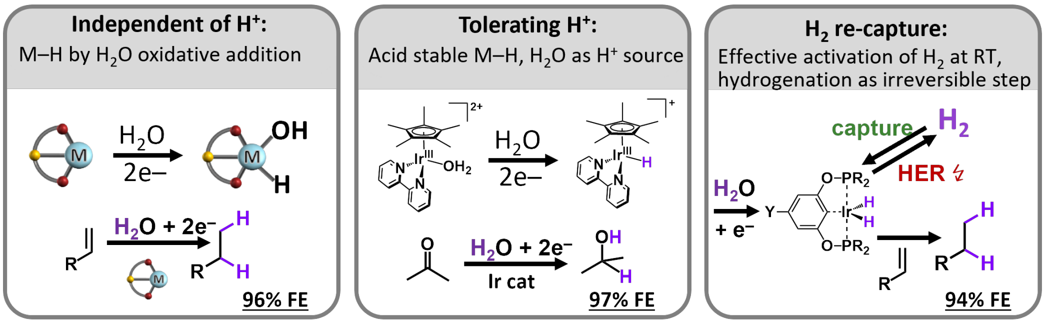
Mechanistic Insights and Reactivity Tuning in Electro-Hydrogenation of Organic Compounds with H_2O at Organometallic Iridium Catalysts

D. P. Halter[1,2], P. Mollik[1]*, J. Chen[1]*, T. Huang[1]*

[1]Technical University of Munich, TUM School of Natural Sciences, Department of Chemistry & Catalysis Research Center (CRC), Lichtenbergstr. 4, 85748 Garching, Germany., [2]University of Antwerp, Faculty of Applied Engineering, Department of Biochemical and Chemical Engineering, Research Group Applied Electrochemistry & Catalysis (ELCAT), Universiteitsplein 1, 2610 Antwerp, Belgium.

Despite multiple applications for H_2 gas as energy carrier and reagent, its large-scale storage and handling is challenging and expensive—a long-standing problem towards a hydrogen economy. Liquid organic hydrogen carriers (LOHCs) emerged as potential solution, for which we develop direct electro-hydrogenation of alkenes and organic carbonyls with H_2O in one step, mediated by molecular iridium complexes.[1-3]

Besides conveying strategies to enable H_2O as desirable—but in the literature still rare—proton source in homogeneous *e*-hydrogenation catalysis,[4] based on detailed mechanistic studies and structure-function relationships three concepts to achieve quantitative selectivity for *e*-hydrogenation over parasitic H_2 production are introduced. It will be showcased, how tuning of reaction mechanisms can break traditional correlations of reaction selectivity and thermodynamic driving force, and how co-catalysts can enable e-hydrogenation at a formal electrocatalytic underpotential. *In situ* and *ex stitu* spectro-electrochemistry (UV/Vis, NMR, IR) experiments were used as valuable tools for these studies.



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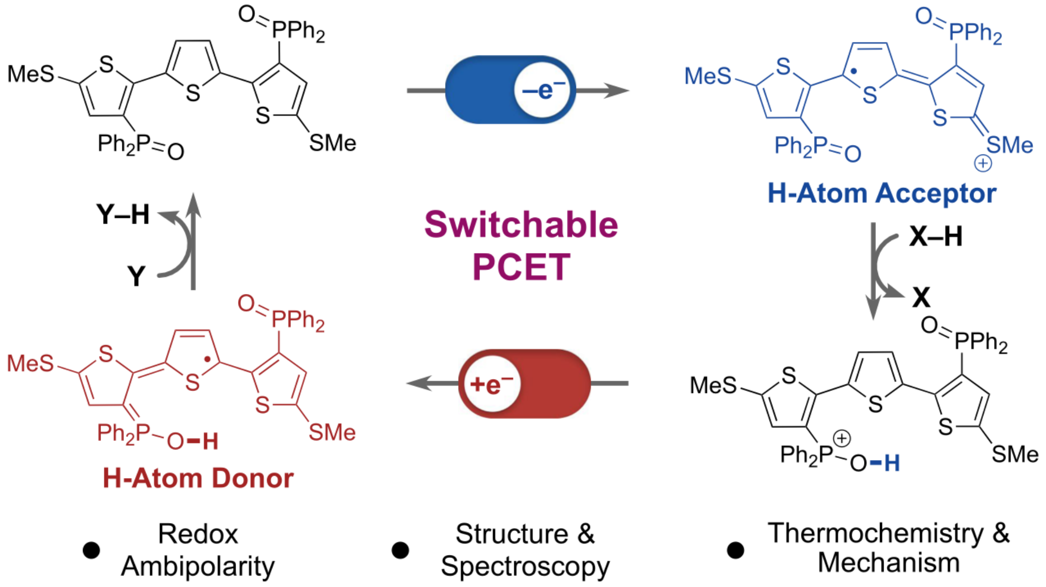
Functionalized Terthiophene as an Ambipolar Redox System: Structure, Spectroscopy and Switchable Proton-Coupled Electron Transfer

M. J. Bezdek[1], D. Käch[1]*, D. Klose[1]*, L. Wettstein[1]*

[1]Department of Chemistry and Applied Biosciences, ETH Zürich

Main group redox systems that can undergo oxidative and reductive (ambipolar) electron transfer are elusive yet attractive for applications across synthetic chemistry and energy science.[1] Specifically, the use of ambipolar redox systems in proton-coupled electron transfer (PCET) reactions is largely unexplored but could enable "switchable" reactivity wherein the uptake and release of hydrogen atoms are controlled using a redox stimulus. In this presentation, an ambipolar functionalized terthiophene (TTH) bearing methyl thioether and phosphine oxide groups that exhibits switchable PCET reactivity will be discussed.[2] Combined structural, spectroscopic and computational investigations revealed the influence of the methyl thioether and phosphine oxide moieties on the TTH electronic structure that results in the stabilization of both cationic and anionic radicals. Upon single-electron oxidation, the functionalized TTH serves as a hydrogen atom acceptor and undergoes PCET with 1,4-dihydroquinone to generate a TTH hydroxyphosphonium species. The process was found to be reversible upon single-electron reduction, with functionalized TTH acting as a hydrogen atom donor in a PCET reaction with 2,3-dimethylanthraquinone. The thermochemistry of the O–H bond formed and cleaved in functionalized TTH during the reaction sequence was investigated, revealing that a bond weakening of 30 kcal/mol underpins the switchable PCET reactivity. Overall, these studies provide an electrochemical, structural, spectroscopic, and thermochemical foundation for the use of ambipolarity to control PCET reactions in main group redox systems. Ongoing efforts targeting the application of functionalized terthiophenes in energy storage and synthesis will also be presented.



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Talks

Session 4A

New Generation Olefin Metathesis Catalysts fostering Eco friendly Innovations

R. Tuba[1,2]

[1]Institute of Materials and Environmental Chemistry, Hungarian Research Network, Research Centre for Natural Sciences, Magyar tudósok körútja 2., Budapest H-1519, Hungary, [2]Research Centre for Biochemical, Environmental and Chemical Engineering, Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, Egyetem u. 10., Veszprém H-8210, Hungary

Growing concerns over plastic waste management are driving the need for diverse strategies and advanced technologies to enable a transition toward sustainable, circular materials. A particularly promising solution to the persistent issue of fossil-based plastic waste – such as polyolefins – is the development of innovative catalytic processes that can upcycle waste into more sustainable, value-added products. Among these, olefin metathesis catalysis has emerged as a powerful tool for converting durable polyolefin waste into valuable chemical intermediates. These intermediates can serve as precursors for high-value materials, including chemically recyclable and compostable plastics. This work centers on the design and application of N-alkyl-substituted Cyclic(Alkyl)(Amino)-Carbene (CAAC)-Ru catalysts with "inverted" structures, as well as bicyclic (Alkyl)(Amino)Carbene (BICAAC)-Ru complexes. These catalysts exhibit improved performance in isomerization-metathesis (ISOMET) reactions. When used in combination with a ruthenium-based double bond isomerization co-catalyst, $(RuHCl)(CO)(PPh_{3})_{3}$, the system efficiently converts olefins derived from the pyrolysis of post-consumer polyolefin waste to high value platform chemicals. The initial pyrolysis step yields olefin-rich oils, which are then selectively transformed into propylene and isobutylene through ISOMET catalysis. Metathesis of sterically hindered alkenes – including olefinic polypropylene pyrolysis oil components – remains a major challenge due to limited catalyst accessibility and reduced reactivity at crowded double bonds. These substrates often suffer from low reaction rates, poor conversion, and catalyst deactivation. Addressing this issue requires the development of more robust and selective catalysts that can tolerate steric bulk while maintaining high activity and functional group compatibility. Advances in ligand design – especially the use of novel BICAAC-based catalysts – are proving to be a promising path forward for tackling branched polymer substrates, significantly broadening the scope of polymer chemical recycling. This olefin metathesis/isomerization catalytic system has shown exceptional efficiency in converting post-consumer plastic waste into propylene and isobutylene. Scale-up to a 900 mL reactor and repeated batch testing have confirmed the system's long-term operational stability. This presentation will highlight recent advancements in olefin metathesis-driven recycling approaches, as well as key challenges that remain in expanding their applicability and efficiency.

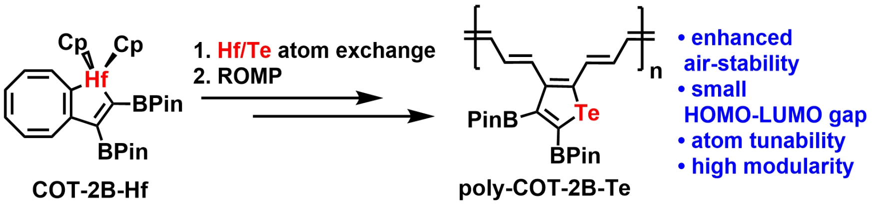
Linking metallacycle transfer with ring-opening metathesis to generate polyacetylenes of unprecedented structure

A. Vayalillath Madom Muralidharan[1], M. J. Ferguson[1]*, E. Rivard[1]*

[1]Department of Chemistry, University of Alberta

Polyacetylene [-CH=CH-]$_n$ (PA) is a landmark macromolecule that adopts metal-like conductivity when doped.[1] This discovery led to the 2000 Nobel Prize in Chemistry. However, polyacetylene's insolubility and rapid degradation in air places it outside of the realm of utility in modern optoelectronics. A few years ago, we disclosed a route to prepare soluble polyacetylenes bearing the inorganic side groups boryl (-BR$_2$), phosphoryl (-P(O)R$_2$) and amine (-NR$_2$), enabling polymer film formation from solution and enhanced air-stability.[2] Furthermore, it is well known that incorporating heavy main group elements, such as tellurium (Te), into π-scaffolds led to improved crystallinity and lower LUMO levels, enhanced phosphorescence and increased charge transport in relation to lighter element congeners.[3]

Herein, we demonstrate a modular approach to afford a hybrid polymer in which, 6π tellurophene ring is fused to PA backbone by linking metallacycle transfer (metal/element atom exchange) with ring-opening metathesis polymerization (ROMP). We have developed a hafnium-based bicyclic precursor, **COT-2B-Hf**, that enables tandem Hf/E metallacycle transfer (E = main group element) and the ring-opening metathesis polymerization (ROMP) of a cyclooctatetraene (COT) unit (Scheme 1). Overall, the synthetic methods introduced in this study greatly expand the scope and structural variety of soluble/processable π-conjugated polyacetylenes with unique architectures as well as tailored optoelectronic properties.



Scheme 1. Synthesis of tellurophene-fused polyacetylene **poly-COT-2B-Te**.

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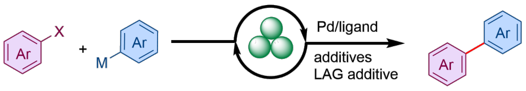
Mechanochemically Facilitated Palladium-Catalyzed Cross-Coupling and Carbonylation Reactions

R. Sebesta[1]

[1]Comenius University Bratislava, Faculty of Natural Sciences, Department of Organic Chemistry, Mlynska dolina,
Ilkovicova 6, 842 15 Bratislava, Slovakia

Metal-catalyzed cross-coupling reactions enable the synthesis of various complex molecules. Despite their widespread use, there are several challenges that hinder their application. The use of sensitive transition metal catalysts and organometallic reagents are significant limiting factors. Mechanochemistry seeks to address these issues. Recent studies have demonstrated that metal-catalyzed cross-coupling reactions can be performed effectively under mechanochemical conditions [1].



Our team examined the mechanochemical cross-coupling of organozinc pivalates with aryl halides [2]. We continued this work by forming other organozinc species in situ, such as Reformatsky enolates under mechanochemical conditions, followed by mechanochemical Pd-catalyzed cross-coupling [3]. Recently, we have also studied the application of arylthianthrenium salts as alternative electrophiles in Pd-catalyzed cross-coupling reactions with organoboron and organozinc compounds [4]. Additionally, we discovered that Pd-catalyzed carbonylation of arylhalides with amines and phenols can be achieved under mechanochemical conditions. A crucial aspect of using mechanochemistry in these instances was employing solid FeBr2(CO)4 as a CO source [5]. Our findings indicate that metal-catalyzed cross-coupling reactions can be performed in a more sustainable manner using mechanochemistry, allowing for operations under ambient conditions in air, even with sensitive organometallic reagents.

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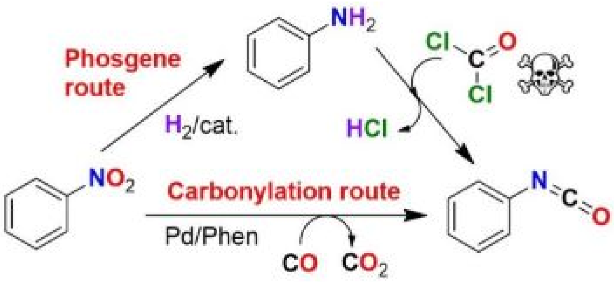
Carbonylation of nitrobenzene to phenyl isocyanate: new life in an old field

F. Ragaini[1], D. R. Ramadan[1,2]*, M. A. Fouad[1,2]*, F. Ferretti[1]*, A. Brotons Rufes[3]*, C. Costabile[3]*, P. Macchi[4]*

[1]Dipartimento di Chimica, Università di Milano, V. C. Golgi 19, Milano, [2]Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Alexandria 21321, Egypt., [3]Dipartimento di Chimica e Biologia “A. Zambelli”, Università di Salerno, V. Giovanni Paolo II, Fisciano (SA), [4]Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, V. Mancinelli 7, Milano

Organic isocyanates are fundamental intermediates in the synthesis of many products, including polyurethanes, pesticides and many others. Aromatic isocyanates, accounting for more than 80% of the market, are actually produced by reduction of nitroarenes to anilines, followed by reactions of the latter with phosgene. However, phosgene is a very toxic substance and avoiding its use is highly desirable.

The most direct way to get isocyanates from nitroarenes is their reaction with CO, which only affords CO_2 as a stoichiometric byproduct. However, the direct catalytic carbonylation reaction of nitroarenes to isocyanates is a difficult reaction, which only proceeds with high catalyst loadings and often affords only moderate yields. Consequently, during the last three decades, most efforts have concentrated on an indirect route in which nitroarenes are carbonylated in the presence of methanol to give the corresponding carbamate, which can be later cracked to isocyanate and methanol in a subsequent step. However, a single-step synthesis would be more appealing if its efficiency can be improved.



We took advantage of our experience in the synthesis of carbamates[1-3] to reconsider one of the best catalytic systems for the direct synthesis of isocyanates from nitroarenes, based on the use of a palladium catalyst with phenanthroline as a ligand.[4] In this communication we will describe the results we obtained, which allowed us to increase the substrate/catalyst ratio by an order of magnitude, while maintaining high selectivities. Furthermore, both experimental and computational studies provided deeper insights into the reaction mechanism.

This work was supported by MUR and Next Generation EU (PRIN2022ZJSCW3)

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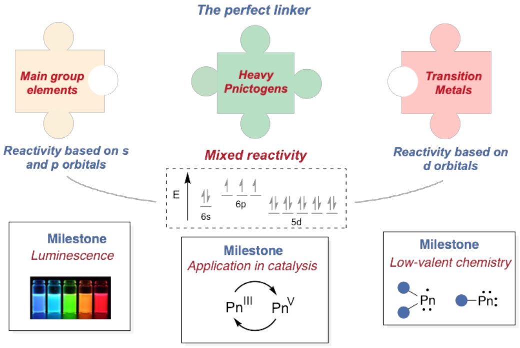
Exploring the Potential of Heavy Pnictogens

A. Bismuto[1]

[1]Institute for Inorganic Chemistry, University of Bonn

Bismuto Group

The chemistry of light main group elements has been widely investigated with singular electronic and bonding motifs.[1] In contrast, heavy pnictogens are still underexplored.[2] Due to the large number of electrons available, the energy gap between their orbitals is considerably lower than that of lighter main-group elements. This allows them to span several oxidation states, mimicking transition metal reactivity.[3] In addition, the ability of antimony and bismuth to expand its valence shell (hypervalency) can lead to materials with unusual electronic properties.[4] Heavy pnictogens show thus high potential to merge the benefits of both main-group and transition metal properties to unveil new applications in several fields such as catalysis and optoelectronics.



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Talks

Session 4B

Mid- to High-Valent Iron Nitrido and Oxido Complexes in tris-Carbene Ligand Environments, Including a Reactive Fe(VII) Nitride

K. Meyer[1]

[1]Department of Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) Egerlandstr. 1, 91058 Erlangen,
Germany, e-mail: karsten.meyer@fau.de

Iron nitrido complexes $[(\mathrm{TIMMN^{mes}})\mathrm{Fe(N)}]^{1+/2+}$ and $[(\mathrm{TIMMNmes})\mathrm{Fe(N)(X)}]^{2+/3+}$ (X = F, Cl) in oxidation states Fe(IV), Fe(V), Fe(VI), and Fe(VII), as well as the tetravalent iron oxide $[(\mathrm{TIMMN^{mes}})\mathrm{Fe^{IV}(O)}]^{2+}$, were synthesized using the sterically encumbered, N-anchored *tris*-N-heterocyclic carbene ligand $\mathrm{TIMMN^{mes}}$. The mid-valent Fe(IV) and high-valent Fe(V) and Fe(VI) nitrido complexes are isolable, air- and temperature-stable. In contrast, the super-oxidized Fe(VII) nitrido species is highly reactive and undergoes ligand rearrangement, akin to skeletal editing. The Fe(IV) oxo complex represents, to the best of our knowledge, the first isolable and fully characterized closed-shell Fe(IV)=O molecular complex. Comprehensive spectroscopic, magnetochemical, electrochemical, and crystallographic analyses, supported by computations, provide deep insight into the electronic structures across this unique series of iron nitrido and oxido complexes spanning oxidation states +4 to +7 within the same tris-carbene coordination environment. Progress toward the synthesis of an isolable Fe(VII) nitride and a complete series of Fe(III), Fe(IV), and Fe(V) oxides is presented

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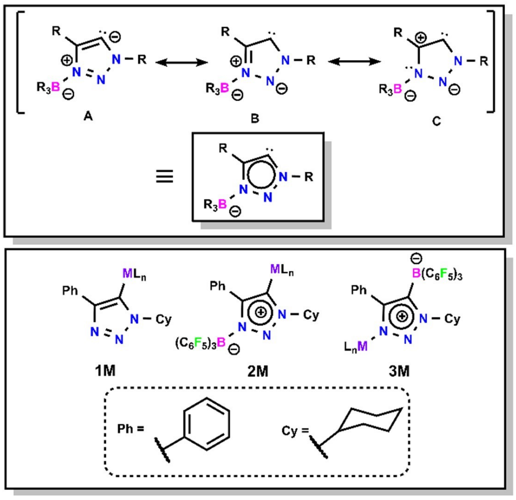
Triazole-Based Anionic Mesoionic Carbenes

B. Sarkar[1]

[1]Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195, Berlin, Germany

Mesoionic carbenes (MICs) of the 1,2,3-triazolylidene type have had a huge impact in synthetic organometallic chemistry over the past 15 years with applications in fields such as homogeneous catalysis, electrocatalysis, and photochemistry/photophysics. [1] Most reported MICs are neutral with examples of cationic and anionic MICs being extremely rare. [2] In this contribution, we will present a facile synthetic route for accessing anionic MICs based on a borate backbone, and report on their stability and follow-up reactivity. We will show that both the anionic MIC (C-donor) as well as the carbene-borane substituted amides (N-donors), formed from the anionic MICs, are versatile ligands for main group elements and transition metals. We will also report on the first examples of their applications in homogeneous catalysis.[3]



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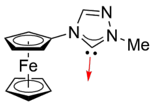
Synthesis and properties of novel ferrocenyl-tagged triazolylidene carbenes

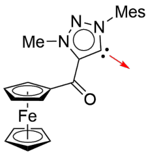
P. Stepnicka[1]

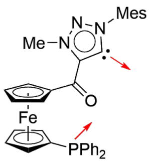
[1]Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic

Thanks to its chemical stability and unique steric and electronic properties, the ferrocene scaffold has become indispensable in the design of ligands for coordination chemistry and catalysis. To date, there has been reported an enormous number of ferrocene-based ligands containing conventional donor groups, mostly phosphines. Comparatively less attention has been paid to alternative donor types such as heteroatom-stabilized carbenes.[1] This contribution describes the synthesis of complexes with new simple and P-chelating, ferrocenyl-substituted triazolylidene ligands, their detailed structural characterization, and catalytic properties.

In particular, presented will be the synthesis and characterization of transition metal complexes with carbene ligands derived from 4-ferrocenyl-1,2,4-triazole, and an analysis of the bonding situation in these compounds.[2] Also reported will be the preparation of group 11 metal complexes with ferrocenyl-substituted 1,2,3-triazol-5-ylidene ligands homologated by an inserted carbonyl moiety and an assessment of the impact of the homologation on the donor properties of these carbene ligands. Further results will include those from catalytic evaluation of these complexes in the model Au-catalyzed cyclization reactions and the preparation of structurally unique trans-P,C chelating Pd(II) complex featuring phosphinoferrocenyl-substituted ligand of this types.







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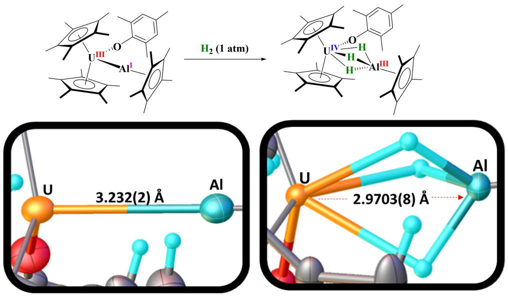
The Marriage of Actinide and Main Group Elements

J. R. Walensky[1], H. Kumar[1]*, P. Mahawar[1]*

[1]University of Missouri, Columbia

While actinides are large electropositive metals, they prefer hard Lewis bases and hence their coordination chemistry and reactivity with softer main group elements is less studied. Our group has been interested in combining actinides with heavier main group complexes (P, As, Al) in order to examine their reactivity, which is far more enhanced compared to a hard Lewis base since the actinide-element bond with soft donors is weak. For example, the reactivity of thorium-phosphido bonds in $[(C_5Me_5)_2Th\{P(H)Mes\}_2]$, Mes = 2,4,6-$Me_3C_6H_2$, with CO shows proton transfer reactivity from both phosphorus to the carbon of CO, forming a formyl-like species.[1] Another example is $[(C_5Me_5)_2(MesO)UAl(C_5Me_5)]$ which has a U-Al bond and can functionalize H_2 to form a trihydroaluminate complex.[2] In this presentation, our latest results will be presented to show the fascinating structure, bonding, and reactivity of actinide-main group bonds!



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Metal-Functionalized Polymers

P. W. Roesky[1], S. Gillhuber[1]*, C. Barner-Kowollik[2]*

[1]Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany, [2]Queensland University of Technology (QUT) 2 George Street, 4000 Brisbane, QLD, Australia

Single chain nanoparticles (SCNPs), which consist of individual polymers folded intramolecularly into discrete nanoparticles, have been used as one of many “bio-inspired” polymeric catalysts.[1] Catalytic SCNPs can combine the advantages of homogeneous and heterogeneous catalysts, such as homogeneous reaction conditions, improved recyclability, high activity and potentially high substrate specificity. The folding of a linear chain *via* intramolecular crosslinking into an SCNP can give rise to the formation of local domains within the nanoparticle which, when decorated with catalytic moieties, can afford ‘catalytic pockets’, analogous to enzymes.[2] Initially, we reported the synthesis and characterization of platinum(II)-crosslinked SCNPs (Pt^{II}-SCNPs).[3] These Pt^{II}-SCNPs were used as recyclable homogeneous catalysts for the amination of allyl alcohols. Although the platinum complex is anchored to the polymer backbone, the Pt^{II}-SCNP system is as active and selective as a small molecule reference catalyst. More recently, our group demonstrated the first successful continuous production of metal-functionalized SCNPs in photoflow.[4] The flow synthesis approach enables the continuous production of catalytically active SCNPs, thereby addressing the scalability issue prevalent in SCNP synthesis, hence critically enhancing the applicability of SCNPs in catalysis (Figure 1).

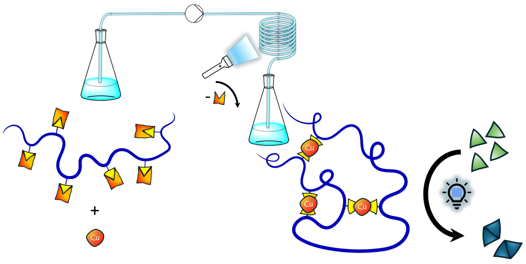

Figure 1: Schematic illustration of the experimental setup used for the photoflow synthesis of catalytically active single-chain nanoparticles (SCNPs).

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Talks

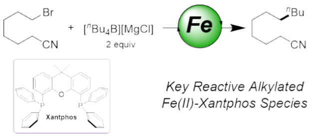
Session 5A

Intermediates and Mechanism in Iron-Catalysed Cross-Couplings

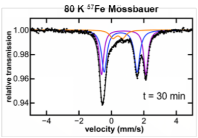
M. Neidig[1]

[1]Department of Chemistry, University of Oxford, Oxford, United Kingdom

Iron catalysts continue to attract significant attention for use across the breadth of bond making (C-C, C-N, C-O, etc.) and bond breaking reactions (ex. C-H) central to modern organic synthesis. Iron-based methods for C-C cross-couplings reactions have been of particular interest due to the broad importance of such transformations in the synthesis of fine chemicals and pharmaceuticals. Significant advances in the development of iron-based methods for C(sp^2)-C(sp^3) cross-couplings have occurred over the past two decades, which have been followed by critical insight into their molecular-level mechanisms that enable effective catalysis.1 However, numerous challenges exist beyond these reactions that remain difficult to overcome without further detailed mechanistic insight. Of particular note are the limited number of effective iron-based methods for C(sp^3)-C(sp^3) and C(sp^2)-C(sp^2) cross-couplings as well as limited reports of reductive cross-couplings with iron that do not require organometallic nucleophile coupling partners. This presentation will focus on recent studies from our group using our physical-inorganic approach to elucidate organoiron intermediates and mechanism underlying iron-catalysed two- and three-component cross-couplings,2 as well as reductive cross-couplings.



Key Reactive Alkylated Fe(II)-Xantphos Species



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Innocent until proven guilty: DFT investigation into the mechanism of NacNacZn catalysed electrophilic C–H functionalisation

J. Łosiewicz[1], M. K. Bisai[1]*, G. S. Nichol[1]*, A. P. Dominey[2]*, S. P. Thomas[1]*, S. A. Macgregor[3]*, M. J. Ingleson[1]*

[1]EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh, EH9 3FJ, UK, [2]GSK Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2NY, UK, [3]EaStCHEM School of Chemistry, University of St Andrews, St. Andrews, KY16 9ST, UK

Direct C–H functionalisation offers an atom-economic route to install a variety of synthetically useful functional groups, which can be further transformed to increase molecular complexity. One prominent example is C–H metalation affording organonucleophiles, which are of particular interest as cross coupling partners.[1] We have recently developed a novel catalytic transition metal-free protocol to form C(arene)–[M] bonds, where [M] = ZnNacNac, Al(Me)NacNac (NacNac = $\{(Ar)N(CH_3)C\}_2CH$).[2] This talk will present our DFT investigations of the reaction mechanism which revealed that combining an uphill electrophilic C–H metalation step with a sufficiently exergonic dehydrocoupling step is key for enabling experimentally observed reactivity. Expanding this work, we achieved a main group catalysed C–H borylation of heteroarenes using 9-borabicyclo-[3.3.1]-nonane, $(H–BBN)_2$ (**Figure 1**).[3] This borane is under-explored in catalytic C–H borylation but exists as a dimer, in contrast to ubiquitous dioxaborolanes (e.g. BPin, BCat derivatives).

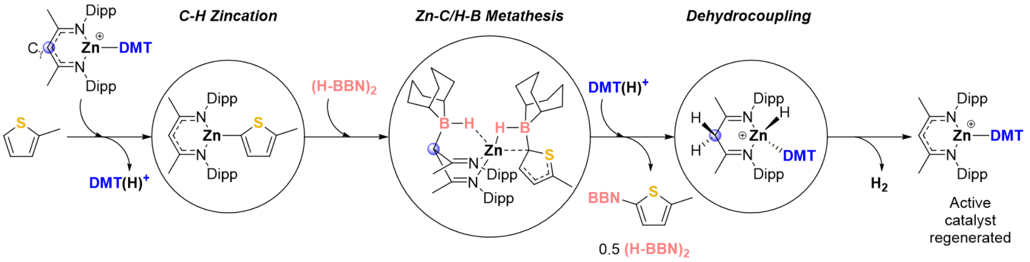

Figure 1: Overview of the computed reaction mechanism for C–H borylation including structural representatives of three key steps: C–H zincation, Zn–C/H–B metathesis and dehydrocoupling.

We will show that in both processes,[2,3] ligand non-innocence proved vital. Our results indicate that the C_{gamma}-position on the NacNac ligand backbone assists with both the Zn–C/H–B metathesis between NacNacZn–Aryl and the hydroborane, as well as in the dehydrocoupling step required to complete the catalytic cycle and regenerate the active catalyst, $[NacNacZn–DMT]^+$.

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Low valent s-block Nickelates: Synthesis, Structure, and Reactivity

L. Vedani[1], A. M. Borys[1]*, E. Hevia[1]*

[1]DCBP, Universität Bern, Freiestrasse 3, Bern, Switzerland

Ever since the discovery of nickel olefin complexes by Wilke in 1960,[1] they have served as ubiquitous precursors in nickel chemistry. Early reports in the 1970's showed that combinig this Ni(0) precursors with polar organometallics gives rise to highly electron rich nickelate complexes which can activate small molecules such as N_2.[2] For decades research in this area has been neglected, however recent reports have shown that lithium nickelates can be key intermediates in key Ni catalysed C–C bond forming processes.[3]

Advancing the understanding on structure/reactivity correlations, this presentation will discuss recent developments in our group assessing the synthesis of alkalimetal Ni(0) and highly reduced Ni(-II) nickelates. Their ability to cleave highly challenging C–C and C–F bonds will also be discussed.[4] Furthermore, their implication in catalytic transformations such as reductive couplings and alkene isomerisation will be assessed.

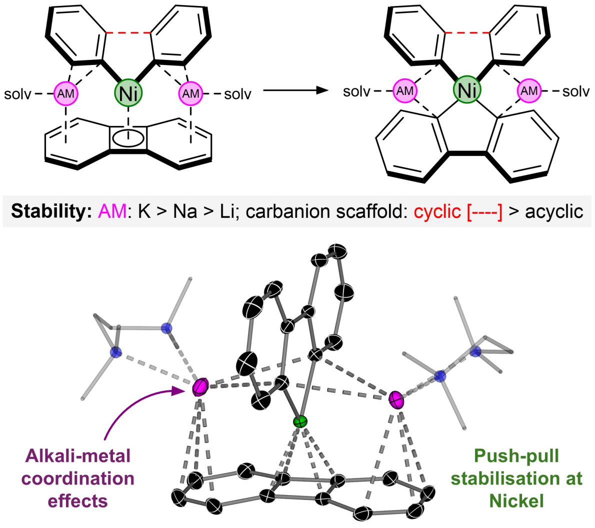

Figure 1) Biphenylene coordination and ring opening by alkali metal nickelates.

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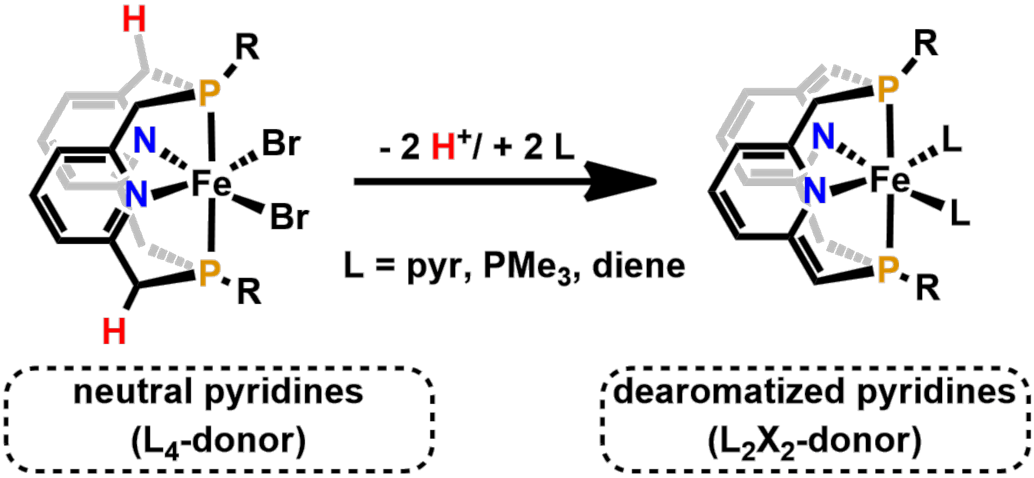
Iron Complexes Supported by a Double Dearomatized PNPN Ligand

S. Weber[1,2], A. M. Pavelic[2]*, J. C. Peters[2]*

[1]TU Wien, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060, Vienna, Austria , [2]Caltech, 1200 E California Blvd., Pasadena 91125, Ca, United States

The activation of weakly (or non-) polarized bonds represents a challenging task in the field of modern organometallic chemistry. In order to facilitate such transformations, the metal center can be supported by ligands containing an acidic site which can be reversibly (de)protonated in order to achieve metal-ligand cooperativity (MLC). This process may lead to a dearomatized system which is capable of activating strong bonds.[1] Such mono dearomatized systems were intensively studied over the last decades for a broad variety of transition metals. However, reports of double dearomatized systems are thus limited to manganese[2] and ruthenium[3] supported by NSNS ligands.



Scheme 1: Synthesis of iron complexes supported by a double deprotonated PNPN ligand.

This contribution will focus on iron(II) complexes supported by a macrocyclic PNPN ligand containing two acidic sites. Deprotonation leads to double dearomatization in conjunction with uptake of π-acidic ligands. A library of iron complexes containing pyridines, phosphines and isonitrile was synthesized. Delightfully, the double dearomatized system could be stabilized upon coordination of norbornadiene. Iron(II) alkene complexes are rare and a diene complex has thus far not been reported. The structure of these systems was elucidated by e.g., multinuclear NMR- ^{57}Fe-Mößauer spectroscopy and single crystal analysis. The reactivity of these complexes with small molecules e.g., H_2, CO and ligand substitution reactions will be discussed.

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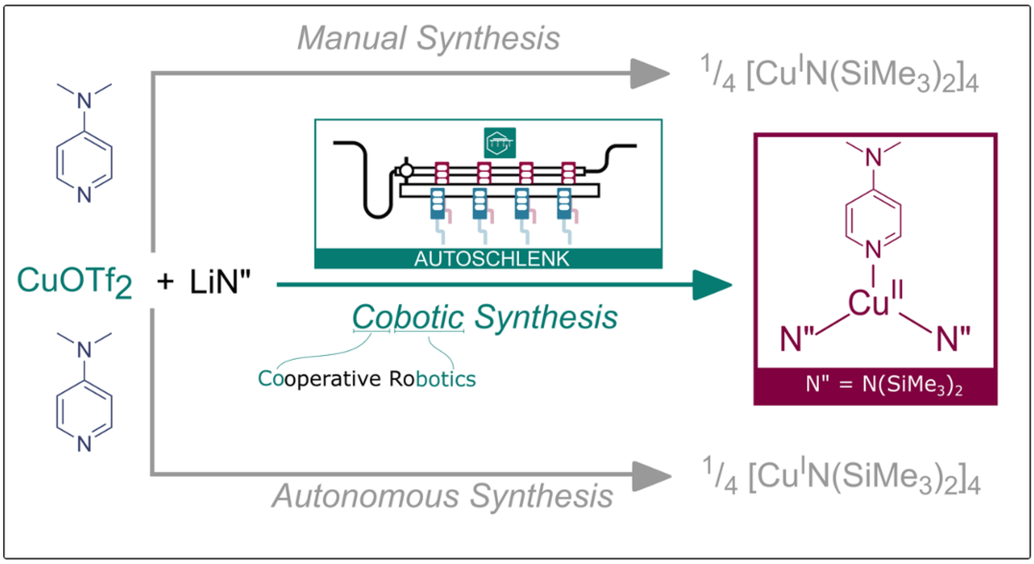
Automating Organometallic Chemistry unlocks access to elusive Cu(II) silylamides

N. L. Bell[1]

[1]University of Glasgow, Glasgow, UK, G12 8QQ

Digital Chemistry has demonstrated significant advances towards autonomous labs over recent years with systems able to work around the clock, unsupervised to generate high quality scientific data and chemical products.[1-3] Despite these advances organometallic chemistry, which often must be conducted under inert-atmospheres, has remained primarily a manual field. [4]



Herein, we will discuss our advances towards developing low-cost, cooperative digital tools for conducting organometallic chemistry[5] and show how implementation of new technologies has allowed us to synthesise and isolate the long targetted a Cu(II) bis-hexamethyldisilazide complex which could not be accessed by traditional manual Schlenk techniques.[6]

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Talks

Session 5B

Developing Heterobimetallic Complexes for Organometallic Catalysis

C. Lu[1], L. Gomm[1]*, F. Lam[1]*, T. M. Schwartz[1]*, H. Zhu[2]*, S. Grimme[2]*

[1]Institute of Inorganic Chemistry, University of Bonn, Gerhard-Domagk-Str. 1, 53177 Bonn, Germany, [2]Mulliken Center for Theoretical Chemistry, University of Bonn

e-mail: clu@uni-bonn.de

Many challenging chemical reactions require precious metal catalysts to proceed. Our research group develops main-group metalloligands (Groups 13 and 14) as an electronic lever for tuning a reactive transition metal active site via a direct metal–metal interaction. This approach has allowed for the development and optimization of highly efficient transition metal-main group bifunctional catalysts. The bimetallic catalysts display remarkably enhanced activity compared to the analogous single metal centers. In this talk, I will detail the roles of the main group support in substrate binding, activation of strong bonds (C−F and C−H), and their applications in catalysis.

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Probing pyridine C2(sp^2)–H bond activation and H_2 reductive elimination at a heterometallic nickel–aluminium dihydride complex

B. Stadler[1], J. A. Zurakowski[2,3]*, M. W. Drover[2]*, M. R. Crimmin[1]*

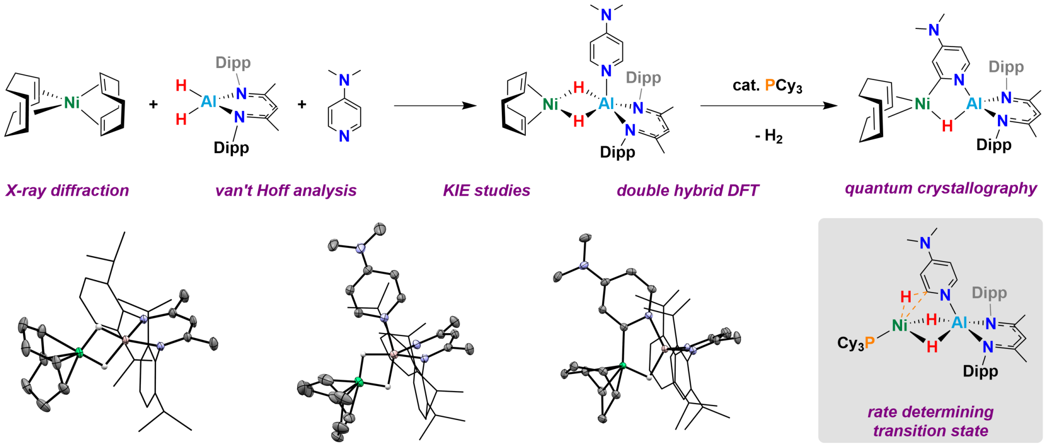
[1]Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, 82 Wood Lane, Shepherds Bush, London, W12 0BZ, United Kingdom, [2]Department of Chemistry, Western University, 1151 Richmond Street, London, ON, N8K 3G6, Canada, [3]Department of Chemistry and Biochemistry, The University of Windsor, 401 Sunset Avenue, Windsor, ON, N9B 3P4, Canada

Bimetallic complexes and their reactivity distinct from monometallic counterparts have received considerable attention in recent years.[1] Herein, we present a mechanistic study that takes advantage of a novel nickel-aluminium μ_2-dihydride heterometallic complex for the C2(sp^2)–H activation of 4-dimethylaminopyridine (DMAP) as a model substrate with concomitant H_2 reductive elimination. Through crystallographic and spectroscopic analysis we present snapshots along the reaction, starting from the association of the two monometallic fragments to form a *bis*-σ-complex, coordination of the DMAP substrate, and finally, C–H activation and reductive elimination of H_2.

The OA/RE steps were found to be slow in the presence of excess cyclooctadiene, whereas the reaction could be catalysed by tricyclohexylphosphine with a 1st order in the catalyst. While pyridine showed similar reactivity to DMAP, quinoline gave C2–C3 hydroalumination instead of C2–H activation reactivity.

DFT analysis of the mechanism established that the oxidative addition of the C2(sp^2)–H bond precedes the reductive elimination of H_2. The rate-limiting C–H activation transition state is ca. 10 kcal/mol more accessible in the presence of the PCy_3 catalyst with the low $k_H/k_D = 1.1$ measured for pyridine/pyridine-[D_5] being a consequence of compound effects for the OA and the RE steps.[2]

In summary, we report a stepwise C–H activation-reductive elimination process for a nickel-aluminium bimetallic complex, highlighting the differences in the fundamental reactivities of monometallic and bimetallic complexes.



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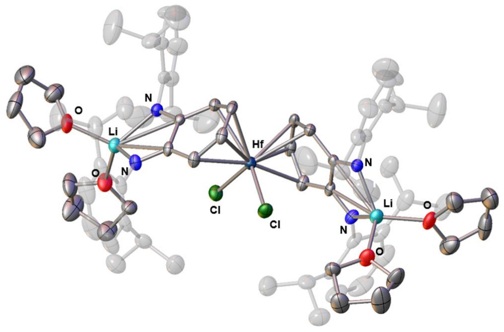
Unveiling the reactivity of hafnium (IV) complexes supported by redox active ligands

E. Alvarez-Ruiz[1], I. Sancho[1]*, M. Navarro[2]*, C. Santamaria [1]*, A. Hernán-Gómez[1]*

[1]Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Río" (IQAR), Universidad de Alcalá, Campus Universitario, E-28805, Alcalá de Henares, Madrid, Spain, [2]Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias y tecnologías químicas, Universidad de Castilla-La Mancha, 13071-Ciudad Real, Spain

Electron transfer processes play a crucial role in the development of new synthetic and catalytic procedures, such as carbon-carbon coupling reactions or small molecule activation.[1] This research field has primarily been developed using late transition metals catalysts.[2] On the contrary, early transitions metals (ETM) in low oxidation state have been less studied due to their typical lack of stability. As an alternative, the combination of early transition metals in their highest oxidation state and redox-active ligands has enabled multiple applications in synthesis.[3] Among the variety of these type of ligands, *ortho*-phenylendiamido (*o*-PDA) fragments are known to enable one or two electron redox processes.[4] While these type of complexes have recently been reported for titanium,[5] studies on the heavier group IV elements remain scarce.

Herein, we report the preparation and structural characterization of a series of hafnium (IV) complexes supported by two *o*-PDA ligands. Solid state studies display two possible coordination modes for the PDA moieties: i) via the nitrogen atoms or ii) through the phenylene central fragment. Furthermore, analysis of the structural-reactivity relationship reveals that the coordination mode of the *o*-PDA fragments is key for enabling electron transfer processes upon reaction with benzophenone or hypervalent iodine species.



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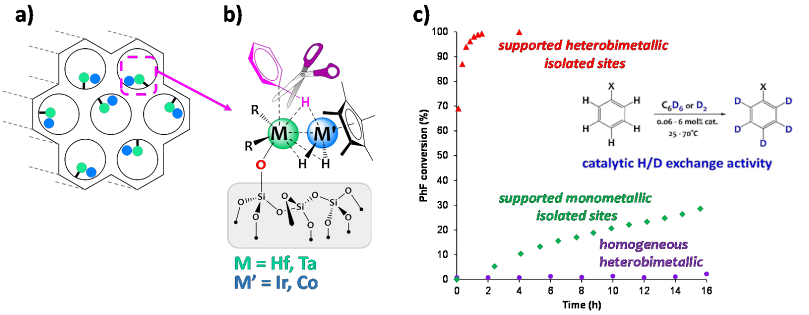
Surface Organometallic Chemistry Engineering of Heterobimetallic Catalysts for Selective H/D Isotope Exchange

C. Camp[1], A. V. Pichugov[1]*, A. Lachguar[1]*, S. Lassalle[1]*, L. Veyre[1]*, C. Thieuleux[1]*, L. Escomel[1]*

[1]Laboratory of Catalysis, Polymerization, Processes and Materials , CNRS, Universite Claude Bernard Lyon 1, CPE-Lyon,
3 rue Victor Grignard, 69616 Villeurbanne, France

One of the current frontiers in organometallic catalysis is to study the combined action of two metal centers to promote novel modes of reactivity, where the two metal centers act in synergy, in order to access a chemistry not possible with monometallic species. The association of late transition metal centers (eg. Ir, Os, Co) with Lewis acidic metals (such as Al, Hf, Ta) is particularly interesting to create polarized metal-metal pairs presenting original electronic structures, and thus potentially novel reactivity. Recently, we have shown that these heterobimetallic complexes are able to activate carbon dioxide[1-3] as well as C-H bonds (Fig. 1b)[4-7] in a concerted way on both metal centers. Using a Surface OrganoMetallic Chemistry (SOMC) approach, these heterobimetallic complexes are used to prepare original heterogeneized catalysts featuring well-defined active sites (Fig. 1a).[5,6] The SOMC methodology allows to access unique low-coordinate surface species not attainable in solution. These original silica-supported M/M' (M = Hf, Ta ; M' = Ir, Co) species exhibit drastically enhanced catalytic performances in H/D exchange reactions with respect to (i) monometallic analogues as well as (ii) homogeneous systems (Fig. 1c). In particular, deuteration of C(sp²)−H[5,7] and challenging C(sp³)−H[6] bonds is achieved with excellent productivity under mild conditions . In this presentation we will describe our latest results.

Figure 1.



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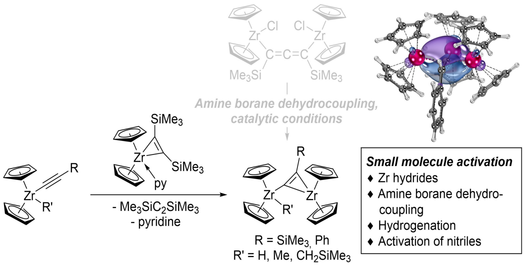
Dinuclear group 4 metallocene alkynyl complexes as versatile platforms for small molecule activation and catalysis

T. Beweries[1], H. Al Hamwi[1]*, F. Reiß[1]*

[1]Leibniz-Institut für Katalyse Rostock e.V. (LIKAT Rostock), Albert-Einstein-Str. 29a, 18059 Rostock, Germany

The concept of multinuclear transition metal complexes is a well-established but still intriguing field in organometallic chemistry and homogeneous catalysis. The idea of multinuclear complexes has gained renewed interest due to their potential to enhance orthogonal catalytic activity and selectivity in various reactions.[1] Cooperative effects of polynuclear catalysts affect catalytic performance through multiple factors such as steric hindrance, electronic effects, heteroatom effects, non-covalent interactions and the distance between metal centres in polynuclear metal catalysts.

We have recently reported the dehydrocoupling of amine boranes using a dinuclear zirconocene complex $[Cp_2Zr(Cl)(\mu\text{-}Me_3SiC_3SiMe_3)Zr(Cl)Cp_2]$[2], activated with MeLi, and found that under reaction conditions transformation of the allenediide bridging unit into an alkynyl fragment occurs.[3] The thus formed dinuclear zirconocene alkynyl complex displays catalytic activity for the dehydrocoupling reaction. Based on this finding, we now present a set of related dinuclear group 4 metallocene complexes that can be readily prepared by highly modular reaction of suitable metallocene(IV) alkynyl precursors with metallocene(II) sources.[4] In this contribution, we discuss the synthesis as well as structure and bonding of these complexes and give insights into the unique reactivity of these species.



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