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Talks

Session 8

Alkali metal heavyweights: big contenders for homogeneous catalysis?

R. Mulvey[1]

[1]University of Strathclyde, Glasgow, Scotland

Lithium, the lightest alkali metal, has long punched above its weight in synthesis, with organolithium compounds displaying exceptional versatility as brilliant bases, nucleophiles, and ligand transfer agents, etc. However, while lithium is an undisputed champion in stoichiometric applications, it has a poor track record in catalytic applications. Though certain organosodium and organopotassium compounds are well known for specialised synthetic tasks, their chemistry, and especially that of rubidium and caesium, still requires substantial fundamental development. The question to address is, "can these heavy metals become viable contenders for lithium's crown in the future and indeed take alkali metal mediation into the more challenging catalytic arena?" This presentation will give a snapshot of our recent progress towards this development. Successful catalytic reactions using both homometallic and heterobimetallic complexes will be discussed and comparisons will be drawn between the performances of lithium and its heavy congeners. Supporting experimental findings, mechanistic insight gained from DFT calculations will also be included.

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An organometallic perspective to first-row transition metal catalysis

A. Casitas[1]

[1]Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg E-mail: casitasm@chemie.uni-marburg.de

Catalysis plays a pivotal role in the development of environmentally friendly and efficient chemical processes towards the synthesis of high-value chemicals from abundant and renewable feedstocks. On the quest of more sustainable synthesis, our research group focuses on the discovery and development of organic reactions catalyzed by middle and late first-row metals (Mn, Fe, Co, Ni). Transition-metal catalyzed nucleophilic allylic substitutions are well-established methods for the construction of carbon-carbon and carbon-heteroatom bonds in organic synthesis. In this communication, I will present our work in regioselective cobalt(I)-catalyzed nucleophilic allylic substitution reactions. This project aims at finding complementary reactivity to the well-stablished methods that involve precious metals, while providing an in-depth mechanistic understanding.[1] In the second part of the talk, I will introduce fundamental insights into the reactivity of organoiron species in high oxidation state, which may ultimately find application in catalysis towards organic synthesis. Thus, synthetic strategies to prepare Fe(III) and Fe(IV) cyanide complexes using cyano λ3-iodanes will be disclosed.[2, 3] In addition, the synthesis of highly reactive organometallic alkynylferrates(III) and Fe(IV) alkynylide complexes and their involvement in carbon-carbon bond-forming reactions will be presented.[4]

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Talks

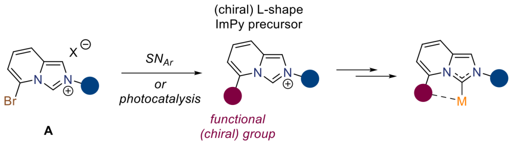
Session 9A

Laterally-functionalized, L-shape N-heterobicyclic Carbene ligands

V. César[1]

[1]Laboratoire de chimie de coordination du CNRS (LCC-CNRS), Université de Toulouse, Toulouse, France, email:
vincent.cesar@lcc-toulouse.fr

L-shape *N*-Heterocyclic Carbene (NHC) based on the imidazo[1,5-*a*]pyridine (ImPy) scaffold have recently gained considerable interest as the true carbene ligand analogues of the popular dialkylbiarylphosphines, better known as Buchwald phosphines.[1] Nevertheless, the substitution pattern of ImPy ligands is still rather limited due to synthetic access issues. We have recently exploited this platform to design new laterally-functionalized N-heterobicyclic carbenes and discovered a versatile, divergent synthetic access towards NHC precursors from the key 5-bromoimidazo[1,5-a]pyridinium salt **A**. Our recent achievements in this area will be discussed, focusing on gold(I) enantioselective catalysis,[2] photocatalysis,[3] and bio-inspired thiolate ligands[4].



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Merging aerobic/moisture-compatible *s*-block organometallic reagents (RLi/RMgX) with enzymes for the enantioselective synthesis of chiral alcohols

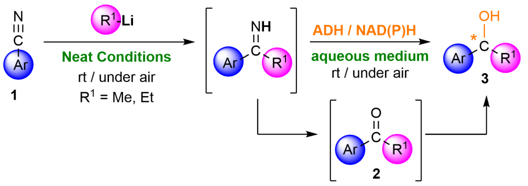
J. García-Álvarez[1], N. Ríos-Lombardía[1]*, G. Morís-Menéndez[1]*, I. Lavandera[2]*, V. Gotor-Fernández[2]*

[1]Laboratorio de Química Sintética Sostenible (QuimSinSos), Organic and Inorganic Chemistry Department, Instituto de Química Organometálica Enrique Moles, University of Oviedo. Avenida Julián Clavería 8, 33006 Oviedo, Asturias (Spain),
[2]Organic and Inorganic Chemistry Department, Instituto de Química Organometálica Enrique Moles, University of Oviedo. Avenida Julián Clavería 8, 33006 Oviedo, Asturias (Spain)

Recent innovations from our research group and others have demonstrated that, in contrast with the conventional wisdom, polar *s*-block organometallic reagents (RLi/RMgX) can be used: *i*) under air; *ii*) in sustainable, protic, non-toxic, and non-dried solvents [such as Deep Eutectic Solvents (*DESs*) or even water]; and *iii*) at room temperature and under air/moisture.[1] Consequently, this paradigm shift in polar organometallic chemistry illustrates the capability of RLi/RMgX reagents to operate under conditions compatible with other catalysts, such as enzymes, thus opening new avenues for the design of one-pot hybrid chemoenzymatic cascades.[2]

Here, we present, for the first time, a hybrid chemoenzymatic approach that integrates organolithium- or Grignard-mediated synthesis of prochiral ketones with a concomitant enantioselective biocatalytic step in a one-pot fashion, performed under air and at room temperature.[3] Unlike previous chemoenzymatic strategies, which have primarily combined transition metals or organocatalysts with enzymes, our methodology explores the unexploited potential of using polar organometallic reagents in combination with asymmetric biotransformations.

This novel approach enables the conversion of nitriles into enantiopure chiral secondary alcohols through a streamlined two-step sequence. The key challenge was to harmonize the reactivity of organolithium/organomagnesium reagents and alcohol dehydrogenases (*ADHs*) within the same reaction vessel. The RLi/RMgX addition proceeded with complete chemoselectivity, yielding prochiral imines under neat conditions. Subsequent hydrolysis, followed by precise pH adjustment, set the stage for the biocatalytic reduction.



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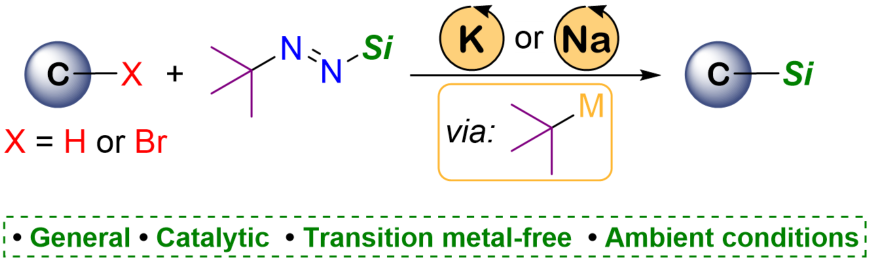
Organoalkali-Catalyzed C–Si Cross-Couplings with *N-tert*-Butyl-*N*'-Silyldiazenes

C. Chauvier[1]

[1]Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, 75005 Paris, France

Organosilicon compounds have become indispensable tools in the chemical sciences, as evidenced by their growing applications in organic synthesis, drug discovery, and materials science. Among the conventional methods for C–Si bond formation, cross-coupling reactions provide a particularly versatile route to organosilicon compounds due to the broad range of organic substrates and silylating reagents that can be used.[1] However, many of these methods are limited by the specific nature and/or amount of promoters required to facilitate the key C–Si bond formation.

This communication will describe the invention and development of a novel C–Si cross-coupling strategy through the design of a new class of silylating reagents, namely silylated *tert*-butyl diazenes (*t*Bu–N═N–SiR$_3$). The synthetic utility of these reagents will be demonstrated in their ability to rapidly assemble diverse organosilicon compounds *via* silylation of C–H[2] and C–Br[3] bonds upon simple treatment with catalytic amounts of alkali metal alkoxides. Mechanistic considerations highlighting the involvement of alkali metal-stabilized *tert*-butyl carbanion intermediates will also be discussed along with their conceptual implications, notably for transposing the stoichiometric metalation chemistry of group 1 polar organometallic reagents (e.g. organolithium compounds) into a catalytic framework.



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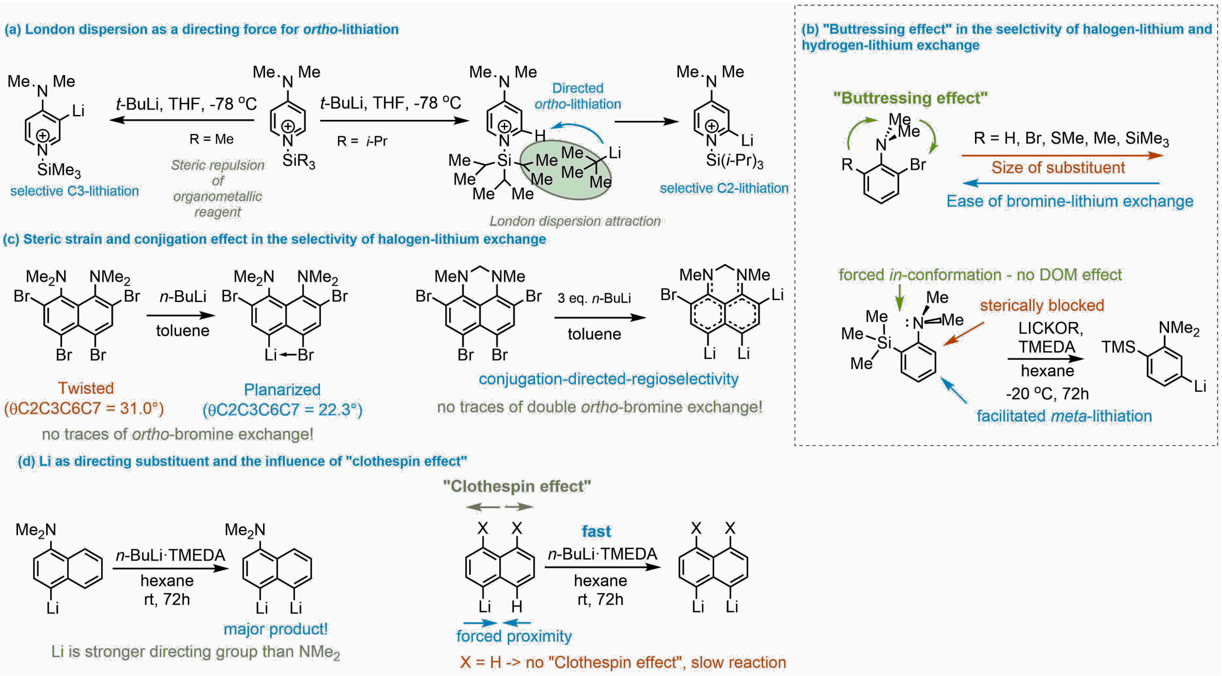
Modulating Organolithium Reactivity with Steric Interactions

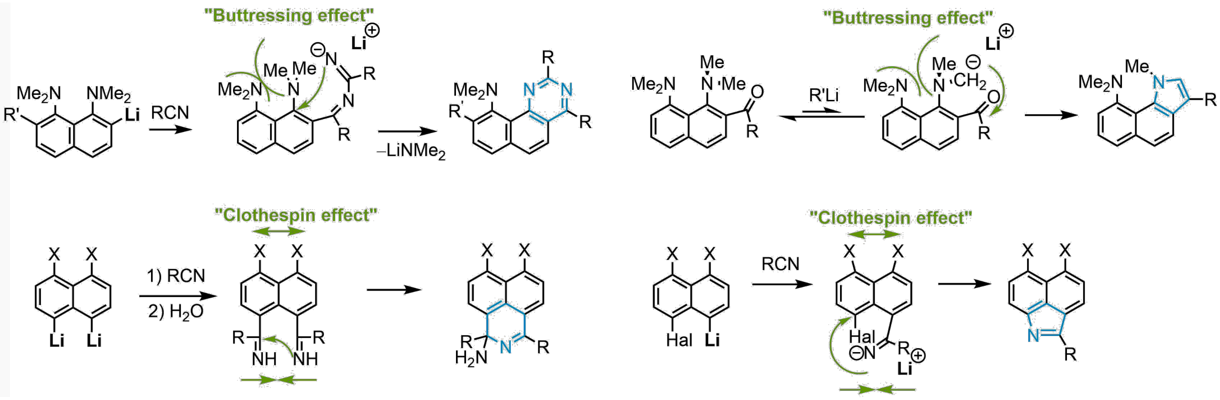
A. S. Antonov[1]

[1]Universität Regensburg, Universitätsstr. 31, 93053 Regensburg

Pioneered by Wilhelm Schlenk in 1917, organolithium reagents drastically elevated their role in synthetic chemistry over the past hundred years and solidified their position among the most versatile and widely used reagents in organic synthesis. The ability to adjust the reactivity of organolithium compounds through different non-covalent interactions is their most fascinating feature. In this study, we explore how steric interactions influence the efficiency and selectivity of halogen-lithium exchange and CH-lithiation in carbo- and heteroaromatic amines with significant steric hindrance (Scheme 1).



We demonstrate the effective utilisation of sterically hindered lithionaphthalenes as a versatile scaffold for simple synthesis of challenging heterocyclic systems (Scheme 2).



More is different: anion-encapsulating sodium alkoxide clusters (X@RONa) as multi-functional Lewis acid catalysts

Z. Li[1]

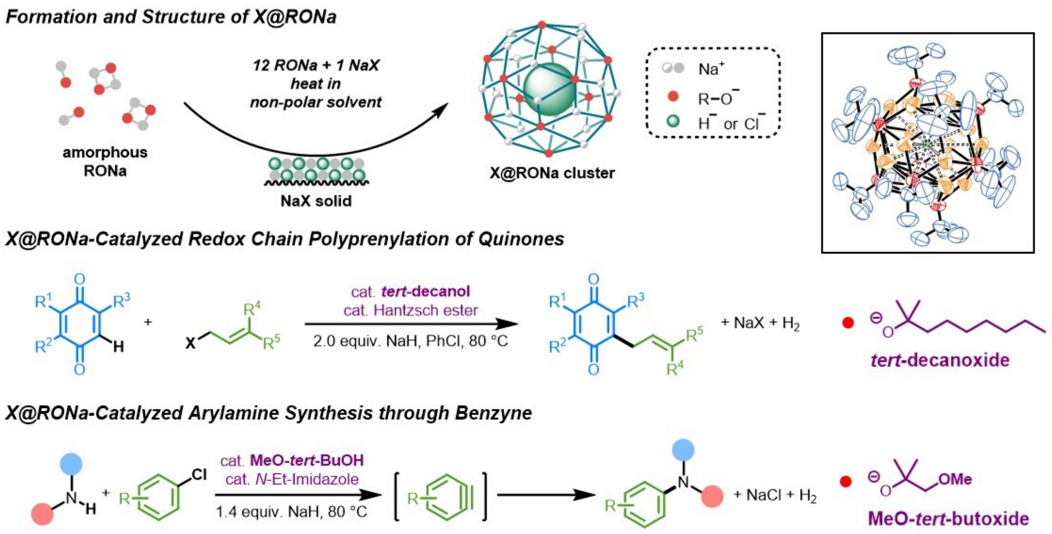
[1]School of Physical Science and Technology, ShanghaiTech University, 393 Middle Huaxia Road, Shanghai

At the presence of halide or other small anions, sodium *tert*-butoxide self-assembled into dodecameric anion-encapsulating molecular clusters $(NaOt\text{-}Bu)_{12}NaX$, where X is the encapsulated anion. Many sodium alkoxides (RONa) are capable of forming the same type of X-encapsulating clusters, which could be generalized as "X@RONa". Such clusters were first discovered and characterized in 2010[1] but catalytic reactivities were not explored.

Herein, we report that they indeed showed distinct reactivity from the monomeric or other oligomeric sodium alkoxides. They can be designed to accomplish different catalytic functions as Lewis acids in organic synthesis.

First, we demonstrated that X@RONa was able to promote transition-metal-free polyprenylation of quinones through redox chain mechanism. Many biologically important polyprenylquinones were synthesized from corresponding parent quinone and polyprenyl halide in one step and high yield. In this case, the best catalyst was found to be X@RONa based on *tert*-decanol.[2]

Second, X@RONa was applied in catalytic scalable, transition-metal-free C-N bond formation. X@RONa was capable of catalytically promoting benzyne formation from simple aryl chlorides, as well as the subsequent arylation of amines. From very simple and cheap aryl chlorides, aryl amines can be easily synthesized in large scale. It is also a rare case of large-scale application of benzyne. In this case, the best catalyst was found to be X@RONa based on 1-methoxy-2-methyl-2-propanol.[3]



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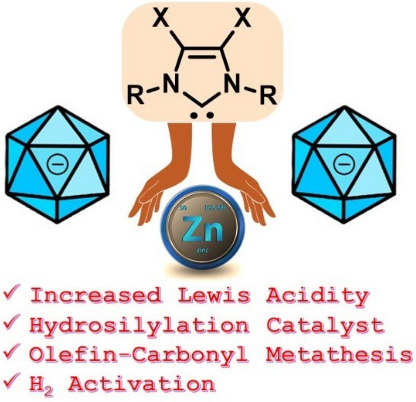
Unprecedented Low-coordinate Zn(II) Cations and Di-cations: Synthesis & Catalytic Exploration

S. Munshi[1], V. Timofeeva[1]*, S. Dagorne[1]*

[1]Institut de Chimie (UMR CNRS 7177), Université de Strasbourg, 4, rue Blaise Pascal, 67000 Strasbourg, France

Lewis acid catalysis is an effective and versatile approach for a variety of organic transformations.[1] The catalytic activity of a metal complex in these reactions is primarily influenced by its Lewis acidity, which is determined by the coordination number and charge of the central atom. Due to their enhanced electrophilicity, cationic Zn(II) complexes, particularly organozinc species, serve as valuable reagents and catalysts in organic synthesis, especially for functionalizing unsaturated substrates.[2] Our group specifically focuses on low-coordinate and/or weakly coordinated Zn(II) cations to enhance electrophilic activation, thus facilitating effective substrate functionalization in both stoichiometric and catalytic contexts. In particular, to maximize electrophilicity, a "pseudo-naked" Zn^{2+} cation only stabilized (in solution) by weakly coordinating anions was recently reported, and found to exhibit higher Lewis acidity than the well-established Lewis acid $B(C_6F_5)_3$.[3] In this study, we demonstrate that the enhanced σ-donating abilities of N-heterocyclic carbene (NHC) ligands[4] enable the stabilization and isolation of a wide range of Zn(II) di-cationic-like complexes with tuneable and enhanced Lewis acidity. These complexes exhibit high reactivity in hydrosilylation reactions involving alkenes, alkynes, and CO_2, as well as in carbonyl–olefin metathesis reactions. Moreover, the Lewis acidity of the metal centres has been adeptly utilized for the activation of H_2 and the subsequent hydrogenation of imines. This research not only highlights the versatility of Zn(II) complexes but also paves the way for new explorations in catalytic processes involving main-group metal cations.



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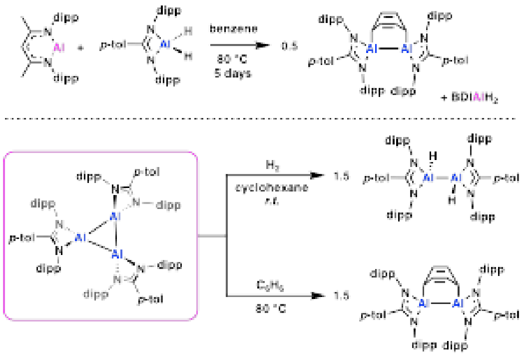
A neutral aluminium (I) trimer

C. Bakewell[1], I. Squire[1]*, M. Tritto[1]*, M. de Vere-Tucker[1]*, T. Kramer[1]*

[1]King's College London

Low oxidation state aluminium (Al) compounds are a class of molecule that have received considerable attention in recent years, owning to their ability to oxidatively cleave a host of strong chemical bonds and activate many industrially and environmentally relevant small molecules. Whilst challenging to isolate, there are now numerous examples of neutral monomeric Al(I) species, and more recently aluminyls Al(I)$^-$ [1]. However, fewer examples of dimeric Al(I) molecules, dialumenes, that feature an Al=Al double bond are known. Over recent years, we have reported the reactivity of a dialumene, formed transiently under reductive conditions, with a variety of aromatic molecules [2, 3]. In all cases, the dialumene is trapped as a dialumene-benzene adduct (Figure 1 top).



Despite the formation of oxidative addition products, we were unable to observe any transient Al(I) species experimentally. We therefore sought to directly isolate the low oxidation state species. Herein, we present the isolation and characterisation of an unprecedented neutral Al(I) trimer, a trialumane (Figure 1 bottom). The electronic structure has been interrogated using DFT and the reactivity towards a variety of small molecules is presented [4].

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Talks

Session 9B

Synergistic approaches to overcome some limitations in asymmetric hydrogenation. New tricks for an old reaction

M. Dieguez[1]

[1]Universitat Rovira I Virgili. Departament de Química Física I Inorgànica. C/Marcel·lí Domingo 1, 43007 Tarragona. Spain

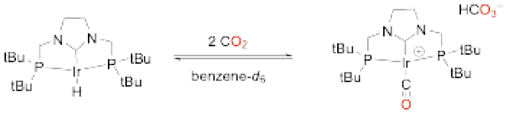
Asymmetric hydrogenation has become a highly reliable and powerful method for synthesizing chiral compounds. A key challenge is expanding the range of substrates that can be effectively converted to enantiopure products, which is crucial for synthesizing a wide variety of molecules whose stereochemistry is critical (i.e., pharmaceuticals, biologically active compounds …). Another important challenge in asymmetric hydrogenation is to increase the sustainability of the process. For instance, the tolerated threshold of metals in APIS is very low, which increases the purification costs. Herein, we will present our latest developments focused on overcoming these drawbacks still present for this old reaction.

Room temperature reverse water gas shift reaction mediated by an iridium pincer complex

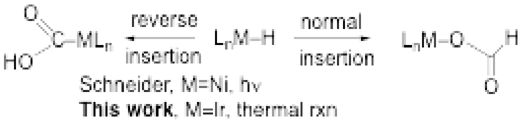
O. F. Wendt[1]

[1]Department of Chemistry, Lund University, LUND, Sweden

Making chemicals from carbon dioxide is very attractive as CO_2 is abundant, inexpensive, non-flammable and non-toxic. Its use is of course CO_2-neutral and can even reduce atmospheric CO_2 levels on the margin. Among the reactions involving CO_2 that have the highest success probability in the short run are those where the reduction is modest, including products such as carboxylic acids and CO. Syngas ($CO+H_2$) is a very useful starting material for the chemical industry and is currently primarily produced from fossil starting materials (mainly methane) in so called steam reforming.[1]Alternative routes will require access to green hydrogen and this contribution describes a metal mediated low temperature reverse water gas shift reaction (rWGS) where CO_2 is reduced with hydrogen to CO and water. This is a reaction that can be performed using heterogenous catalysts but such reactions require very high temperatures, typically above 700 °C.[2] These high temperatures are required both for good catalytic activity but also to drive the highly endothermic rWGS. We have developed iridium catalysts that operate with very high efficiency in both hydrogenation and dehydrogenation.[3] Recently we discovered an iridium pincer complex that is able to hydrogenate CO_2 to CO under ambient conditions, Scheme 1.



The driving force is the coordination of CO to the metal and the key step is a reverse insertion of CO_2 into a metal hydride bond. Such insertions are extremely rare and has previously only been reported under photochemical conditions, Scheme 2.[4] In this contribution we will report on the mechanistic details for both the reverse insertion and the connected rWGS reaction.



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Elucidating Electron Transfer Events in Polypyridine Nickel Complexes

C. S. Day[1], A. Rentería[2]*, S. Ton[3]*, A. Gogoi[2]*, R. Martin[3]*, O. Gutierrez[2]*

[1]University of Copenhagen, Department of Chemistry, Copenhagen, Denmark, [2]University of California, Los Angeles, Department of Chemistry, California, USA, [3]ICIQ, Tarragona, Spain

Polypyridine ligated nickel complexes have found considerable utility as privileged catalysts in a wide variety of cross-coupling reactions.[1] The rapid adoption of these complexes is tentatively attributed to their ability to shuttle between different oxidation states that is enabled by facile electron-transfer. While disproportionation, comproportionation or reduction events play an important role in Ni-catalyzed cross-coupling reactions, the factors responsible for enabling electron-transfer are poorly understood in mechanistic terms.[2] Indeed, progress in this field is mainly based on empirical discoveries. Herein, we disclose an unprecedented look into the reactivity of pseudohalide and halide ligated Ni(II) complexes supported by polypyridine ligands.[3] We have found that the nature of the anionic ligand has a striking impact on the key electron-transfer events. From a broader perspective, this study provides rationalizations to previously overlooked and fundamental steps within the Ni-catalyzed cross-coupling arena, thus offering a new gateway for designing future Ni-catalyzed endeavors.

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Reversible P–P bond cleavage in piano-stool iridium(III) complexes

M. B. Smith[1]

[1]Department of Chemistry, Loughborough University, Loughborough, Leics, LE11 3TU, UK. E-mail address: m.b.smith@lboro.ac.uk

Unlike tertiary phosphines, the coordination chemistry of diphosphanes bearing a P–P single bond has been very poorly studied [1,2]. Herein a novel class of readily accessible diphosphanes, based on a rigid bicyclic framework (Figure 1), will be presented. Furthermore, it will be shown these air stable ligands represent an excellent scaffold for supporting late transition metal fragments such as the ubiquitous "$IrCl_2(C_5Me_5)$" half sandwich group [3,4].

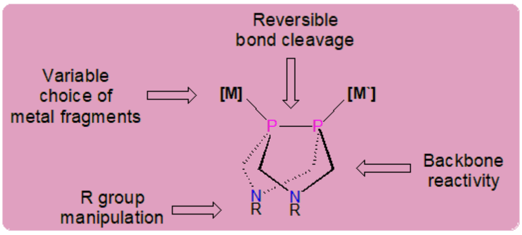

Figure 1.

A striking feature of this work is the reversible nature by which the P–P bond can be cleaved, and reformed, within a series of bridging Ir^{III}/Au^{I}-heterodinuclear complexes. The unusual reactivity of such compounds towards C–C bond formation across both $P_2C_2N(R)$ five-membered rings will also be demonstrated.

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Interrogating the *anti*-Insertion of Alkynes into Gold(III)

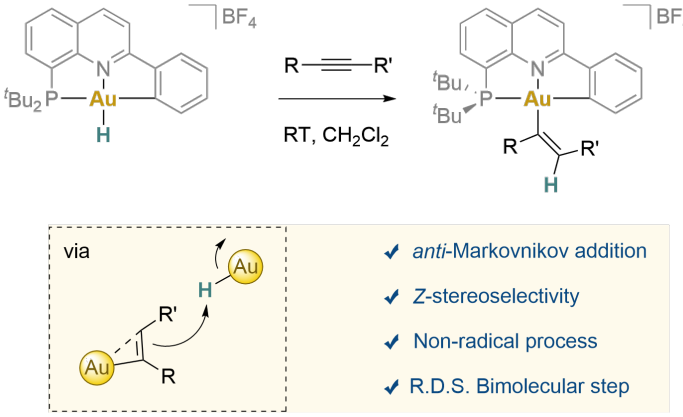
J. Martín[1], J. Schörgenhumer[1]*, C. Nevado[1]*

[1]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, CH 8057, Switzerland

The hydrofunctionalization of alkynes is one of the most synthetically valuable and widely used transformations catalyzed by metals. Over the past decades, the organometallic community has made significant progress in elucidating the insertion of alkynes into transition metal-hydride bonds—a key step in this transformation—leading to the development of more efficient and selective catalytic processes.[1] While *syn*-insertions are well-characterized, *anti*-insertion pathways remain poorly understood and are often proposed based on literature precedents rather than direct experimental evidence.

Gold has played a pivotal role in the efficient hydrofunctionalization of unsaturated moieties, including alkenes, allenes and alkynes.[2] However, in depth mechanistic understanding of the specific alkyne insertion step into gold is still lacking, which stands in stark contrast to the extensive knowledge amassed for other transition metals in similar processes. This paucity is largely due to the scarcity of stable gold hydrides.

We have recently reported a novel class of (P^N^C) pincer ligands capable of stabilizing gold(III)-hydrides under very mild conditions.[3] Here we present that, despite their non-hydridic character, (P^N^C)gold(III) hydrides are able to insert both terminal and internal alkynes yielding the corresponding *anti*-Markovnikov addition *Z*-vinyl configured complexes in the absence of external additives. Despite the apparent simplicity of this two-component reaction, a combination of control experiments, kinetic studies, and computational analyses reveals a more complex scenario in which water plays a prominent role in the formation and stabilization of coordinatively unsaturated gold species, likely implied in other gold-mediated transformations.[4]



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B_2pin_2-mediated Ligand Deprotonation Enables Selective Iridium-catalyzed C-H Borylations Revealed by Click Ligands

V. Delahaye[1], S. Derien[1]*, M. Achard[1]*, R. Gramage-Doria[1]*

[1]University of Rennes, CNRS, Rennes Institute of Chemical Sciences, 263 avenue du General Leclerc, 35042 Rennes, France

Iridium-catalyzed C-H bond borylation reactions have revolutionized the way of conceiving chemical synthesis by providing step- and atom-economy methodologies using bench stable boron precursors such as bis(pinacolato)diboron (B_2pin_2).[1] Indeed, the access to boron-containing building blocks is highly attractive since straightforward post-modifications can lead to new carbon-carbon and carbon-heteroatom bond formations. Iridium-catalyzed C-H borylation of aromatics have been developed and the regioselectivity is controlled by the steric and electronic nature of the substrate as pioneered by Hartwig.[2] To bypass the inherent reactivity of iridium at sterically accessible sites, catalyst-to-substrate coordination appears as a promising strategy.[3] For that, well-defined, and typically sensitive, anionic ligands have been developed in order to form catalytically active iridium species allowing substrate-coordination towards proximal selectivity.[4-5] Herein, we present a fundamentally new approach in which the anionic ligand forms *in situ* upon reaction of the iridium pre-catalyst with the boron reagent B_2pin_2. This new action mode has been exploited to control the regioselectivity in unbiased substrates that impose selectivity issues when using standard iridium catalysts. As such, these results disclose the manifold role of B_2pin_2 and rises questions about previous, postulated action modes[6] in which the ligand could eventually *in situ* switch from neutral to anionic during the catalysis.

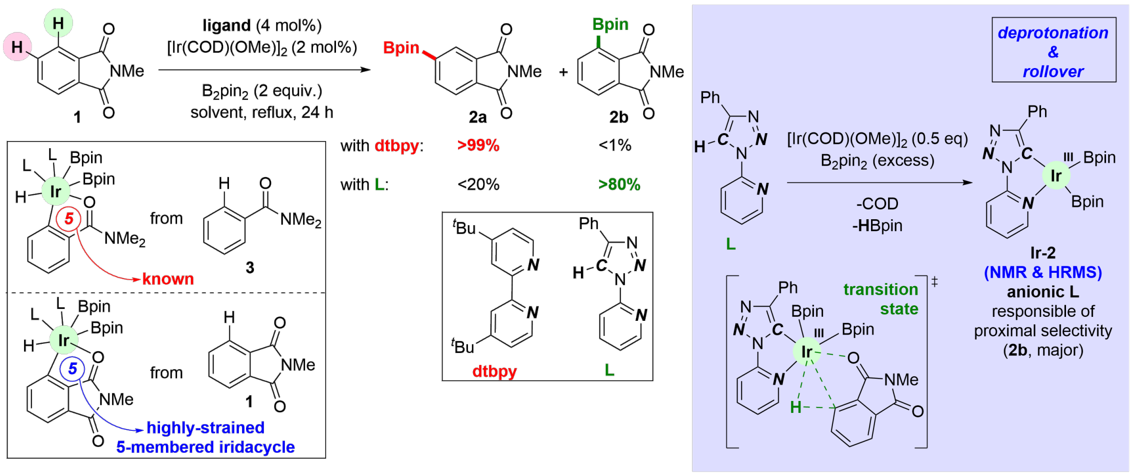

Figure 1 Click ligands enabling proximal C-H bond borylation selectivity via a unique action mechanism mediated by B2pin2.

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DFT Studies on Cross-coupling Reactions Catalyzed by Gold (I/III) complexes

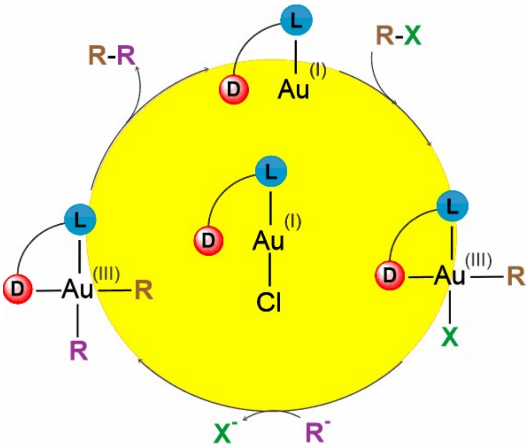
C. Costabile[1], G. Galdi[1]*, A. Brotons-Rufes[1]*

[1]Department of Chemistry and Biology "A. Zambelli", University of Salerno Via Giovanni Paolo II, 84084 Fisciano (SA), Italy

In the past two decades, gold emerged as one of the most important metal in catalyzed organic reactions.[1] After the pioneering work of Bourissou on diphosphine gold complexes, many efforts were focused on the development of ligands able to stabilize Au(III) species [2], in order to promote cross coupling reactions (Scheme 1).

Inspired by the experimental work of Russell and coworkers, [3] we performed a DFT study on the mechanism involved in 1,2-oxyarylation of ethylene promoted by gold catalysts bearing hemilabile N-Heterocyclic Carbene (NHC^X) ligands. In the attempt to design a promising catalyst, electronic and steric NHC properties were tuned, showing that the NHC^P combination revealed of high interest for the stabilization of Au(III) species involved in the reaction.[4]

Aiming at generalizing the main findings of this investigation, we extended the mechanistic studies to organic challenging reactions, as the synthesis of aryl amides and aryl carbamates by C−N cross-coupling of aryl iodides with alkyl nitriles [5], highlighting the main differences between Au and Pd catalyzed reactions.



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Talks

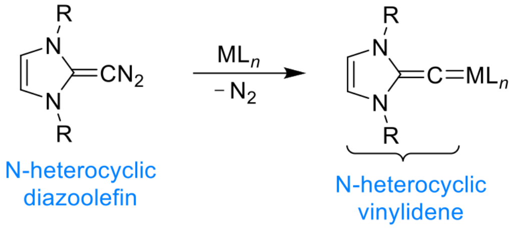
Session 10A

N-Heterocyclic Vinylidene Ligands

K. Severin[1]

[1]Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Diazoolefins of the general formula (NHC)=CN_2 can be obtained by reactions of the corresponding N heterocyclic olefins, (NHC)=CH_2, with the diazo transfer reagent nitrous oxide.[1] Upon combination of diazoolefins with suited metal precursors, complexes with N heterocyclic vinylidene ligands are obtained (see Figure below). Our investigations have shown that N-heterocyclic vinylidenes are unique C-donor ligands.[2-4] They can donate up to 6-electrons to the metal center, making them well-suited for the stabilization of low-coordinate complexes. Complexes with N-heterocyclic vinylidene ligands show a diverse reactivity in reactions with electrophiles and nucleophiles.



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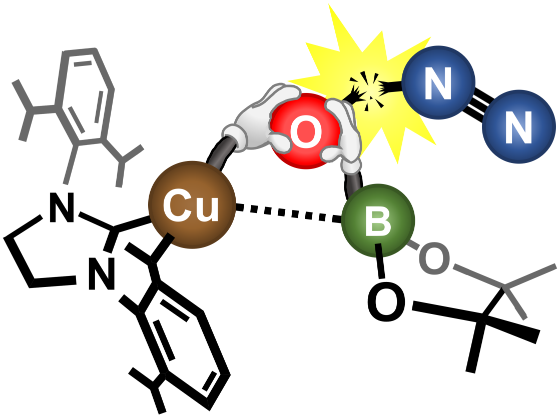
Copper(I) Catalysed Diboron(4) Reduction of Nitrous Oxide

A. B. Chaplin[1], T. M. Hood[1]*, A. C. C. Ward[1]*, R. S. C. Charman[2]*, D. J. Liptrot[2]*, T. Krämer[3]*

[1]Department of Chemistry, University of Warwick, UK, [2]Department of Chemistry, University of Bath, UK, [3]School of Chemistry, Trinity College Dublin, The University of Dublin, Ireland

Nitrous oxide (N_2O) is a long-lived gas that accumulates in the atmosphere, contributing to climate change as a potent greenhouse gas and leading to ozone depletion in the stratosphere.[1] Although chemical activation is challenging, exponentially increasing anthropogenic emissions of N_2O make it imperative that methods are developed for the remediation and repurposing of this atmospheric pollutant.[2,3] Catalytic deoxygenation reactions which liberate N_2 are attractive targets but, despite benefiting from favourable thermodynamics, are poorly established. Inspired by the homogeneous process established by Sadighi for the reduction of isoelectronic CO_2,[4] we proposed that NHC-ligated copper(I) boryl complexes would be effective catalysts for the reduction of N_2O to N_2 using diboron(4) reductants. We herein report on the evaluation of this hypothesis using range of copper(I) precatalysts alongside supporting mechanistic and computational analysis.[5]



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Mechanistic Studies of N–C Bond Formation from Dinitrogen and Hydrocarbons

N. Hidalgo[1], S. M. Bhutto[1]*, B. Q. Mercado[1]*, P. L. Holland[1]*

[1]Yale University, Department of Chemistry, New Haven, Connecticut 06520, USA.

The formation of N–C bonds from dinitrogen (N_2) via organometallic chemistry is severely limited to only a handful of reaction pathways.[1] Performing such N_2 functionalization chemistry using sustainable, first-row metals has proven challenging using carbon electrophiles. Our group has developed a system for the C–H amination of unactivated arenes directly from N_2 by a low-valent iron complex, resulting in formation of anilines in a one-pot reaction that proceeds cyclically.[2] These results point the way toward the use of N_2 as a synthon for N-containing organic molecules without dependence on ammonia as an intermediate.

We have previously studied the N–C bond forming step in this reaction involving migratory insertion of the aryl group.[3] Here, we describe studies on the step with C–H activation of the arene, which are greatly influenced by the alkali metal cation. We have successfully isolated key alkali metal complexes and describe their structures, energetics, and reactivity toward C–H activation.[4]

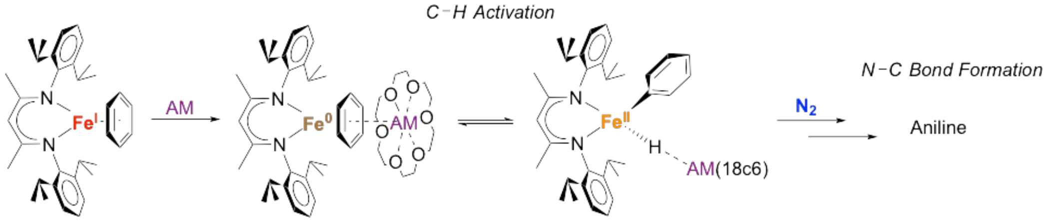

Figure 1. Representative example of N–C bond formation from inactivated arenes and N_2. AM = Alkali Metals.

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Comprehensive Study of Highly Reduced Ruthenium and Iron Carbide Carbonyl Clusters/p

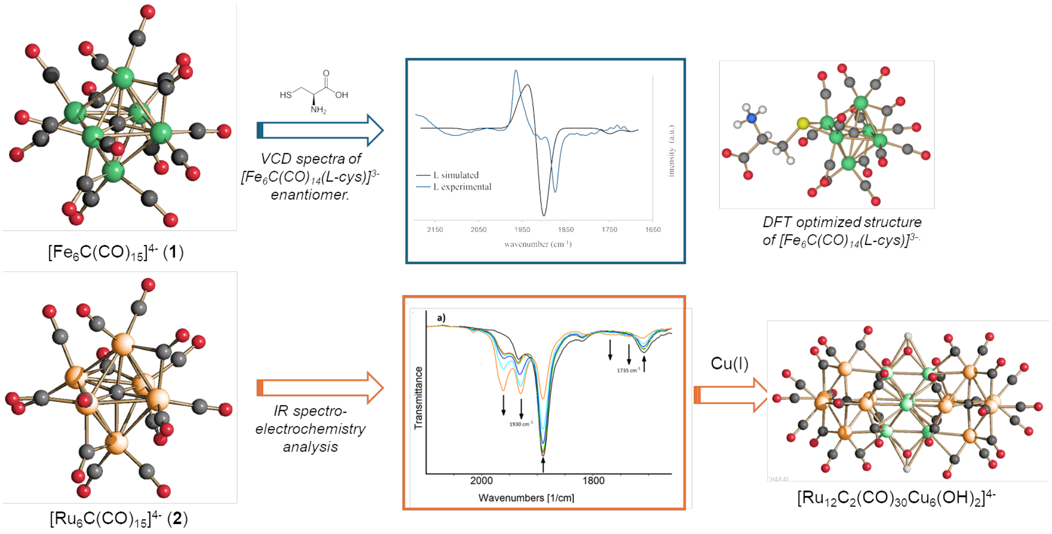
C. Cesari[1], F. Forti[1]*, G. Scorzoni[1]*, M. Bortoluzzi[2]*, T. Funaioli[3]*, S. Zacchini[1]*

[1]Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Via Gobetti 85, 40129 Bologna, Italy, [2] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca’ Foscari Venezia, Via Torino 155, 30175 Mestre (VE), Italy, [3]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy

Metal carbide carbonyl clusters, typically featuring transition metal atoms in low oxidation states bonded to carbonyl ligands and carbide atoms, are important for studying the reactivity of carbon atoms on metal surfaces and metal nanoparticles. Recently, these clusters have gained interest for electrocatalytic applications and as models for enzymes such as nitrogenase.[1]

Within this framework, our research group synthesized and characterized highly reduced Iron and Ruthenium carbide carbonyl clusters $[Fe_6C(CO)_{15}]^{4-}$ (**1**) and $[Ru_6C(CO)_{15}]^{4-}$ (**2**). These hexanuclear clusters exhibit enhanced stability due to a fully interstitial C-atom within the octahedral cage. [2][3]

In this study, we explore their redox behavior using chemical, electrochemical, and IR spectroelectrochemical methods, supported by DFT studies. Thiol addition to the iron cluster **1** leads to oxidative CO substitution, forming tri-anion carbide clusters of the general formula $[Fe_6C(CO)_{14}(SR)]^{3-}$. The chirality of products with enantiopure L- and D-cysteine has been analyzed via vibrational circular dichroism (VCD) and computational studies. Furthermore, the anionic ruthenium cluster **2** can form high-nuclearity heterometallic species with Cu(I) and Ag(I), and react with $Au(PPh_3)Cl$ to form various decorated clusters.



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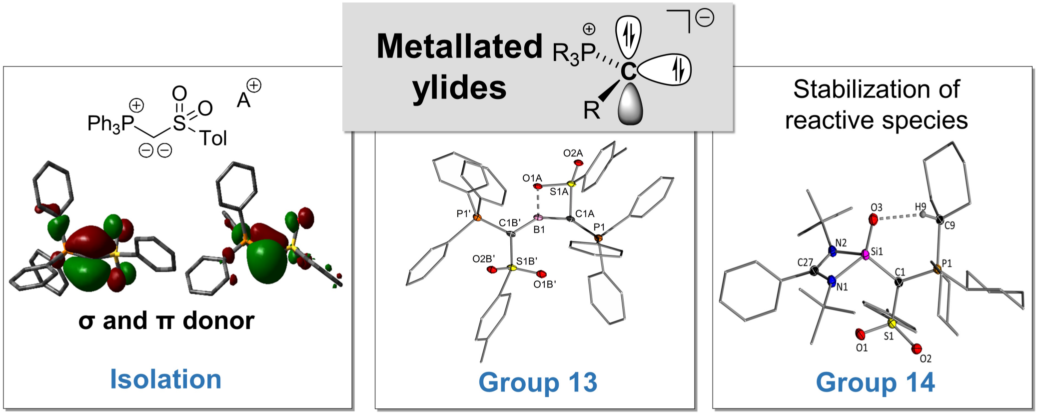
Ylide-Functionalized Low-Valent Main Group Compounds

V. H. Gessner[1]

[1]Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany

Bulky donor substituents, such as amino or alkyl groups, are frequently used in main group chemistry to stabilize reactive species as well as in ligand design to tailor the electronic and steric properties. For example, amino substituents are often applied in low-valent main group compounds (e.g. carbenes) to balance the electron-deficiency of the central atom, while bulky alkyl groups are used in phosphines to enhance their donor capacity and create active homogenous catalysts.[1]

In the past years, our group has established α-metallated ylides as versatile reagents for the introduction of ylide-substituents (Figure 1). Metallated ylides formally possess two lone pairs of electrons at the ylide carbon atom, allowing them to function as monoanionic σ- and π-donor ligands. As a result, they serve as ideal substituents for stabilizing electron-deficient compounds and accessing electron-rich phosphines.[2] Additionally, they showed a unique propensity for exchanging the phosphine group to access novel s-block metal reagents.[3,4] In this presentation, we will showcase the application of metallated ylides in the isolation of reactive main group compounds, discussing their synthesis, properties and reactivities.[5]



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Cationic Polyhedral Heteroboranes – Going from obscure species to metal complexes and catalysis

A. Ruzicka[1], J. Vrana[1]*, V. Nemec[1]*, J. Holub[2]*

[1]Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, Pardubice, CZ 532 10, Czech Republic, [2]Institute of Inorganic Chemistry, Czech Academy of Sciences, 250 68 Řež, Czech Republic

In the hundred-year-history of boron hydrides and their successors (polyhedral boranes, carboranes and other heteroboranes) and derivatives, the number, molecular shape, reactivity and applications of these species have become enormous, thus establishing a self-consistent field of chemistry. Areas of possible applications of these species ranging from energy/hydrogen storage, synthetic organic chemistry, catalysis and medicine to preparation of new materials. Polyhedral boranes and hereroboranes appear almost exclusively as neutral or anionic species, while the cationic ones are protonated at exoskeletal heteroatoms or they are instable.

Taking these considerations into account, one could expect that the addition of a strong σ-donor such as NHCs would increase the electron density on those traditionally taken electron-deficient skeletons and stabilise them like in the many cases of low-valent or cationic main-group elements. Surprisingly enough, the addition of NHCs to 10-vertex closo dicarbaborane species followed by subsequent addition of protonation agent produced cationic cages.[1] Similar strategy has been applied to ionization of thia- and selenaboranes.[2] In this work, we would like to demonstrate the power of NHC donation for stabilization of unusual species, synthesis of various transition metal-containing compounds (Fig. 1) and its use in homogenous catalysis.

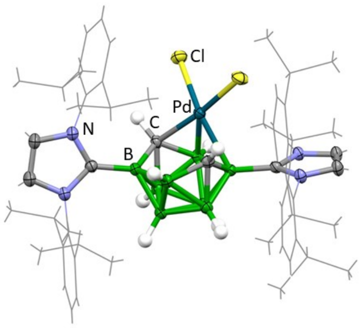

Figure 1 An example of NHC stabilized compound neutral dicarbaborane-$PdCl_2$ complex.

This work was supported by Czech Science Foundation grant nr. 22-03945S.

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Radical Pathways in Hydrogen Activation: Unconventional Reactivity of Palladium(I) Metalloradicals

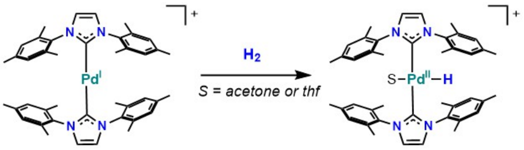
C. Yebra[1], S. de Toro[1]*, A. Lledós[2]*, G. Maties[1]*, P. Gómez-Sal[1]*, A. Martín[1]*, R. Andrés[1]*, E. de Jesús[1]*

[1]Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Rio",
Universidad de Alcalá, Campus Universitario, E-28805 Alcalá de Henares, Madrid, Spain., [2]Departament de Química,
Edifici C.n, Universitat Autónoma de Barcelona,08193 Cerdanyola del Vallés, Catalonia, Spain

Hydrogen typically coordinates with transition metals, initially forming M-(H_2) adducts, which can further evolve into their oxidative addition isomers, metal-dihydrides, depending on the electronic properties of the metal center.[1] Hydride ligands are generally categorized into four types based on the separation between the coordinated hydrogen atoms: Kubas-type dihydrogens, elongated dihydrogens, compressed dihydrides, and classical hydrides.[2] Recent findings highlight uncommon bonding situations, including paramagnetic complexes, in which a non-classical H_2 adduct can act as a precursor for outer-sphere H-atom or hydride transfer. [3]

We recently reported the first air-stable palladium(I) metalloradical featuring an *N*-heterocyclic carbene ligand, $[Pd(IPr)_2]^{\bullet+}$, which reversibly binds and reduces molecular oxygen, forming the three-coordinate superoxide Pd(II) species $[Pd(IPr)_2(\eta^1\text{-OO}\bullet)]^+$.[4]

Building on our ongoing research into the activation of small molecules by mononuclear Pd(I) complexes, we now show that the metalloradical $[Pd(IMes)_2]^{\bullet+}$ activates H_2, ultimately yielding the monohydride complex $[Pd(IMes)_2(H)(S)]^+$ (S = acetone, THF). NMR spectroscopy, isotopic labeling, and theoretical studies support an unconventional radical pathway for H_2 activation, involving the release of an H• radical.



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Talks

Session 10B

Applications of Mn(I) and Fe(II) Complexes involving E-H (E = H, C, Si, B) Bond Activation Reactions

K. Kirchner[1]

[1]Institute of Applied Chemistry

The utilization of base-metal catalysts represents an emerging field in homogeneous catalysis. Among others, manganese-based complexes were proven to be highly competitive catalysts for several (de)hydrogenation reactions.

This lecture outlines the potential of Mn(I)- and Fe(II)-carbonyl alkyl and related complexes for the activation of non-polar and moderately polar E-H (E = H, C, Si, B) bonds and disclose our successful approach for the utilization of complexes in the field of homogeneous catalysis.[1-5] We took advantage of the fact that Mn(I) and Fe(II) alkyl carbonyl complexes undergo migratory insertion of the nucleophilic alkyl ligand into the polarized CO moiety, yielding via a coordinatively unsaturated acyl complex the catalytically active M-E and/or M-H species.

Our investigations unveiled novel insights in reaction pathways of the hydrosilylation and hydroboration of alkenes and alkynes, hydrogenations of alkenes, alkynes, ketones and the selective isomerization of alkenes.

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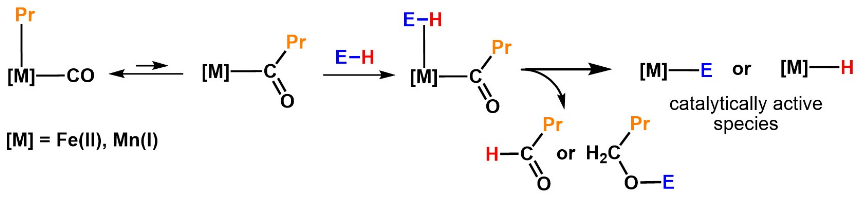
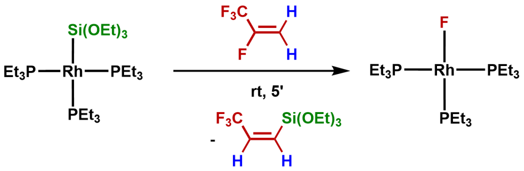


Rhodium-Mediated C-H and C-F Bond Activation to Access Fluorinated Alkene Derivatives

T. Braun[1], C. von Hahmann[1]*, S. Mollasalehi[1]*, M. Talavera[1]*

[1]Department of Chemistry, Humboldt-University Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

Useful methods for a metal-mediated derivatization of fluorinated molecules are often based on C−H or C−F bond activation reactions.[1] In order to make C−F bond cleavage steps feasible, other strong element−fluorine bonds such as H−F or Si−F bonds have to be formed. Thus, at rhodium, highly reactive Rh(I) species such as [Rh(H)(PEt_3)$_3$], [Rh{Si(OEt)$_3$}(PEt_3)$_3$] or [Rh($GePh_3$)(PEt_3)$_3$] can serve as suitable tools to induce a C−F bond activation step, but also C−H bond activation reactions.[2] Stoichiometric studies at the rhodium complexes as well as initial catalytic reactions for the hydrodefluorination, silylation or germylation of olefinic precursors will be described (Figure). In another spin-off catalytic cross-coupling reactions were developed, which are characterized by an outer-sphere C-C coupling step.



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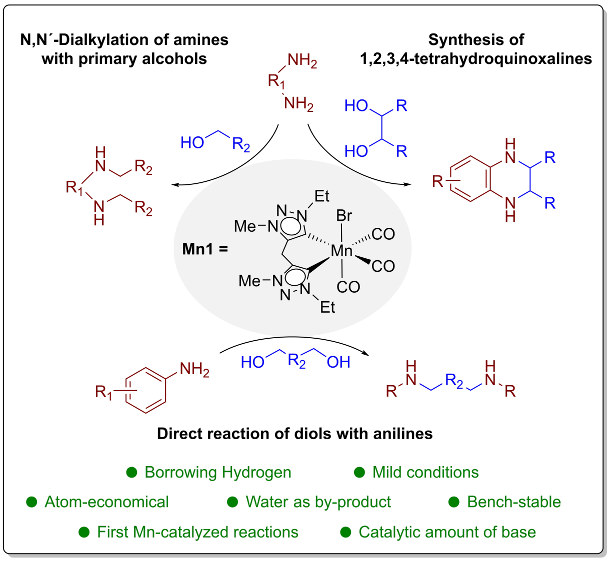
Triazolylidene Mn Complexes in Borrowing Hydrogen Reactions

B. Garcia[1], S. Friães[1]*, D. Raydan[2,1]*, M. M. Marques[2]*, B. Royo[1]*

[1]ITQB NOVA, Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Avenida da República, 2780-157 Oeiras, Portugal, [2]REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa

The borrowing hydrogen (BH) process efficiently forms C-N bonds from alcohols and amines, enabling *N*-alkylation and the direct synthesis of diverse *N*-heterocycles. While early studies relied on noble metal catalysts, recent efforts prioritize earth-abundant metals, particularly manganese. Pioneering work by Beller and Milstein with Mn-PNP pincer complexes spurred research in this area.[1] Though phosphine-based ligands play a key role in Mn-catalyzed BH, developing phosphine-free systems remains crucial for improving sustainability and cost-efficiency.

In our group, we have developed manganese phosphine-free catalytic systems for a range of reactions, utilizing *N*-heterocyclic carbenes as supporting ligands. Recently, we and others reported the excellent catalytic activity of [Mn(bis-NHC)(CO)$_3$Br] (NHC = imidazolylidene or 1,2,3-triazolylidene) complexes in the *N*-alkylation of amines with primary alcohols.[2] Herein, we present a BH method for synthesizing 1,2,3,4-tetrahydroquinoxalines from *o*-phenylenediamine and diols under mild conditions (80 °C) using Mn(bis-1,2,3-triazolylidene)(CO)$_3$Br] as a catalyst. Additionally, this catalyst also enables *N*,*N*'-dialkylation of *o*- and *p*-phenylenediamines with primary alcohols, and the selective dialkylation and monoalkylation of aniline with aliphatic diols, affording amines in high yields under mild conditions (100 °C, 6 h). This air-stable, easily prepared Mn catalyst exhibits broad substrate compatibility.[3]



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Ni(0)-Olefin Pincer Complexes for Catalytic Hydrogenation of Carbonyl Compounds *via* Metal-Ligand Cooperativity

C. Binnani[1], M. E. Moret[1]*

[1]Institute for Sustainable and Circular Chemistry (ISCC), Utrecht University, Utrecht, Netherlands

Catalytic hydrogenation is a fundamental transformation in the industrial production of pharmaceuticals, agrochemicals, and fine chemicals.**[1]** The selective hydrogenation of carbonyl compounds is particularly important, as it enables the synthesis of alcohols, which serves as key intermediates in various chemical processes. Conventional hydrogenation methods typically use precious metal catalysts, which are expensive and can pose environmental concerns.**[2]** Therefore, there is a growing interest in designing and developing efficient catalysts based on 3d transition metals. Current homogeneous nickel catalysts for carbonyl hydrogenation often suffer from low selectivity and require harsh reaction conditions.**[3]** Recent studies have demonstrated that pincer-type nickel complexes can enhance catalytic performance by utilizing metal-ligand cooperativity (MLC), wherein the ligand actively participates in bond activation, enabling milder and more selective hydrogenation.**[4]** The Moret group has recently demonstrated the ability of Ni(0)-olefin complexes to catalyze selective semi-hydrogenation of internal alkynes via a ligand-to-ligand hydrogen transfer (LLHT) mechanism.**[5]** In this contribution, we report on the use of Ni(0)-olefin pincer complexes for the hydrogenation of carbonyl compounds. Kinetic studies, deuterium labelling experiments, and density functional theory (DFT) calculations together support a cooperative mechanism in which LLHT to the olefinic backbone plays a key role. For a deeper understanding of these processes, structure-activity relationship is investigated by introducing structural modifications such as silyl substituents on the olefin backbone.

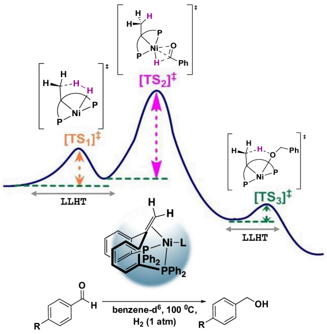

Figure 1. Ni(0)-olefin complex for the catalytic hydrogenation of carbonyl compounds and mechanistic insights.

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Metal amido complexes for kicks, clusters, and catalysis

A. Jacobi von Wangelin[1]

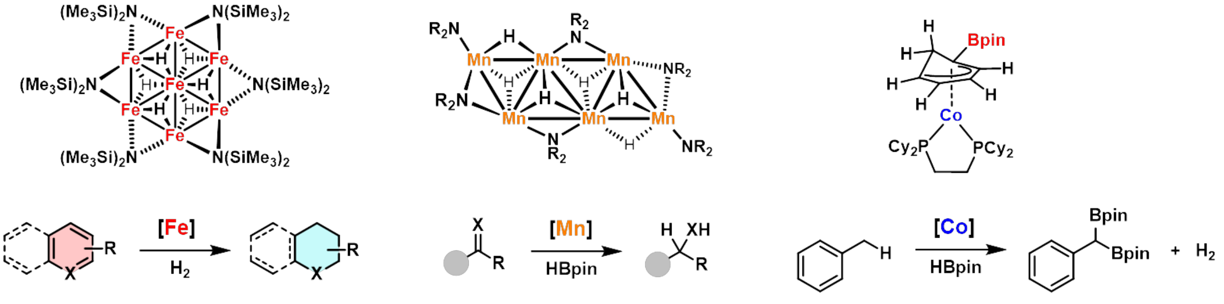
[1]University of Hamburg

This talk discusses various applications of **Fe**, **Mn**, and **Co** amido complexes to the synthesis of novel metal complexes, unusual cluster architectures, and active catalysts.

i) Metal nanoclusters have recently gained a strong foothold in the field of nanoscience due to their unique structural, magnetic, and catalytic properties. **Discrete metal clusters** (Mn, Fe, Co) constitute snapshots of larger cluster growth mechanisms that are especially rare owing to rapid aggregation or decomposition pathways. We have developed a synthetic strategy that enables the rapid and high-yielding access to 3d metal nanoclusters (n = 4-8) with amido, hydrido, and hydrocarbyl ligands.

ii) Amine-bearing **iron hydride species** were demonstrated to act as highly active catalysts in alkene and alkyne functionalizations, including effective hydrogenations of deactivated arenes.

iii) A rapid access to versatile **cobalt(I) complexes** has been developed that exhibit high activity in hydrofunctionalizations, hydrogenations, and cross-coupling reactions.



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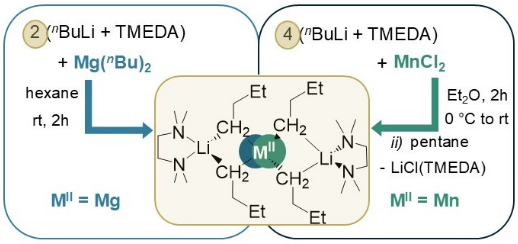
How (dis)similar are Mn(II) and Mg(II) organometallics?

M. Uzelac[1], R. Jones[1]*, J. Kragskow[1]*, T. Kraemer[2]*, M. F. Mahon[1]*

[1]Department of Chemistry, University of Bath, Bath, UK, [2]Trinity College Dublin, the University of Dublin, Ireland

With its high abundance, low supply risk and low inherent toxicity[1] Mn is sustainable and economically attractive, while its many accessible oxidation states imply diverse reaction pathways are within reach, finding widespread application in catalysis. The organometallic chemistry of Mn(II) displays reactivity unique within transition metal chemistry. Due to the predominantly ionic Mn-C bond, such compounds often display behaviour and structural features more comparable to organomagnesium reagents.[2,3] But to what extent are Mn(II) and Mg(II) organometallics similar, and where might we find the differences? This contribution will compare and contrast new, analogous, anionic ate complexes containing Mg(II) and Mn(II) centres. A combination of experimental and computational studies have been employed to comprehend the structural correlations between such magnesiates and manganates. Complementing these findings, investigations into the reactivity of these complexes in selected organic transformations, such as metalation and nucleophilic addition, are also examined.



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Tuning the catalytic activity of cobalt complexes with hemilabile phosphane ligands

M. Iglesias[1], S. García-Abellán[1]*, V. Polo[2]*, J. Munárriz[2]*

[1]Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, [2]Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Universidad de Zaragoza

Over the past decades, homogeneous catalysts based on Earth-abundant metals (EAMs) have gained increasing attention, driven by the demand for more sustainable chemical processes and the opportunity to explore their diverse and less-studied reactivity.[1,2] Among these, cobalt complexes have shown great promise, exhibiting catalytic efficiency in a range of homogeneous transformations, including important industrial processes such as the Fischer-Tropsch reaction, alkene hydroformylation, and methanol carbonylation.

In this presentation, the structure, reactivity, and catalytic activity of new complexes featuring phosphane-triazole ligands, which give rise to hemilabile coordination, will be discussed. Co(III) complexes of the type $[\mathrm{CoCp^{*}(CH_3CN)(P\text{-}N)}][\mathrm{BF_4}]_2$ and $[\mathrm{CoCp^{*}(I)(P\text{-}N)}]\mathrm{I}$ ($\mathrm{Cp^{*}}$ = pentamethylcyclopentadienyl) show ligand-dependent activities in the fluorination of acyl chlorides and alkyl halides,[3] as well as in the [2+2+2] cycloadditon of alkynes and nitriles (Figure 1).[4]

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