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Inspired by Nitrogenase: Dihydride Complexes for the H_2-Releasing Reductive Activation of Challenging Substrates

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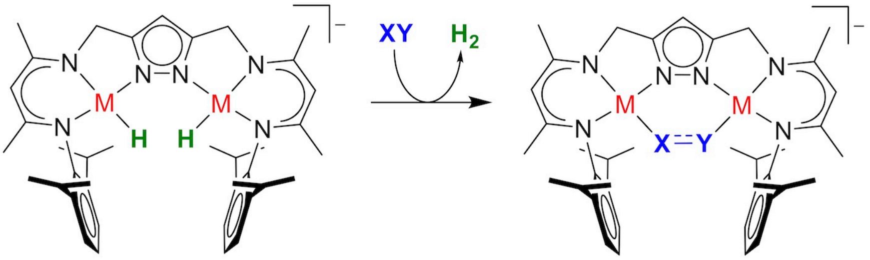
style="font-weight: 400;">Metalloenzyme active sites provide great inspiration for the design of new types of catalysts for the activation of small inert molecules, and for substrate transformations relevant to sustainable energy schemes. Work in our group has exploited the use of compartmental pyrazolate-based ligand scaffolds for preorganizing two metal ions at tunable distances to enable metal-metal cooperativity, to enforce constrained substrate binding modes, and to emulate bioinorganic reactivity and isolate key intermediates [1].

The focus of this lecture will be on systems that use H_2 release from dinuclear metal hydride complexes to provide the required reducing equivalents for the binding and subsequent transformation of ubiquitous molecules such as O_2, H_2O, NO, or N_2 [2], also enabling key reactivity steps observed for multimetallic enzymes such as Acetyl-CoA Synthase (ACS). Spectroscopic and kinetic investigations as well as DFT calculations for these systems are revealing electronic structure contributions to reactivity, and are providing important mechanistic insight.



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Nano onions based on an amphiphilic gold(I) cyclic trinuclear complex

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Coinage-metal-based cyclic trinuclear complexes or CTCs,[1] are a class of trimeric structures with the general formula M_3L_3, where M = Cu(I), Ag(I), Au(I). Gold(I) CTCs are especially interesting due to their tuneable π acidity / basicity[2] and their ability to form strong intermolecular aurophilic interactions, which are comparable in strength with hydrogen bonds.[3] If the ligands have an amphiphilic structure, the self-assembly in aqueous media can be further controlled through hydrophobic and hydrophilic interactions. Combining these two strategies can lead to the formation of complex supramolecular assemblies held together by several types of intermolecular interactions.

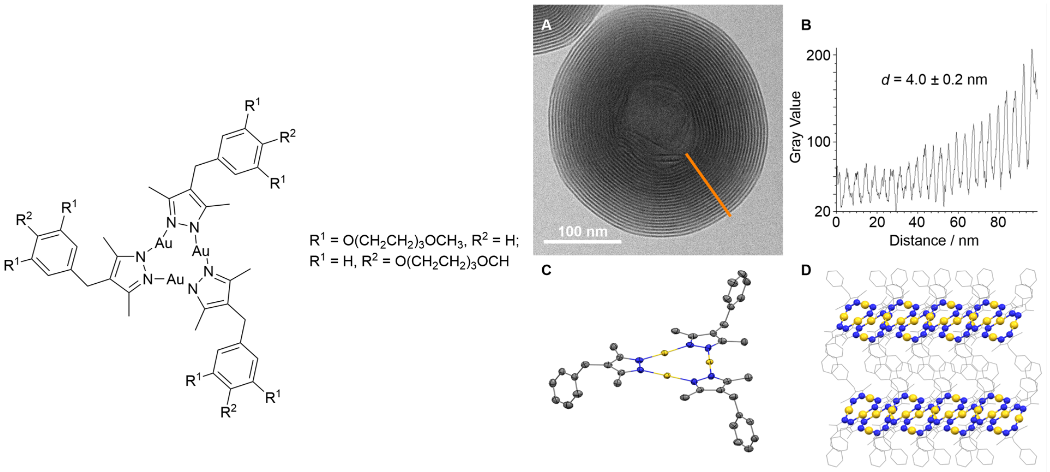

Figure 1. Structure of homoleptic gold(I) CTCs functionalized with PEG side chains (left) and cryoEM image of self-assembled nano-onions based on the synthesised Au(I) CTCs (right, A, B) and the single-crystal X-ray diffraction analysis of the non-amphiphilic analogue (right, C, D; H atoms were removed for clarity).

In this contribution, the synthesis, the characterization and self-assembly of amphiphilic homoleptic and heteroleptic gold(I) CTCs (Figure 1) will be presented. In aqueous solution, one Au(I) complex was found to form multilayer vesicles with an onion-like architecture, a rare example of such assemblies with metalloamphiphiles,[4] and to the best of our knowledge, the first containing Au(I). We have investigated the influence of the metal centre and of the position and number of the amphiphilic side chain(s) on the self-assembly by cryoEM and EDX, revealing the interplay between aurophilic interactions, π-π stacking and hydrophobicity. Single-crystal X-ray diffraction studies on the non-amphiphilic analogue (Figure 1C, D) revealed that the gold trimers are arranged in an off-set, columnar fashion, with Au-Au distances indicating only very weak aurophilic interactions (Figure 1D). Nonetheless, control experiments with the Ag(I) and Cu(I) analogues highlighted the crucial role of Au(I) in the formation of well-defined nano onions.

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Symmetry and Rigidity for Boosting Erbium-Based Molecular Light-Upconversion in Solution

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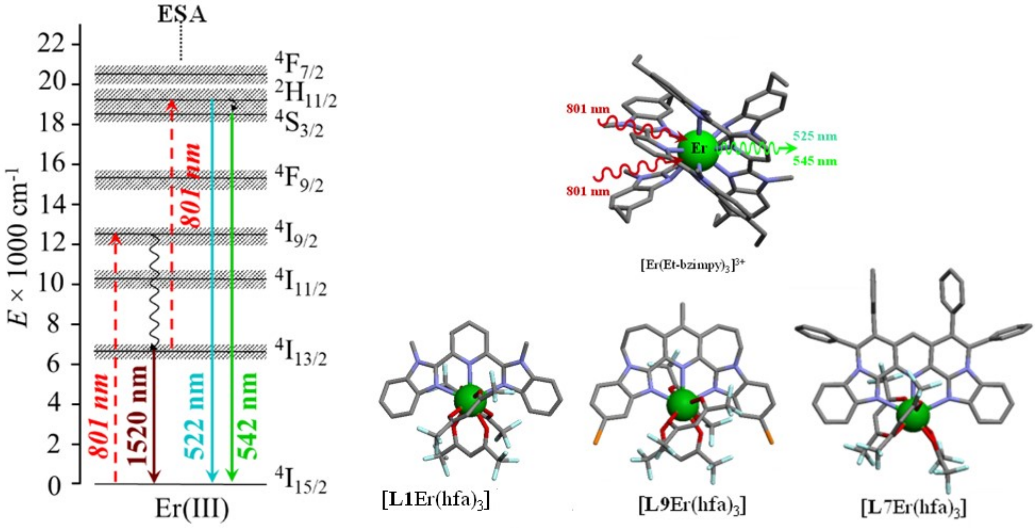
Excited-state absorption (ESA) upconversion,[1] a promising mechanism for photonics and optoelectronics applications, has seen significant advancements through structural modifications of erbium complexes. Achieving this goal requires either the piling up of low-energy near-infrared photons onto a single short-lived lanthanide center via ESA, or the alternative energy transfer upconversion (ETU) mechanism, which combines a short-lived lanthanide activator surrounded with long-lived sensitizers.[2]

In this work we moved from local idealized D_{3h}-symmetrical triple-helical [ErN_9] chromophores,[3] as observed in $[Er(Et\text{-}bzimpy)_3]^{3+}$, to local idealized C_{2v}-[ErN_3O_6] units in C_{2v}-symmetrical [**L*k***Er(hfa)$_3$] adducts.[4] This change led to a remarkable 2-3 orders of magnitude increase in upconversion efficiency. Detailed photophysical studies indicate that this enhancement is attributed to the existence of a long-lived Er($^4I_{11/2}$) level, stemming from the specific lack of efficient relaxation processes in the 3500 cm^{-1} range accompanying the concomitant binding of perfluorinated hfa$^-$ co-ligands and rigid polyaromatic **L*k*** guests to Er(III) in [**L*k***Er(hfa)$_3$] complexes. Ongoing investigations are focused on providing ultimate proof for the dominance of this mechanism, with technical developments aimed at time-gated near-infrared (NIR) detection following intense pulsed NIR excitation of Er($^4I_{9/2}\leftarrow{}^4I_{15/2}$) at 801 nm and Er($^4I_{9/2}\leftarrow{}^4I_{15/2}$) at 966 nm.



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Gold(III)-hydrides stabilized by novel (P^N^C) pincer ligands

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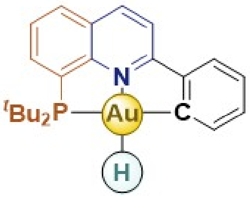
The quest for the isolation and characterization of highly reactive organometallic intermediates to access more efficient catalytic processes remains a major focus of the synthetic community. Transition metal hydrides have been extensively investigated due to their pivotal role as intermediates in numerous catalytic transformations [1]. However, despite their rich chemistry, gold hydrides in high oxidation states have remained largely unexplored. Such scarcity can be attributed to the inherent instability of these species, which results from an electronic mismatch between the highly oxidizing metal and the strong electron-rich hydride ligand [2].To stabilize and study these and other elusive gold(III) species, new ligand designs and improved methods to incorporate them into the metal are esential [3].

Our efforts in the field have resulted in the successful synthesis and structural characterization of a new class of gold(III)-hydrides stabilized by unique, *de novo* designed (P^N^C) pincer ligands [4]. The synthesis of these new (P^N^C)-gold(III)-hydrides has been streamlined by first, incorporating a cycloauration step devoid of toxic metals or harsh conditions and secondly, by using H-Bpin as a mild hydride donor. Our straightforward protocol contrasts with previous methods that rely on toxic metals, harsh conditions, and highly reactive hydride donors.

Interestingly, these gold(III)-hydrides exhibit protic behavior but still react with allenes and alkynes to selectively form *trans* insertion products. Due to the exceptional stability of the gold(III)-hydrides under ambient conditions, we undertook an investigation into the mechanism of this intriguing reaction [5].



- ✓ New (P^N^C) pincer ligands
- ✓ Straightforward acces to gold(III)
- ✓ Stable chloride, hydroxo, formate and hydride gold(III)species
- ✓ X-ray characterization
- ✓ Insertion with alkynes

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Cyclopentadienone Iron Complex-Catalyzed Hydrogenation of Ketones: The Influence of the Charge-Tag on Catalytic Performance

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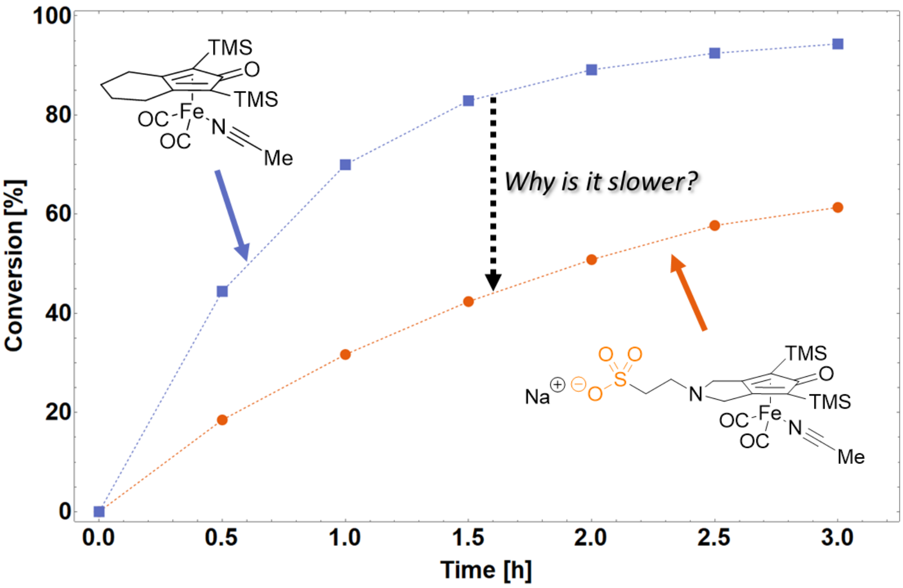
In a recent publication, we reported on a negatively charge-tagged iron cyclopentadienone complex used for the hydrogenation of ketones in aqueous solvent [1]. This compound was used to investigate the reaction mechanism by real-time mass spectrometry, which allowed us to identify the catalytically active species and determine catalyst decomposition pathways. While working with these complexes, we noted that the sulfonate charge-tagged complex showed consistently slower reaction rates in ketone hydrogenation compared to the corresponding neutral complex. In this work, we describe the experimental investigation into the reason for the difference in rate. Using different catalyst derivatives and a variety of experimental techniques such as ^{31}P NMR and kinetics, we could show that blocking of the free coordination site in the active catalyst by the sulfonate group or electric field effects are not responsible for the difference in reaction rate. It was found that the tertiary amine group used to tether the charge-tag to rest of the molecule is responsible, presumably due to inductive effects. The sulfonate charge-tagged complex was found to form micelles in solution, with critical micelle concentrations in D_2O in the range of 1.75 – 17 mM depending on the alkali metal counter ion. The micelles were found to function as microreactors, accelerating the hydrogenation reaction compared to structurally similar neutral complexes, which are not able to form micelles. [2]



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Non-classical azolylidene metal complexes as potential anticancer therapeutics

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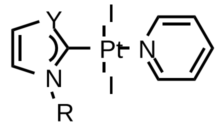
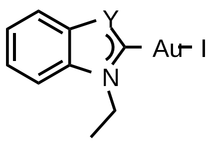
In recent decades, organometallic compounds with N-heterocyclic carbene (NHC) ligands have been studied for their anticancer and antimicrobial properties [1-3]. (Benz)imidazole derivatives, along with cyclic(alkylamino)carbenes, have been the predominant scaffolds for NHC-based anticancer drugs. Modulation of the biological properties is usually achieved by structural modifications, typically introduced through the groups on the nitrogen atoms or within the heterocyclic backbone. However, non-classical azolium-based carbenes ligands, (N,Y)HCs (Y = O, S, Se), remain largely unexplored, either in inorganic medicinal chemistry or general inorganic chemistry.

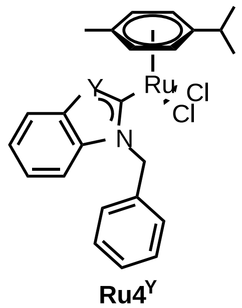
Platinum, gold and ruthenium (N,N)HC complexes were selected for their previously reported biological activity and their proposed mechanisms of action. Their azolium analogues, bearing (benz)oxazole, (benzo)thiazole or benzoselenazole, were successfully synthesised. Upon introduction of the chalcogen, the overall donor strength of the ligands slightly decreases due to the enhanced π-backdonation. The ligands display the characteristic "half-umbrella" shape, providing asymmetric steric crowding and enabling lateral access to the metal centre. Furthermore, the incorporation of the chalcogen opens the possibility to hydrogen bonding and chalcogen interactions which can have significant impact on the binding of biomolecules or small molecules.



Pt1^{Y} **- Pt2**^{Y}
R = Me (**1**), Bn (**2**)
Y = NR, O, S



Au3^{Y}
Y = NEt, S, O



Ru4^{Y}
Y = NBn, S, Se

The therapeutic potential of the (N,Y)HC metal complexes against ovarian cancer cells was evaluated. Two distinct ligand behaviours were observed depending on the metal: for the platinum complexes, the substitution of an alkylated nitrogen in imidazole led to a decrease in toxicity following the trend N > O > S, whereas the trend was O / Se > N > S for the gold and ruthenium compounds. Furthermore, the mechanisms of action of the compounds were studied *in cellulo*. Cell fluorescence microscopy revealed that **Pt1**^{Y} and **Pt2**^{Y} are able to stop DNA replication, possibly forming interstrand DNA crosslinks which could explain their ability to overcome cisplatin resistance. The degree of interaction between the **Ru4**^{Y} family and its protein target correlated well with the observed cytotoxicity. However, no correlation was observed for the **Au3**^{Y} complexes, hinting at a different target or mechanism of action regulating their toxicity.

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Enhancing Energy Research

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Process improvement, mobility, sustainability, and electricity generation are pivotal fields of interest in nowadays energy research. Enhanced development of better membranes, more efficient fuel cell catalysts, and lighter batteries with increased energy density, opto-electronics and photovoltaics got special interest over the years. Such cases for materials development were realized by Chemspeed's high-throughput and high-output solutions. This presentation covers a selection of case studies in these fields for industrially relevant material classes such as thermo-electric materials, battery inks, quantum dots and perovskites. We showcase the beneficial use of our solutions in synthesis, process research, formulation, application, and testing.

The Influence of an ortho-methyl Group in Rhodium-PYA Complex Reactivity and Catalysis

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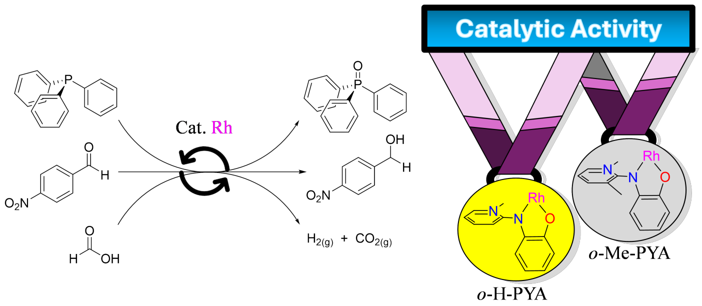
Keywords: Catalysis, Rhodium-PYA complexes, Ligand modification.

Steric and electronic properties of the ligands allow for precise control over complex reactivity.[1] This study examines the impact of an ortho-methyl group in a pyridinium amide[2] (PYA) moiety on the reactivity and catalytic properties of rhodium-PYA complexes. We probed a variety of reactions including phosphine oxidation, transfer hydrogenation of aldehydes, and formic acid dehydrogenation.[3] The results highlight the significant role of ligand modification in tuning the activity and selectivity of rhodium-based catalysts, providing insights for the design of more efficient catalytic systems.



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The Influence of SiO_2 Dehydroxylation on Offline Thermochromatography with ^{202}Tl

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Fused silica is heavily used as a stationary phase in gas-solid chromatography experiments with superheavy elements (SHE, $Z > 103$) [1]. Being used as the stationary phase, it is essential that the fused silica surface remains stable and unaltered throughout the experiment. This is of particular significance in the context of thermochromatography, where the chromatography column is subjected to a negative temperature gradient. An untreated fused silica surface dehydroxylates beyond 190°C up to 1200°C [2]. Consequently, an untreated fused silica surface subjected to a temperature gradient within this range exhibits a temperature-dependent surface hydroxyl concentration, which is unfavorable as a stationary phase. The direct influence of dehydroxylation was observed in recent isothermal chromatography experiments with ^{184}Tl in preparation for the next SHE chemistry experiment with the heavier homolog, nihonium (Nh, $Z = 113$) [1, 3].

To date, three published Nh chemistry experiments have been conducted [4-6], all of them yielding inconclusive results. This prompted a comprehensive re-examination of the Tl/SiO_2 chemistry at the so-called one-atom-at-a-time level. The first experiments highlighted the impact of fused silica dehydroxylation [2]. As the previous offline thermochromatography experiments with long-lived ^{200}Tl did not address nor pretreat the fused silica surface [7], it was deemed necessary to reinvestigate the behavior of this stationary phase in detail. Presented here will be the recent offline thermochromatography experiments with carrier-free ^{202}Tl, focusing on the pretreatment of the fused silica surface. These studies will pave the way toward a next-generation chemical characterization of Nh.

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Stabilization Effect of NH-S Hydrogen Bonds in Synthetic Iron-Sulfur and Iron-Selenium Clusters

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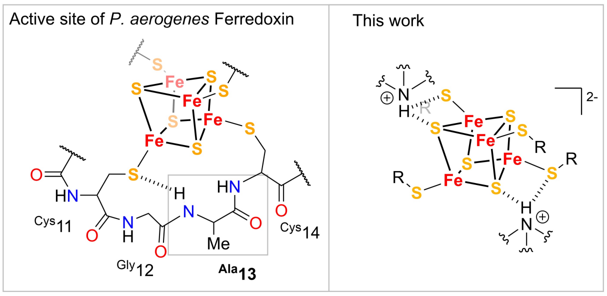
Iron sulfur (FeS) cofactors are integral components in a variety of metalloenzymes and play a key role in many biological processes due to their structural and chemical versatility as well as their unique electrochemical properties.[1] In this context, iron-sulfur cubanes (Fe_4S_4) have been developed as synthetic models of Fe_4S_4 containing metalloenzymes, most notably high-potential iron-sulfur proteins (HiPIP) and bacterial ferredoxins, which respectively act as competent electron transfer mediators in metabolic processes.[2,3] The redox properties of Fe_4S_4 clusters in these complex enzymatic systems are tailored by directional NH-S hydrogen bonding interactions between nitrogen atoms of polypeptide functionalities and sulfur atoms of both the Fe_4S_4 core and cysteine ligands as well as electrostatic interactions.[4] Early work of Nakamura has demonstrated that the spatial proximity of H-bonding donor functionalities in the ligand framework of synthetic Fe_4S_4 clusters enables the modification of the redox potential E via NH-S hydrogen bonds in analogy to natural systems.[5] Previous work in our group has focused on the dynamic modulation of the redox potential E of Fe_4S_4 mimics, exploiting a gated electron transfer (ET) mechanism, by encapsulation of K^+ ions in the second coordination sphere, enabling the stabilization of highly reducing species.[6,7] Inspired by this, our group has recently been able to establish the rational control of the redox potential of synthetic Fe_4X_4 ($X = S, Se$) clusters by NH-S hydrogen bonding interactions between nitrogen atoms of ammonium cations with S or Se atoms of the Fe_4X_4 cubane core and thiolate ligands respectively, which has been extensively studied among a systematic series of acids containing varying numbers of NH hydrogen bond donor functionalities encompassing varying pK_a strengths. The assessment of this stabilization effect has been conducted by spectroscopic- and electrochemical-techniques, concomitant with the isolation of solid-state molecular structures of Fe_4X_4 acid-base adducts. Lastly, we have been able to demonstrate that NH-S hydrogen bonding enables the stabilization of reduced $[Fe_4X_4]^{1+}$ acid-adduct complexes which also exhibit proton-coupled electron transfer (PCET) reactivity.



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Re-Evaluation of the Air-Mediated Response in Bi-Based Perovskite X-Ray Detectors

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Lead (Pb) perovskites dominated X-ray detection for a decade, but toxicity concerns drove research towards safer Pb-free alternatives. Lately, Bi-based halide materials emerged as leading candidates due to their comparable X-ray detection performance. By conducting measurements after heedfully eliminating detrimental effects of crystal quality, crystallographic orientation, and metallization interface, we conclude that $A_3B_2X_9$ materials form intrinsically poor X-ray detectors. The high figure of merits reported in the literature arise from the artefact caused by air-ionization and in turn indicate ill X-ray characterization employed in the past. Utilizing a self-built measurement setup with vacuum chamber, we demonstrate that the chamber environment has a crucial role in the obtained photocurrent. Intentional switching of the environment from vacuum, air and Argon in the chamber could generate a counterfeit 1000-fold higher X-ray response. As an outcome, we have unveiled the existence of a certain threshold for air-ionization. Only Bi-based materials with either low e-h pair creation energy such as BiI_3 or with high mobility 3D crystallographic structure such as $Cs_2AgBiBr_6$ show response above this threshold. In our study, not only we have decoupled air-ionization contribution from the detection response generated by the material but also laid down standard experimental protocols to be followed for reporting reliable X-ray detection performance.

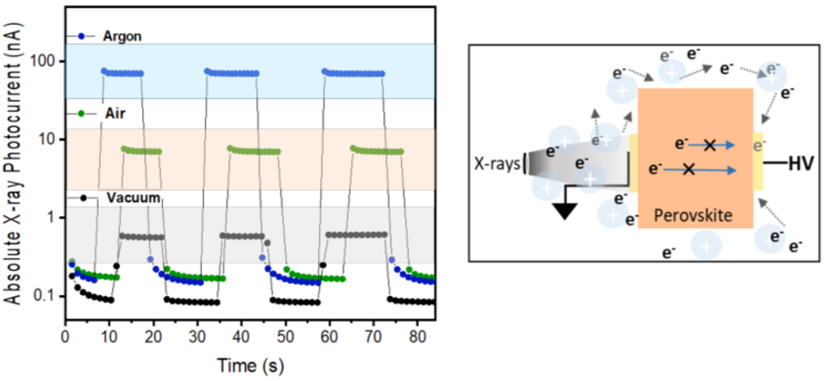

***Figure 1**: Depicts a 1000-fold increase in absolute X-ray photocurrent obtained with the $Cs_3Bi_2I_9$ single crystal when measured under vacuum, air, and argon filled chamber environment. The samples was biased at 150V and 22keV X-ray was turned on after 20-30 seconds leading to increased photocurrent. The schematic depicts the collection of charged ions on the contacts externally instead of photo-generated carrier from the perovskite sensor.*

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Tracking Ag^+ ions from the SilE protein to the silver efflux pump in *E.coli*

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With the worldwide increase of antibioresistance, researchers are looking for alternative therapies to prevent and treat bacterial infections. One example is silver, which has been used for thousands of years for its antimicrobial properties. However, in 1975, a strain of *Salmonella enterica* showing tolerance to silver was discovered in burn patients at a Boston hospital. These bacteria possessed a transmissible plasmid called pMG101 encoding the Sil silver efflux system, which is structurally very similar to the already known Cus copper efflux system. [1,2] However, it differs in the presence of the SilE periplasmic protein necessary for the Sil system to operate correctly. [2]

SilE is not part of the SilA, SilB and SilC tri-protein complex forming the efflux pump but acts as a silver ion sponge. [1] However, the way of transferring silver ions from SilE to the pump is still unknown. It has been shown that SilE does not interact with either SilB or SilF [3,4] (another silver-binding protein that gives ions to SilB), raising the question of a possible intermediary.

To try and find an answer, SilE was expressed in *E.coli*. We will present the results of titration experiments, revealing the number of silver ions that can be captured by SilE. The behaviour of the saturated protein in solution, respectively in presence of competitors derived from other proteins of Sil, will be shown. We will discuss if SilE needs an assistant or if it is in fact a suicide protein that will not release its ions.

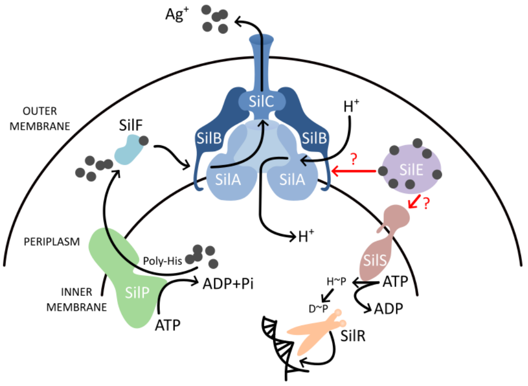

Fig. 1: Sil system, adapted from Asiani et al., 2016

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Neopentyl Sodium as a Tool for Metalation of Non-Activated Alkenes

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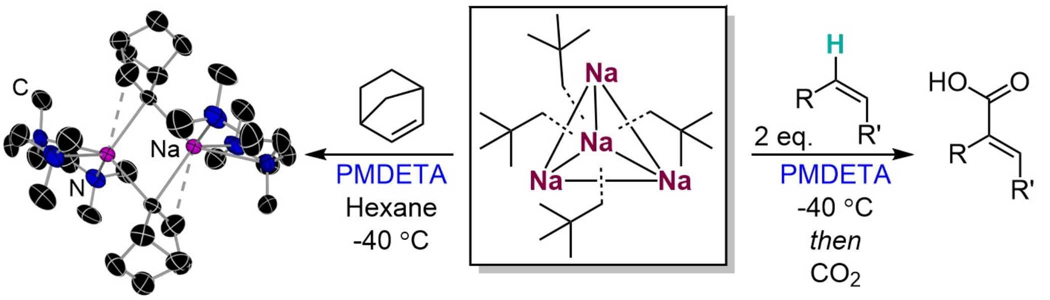
From as far back as the 1940s, alkyl sodium reagents have been examined for their powerful basicity, with the ability to deprotonate unactivated aromatic and vinylic C-H bonds. Pioneering work by the likes of Morton and Finnegan demonstrated how pentylsodium could be synthesised in situ from pentyl chloride and sodium metal to react with alkyl substituted benzene derivatives and various olefins to afford organosodium intermediates which could subsequently be trapped with simple electrophilic quenches.[1] These studies however often required very long reaction times due to the very poor solubility of the sodiated species and the nature of the organosodium intermediates found in these complex mixtures remained unknown. With an increase in understanding of organolithium reagents as powerful bases these organosodiums were left behind as mere curiosities. Combining sodium alkyl $NaCH_2SiMe_3$ with Lewis donor PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine), our group has recently shown that some of these limitations can be overcome, affording a hydrocarbon-soluble organosodium reagent that can be used for benzylic metalation of non-activated alkyl-arenes.[2][3] Advancing the understanding of structure/reactivity correlations in this underexplored family of s-block metal organometallics, here we report on the synthesis and characterisation, in both the solid and solution states, of a highly basic alkyl sodium complex, neopentyl sodium $[\{Na(CH_2tBu)\}_4]$. The enhanced ability of this reagent to metalate stoichiometric quantities of nonactivated substrates such as benzene or simple cyclic olefins with the addition of the Lewis donor PMDETA was examined, with a carbon dioxide quench carried out to demonstrate the high efficiency of the sodiations carried out under these conditions. Remarkably organolithium reagents are inert towards these substrates under the same reaction conditions, demonstrating the influence of the alkali-metal. Key reaction intermediates have been trapped and characterised by X-ray crystallography and ^1H NMR DOSY (Diffusion Ordered SpectroscopY), shedding light into the hidden constitution of these complexes.



Sodiated intermediates characterised by X-ray, ^1H, ^{13}C and ^1H DOSY NMR

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Towards the Elucidation of Ni-Catalyzed Cyclopropanation: MeNiGaL - a Ni(0) Methyl Complex Based on a Ni-Ga Double-Decker Complex

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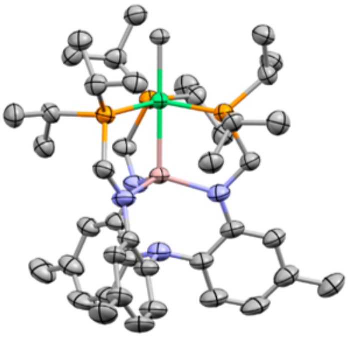
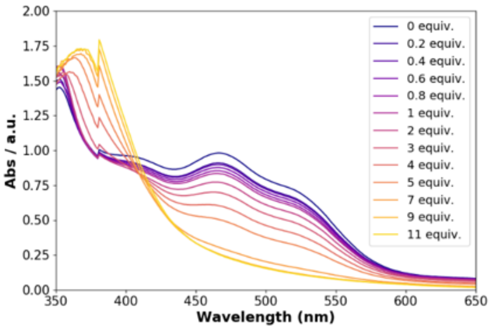
During our efforts to elucidate the reaction mechanism of the nickel catalyzed cyclopropanation reaction of unactivated alkenes using NMe_4OTf/BuLi as the methylene source[1,2], we prepared the Ni-Ga double-decker complex NiGaL, a close derivative to the compound described by Lu et al.[3]. The enhanced Lewis acidity of the nickel center provided by the interaction with the Ga(III) ion was postulated to provide a thermodynamic sink hole which could possibly allow the observation and/or isolation of an ammonium ylide species, which was proposed as an intermediate in the catalytic cycle. Although the introduction of ammonium or phosphonium ylides was unsuccessful, we were able to isolate the corresponding Ni(0) methyl complex MeNiGaL, indicative of the nickel atoms enhanced Lewis acidity.

The Ni(0) methyl complex **MeNiGaL** was synthesized and thoroughly characterized. This compound is prepared from the 16-valence electron complex NiGaL through the addition of MeLi, resulting in the formation of the corresponding lithium salt. Attempts to synthesize the analogous neopentyl or CH_2EMe_3 complexes (E = N, P), as potential intermediates or analogues for the nickel-catalyzed cyclopropanation of unactivated alkenes using NMe_4OTf/BuLi, were unsuccessful.

Manuscript accepted for publication





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Toward predicting silver ion binding in proteins

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Silver ions and nanoparticles are known to possess antimicrobial properties.[1] Yet the Gram-negative bacteria *Salmonella Typhimurium* learned how to tolerate larger amounts of silver by expressing a silver efflux system Sil, encoded on a transferable plasmid pMG101.[2] This silver efflux system is similar to the copper efflux system Cus, except for one specific protein, SilE, which is proposed to act like a silver sponge.[2,3] SilE is a small periplasmic protein composed by 143 amino acids and containing many histidine (His, H) and methionine (Met, M) residues, organized mainly in tetrapeptide (and one tripeptide) entities, which could be expected to bind silver(I) ions.[4] In previous model studies in our group, Chabert *et al.* highlighted that each HX_nM (n=1,2) peptide was able to coordinate to one silver(I) ion, but also that the nature of the amino acid "X" influences the association binding constant $\log(K_{ass})$.[4]

Based on these observations, simple tetrapeptide models inspired by SilE were synthesized and studied, in order to gain a more basic understanding of how different amino acids in between the directly binding amino acids are affecting the binding of silver(I) ions in proteins. Differences and similarities in the coordination behaviour were noticed. We report the results for several different amino acids "X", as well as the first trends to predict the behaviour of the binding sites in proteins.

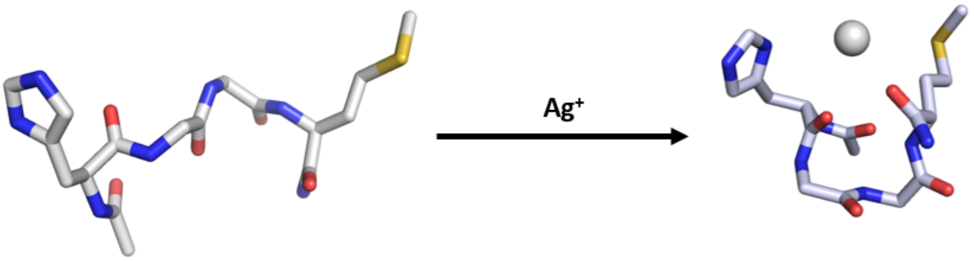

Fig. 1 : Folding of HXXM upon coordination with Ag^+

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Synthesis and Reactivity of Triazolylidene-Group 10 Metal Complexes via Oxidative Addition of 5-Halo-Triazolium Salts

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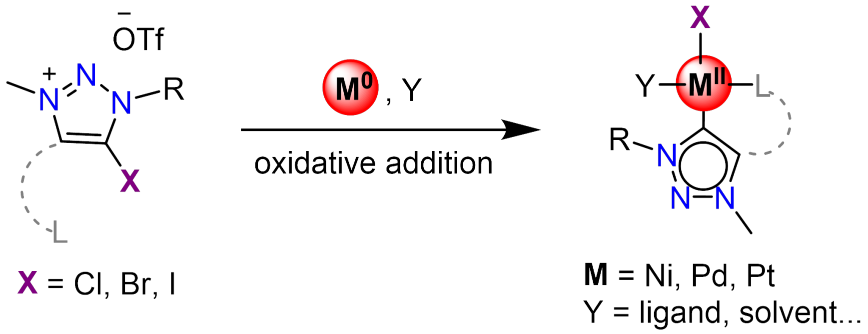
N-heterocyclic carbene (NHC)-supported complexes have been extensively studied in the last decades and now represent the state-of-the-art catalysts for key synthetic applications.[1–3] Among those, 1,2,3-triazol-5-ylidenes complexes demonstrated superior performances in catalysis with respect to the Arduengo-type carbene complexes, thus attracting growing interest in the field.[4,5] However, the metalation reaction of these ligand precursors suffers from poor control over stoichiometry, resulting in homo- or heteroleptic complexes with various nuclearity.[6,7] Here, we investigated for the first time the oxidative addition reaction of halogenated triazolylidene precursors in order to obtain metal-NHC complexes with a controlled molecular structure. We will show the effectiveness of this protocol to synthesize mono- and bidentate triazolylidene complexes of group 10 transition metals and their coordination chemistry and application in homogeneous catalysis will be discussed.



❖ *Coordination chemistry* ❖ *Catalytic applications*

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Cyclopentadienone Monoisocyanide Iron Complexes: Synthesis and Catalytic Performance in Transfer Hydrogenation

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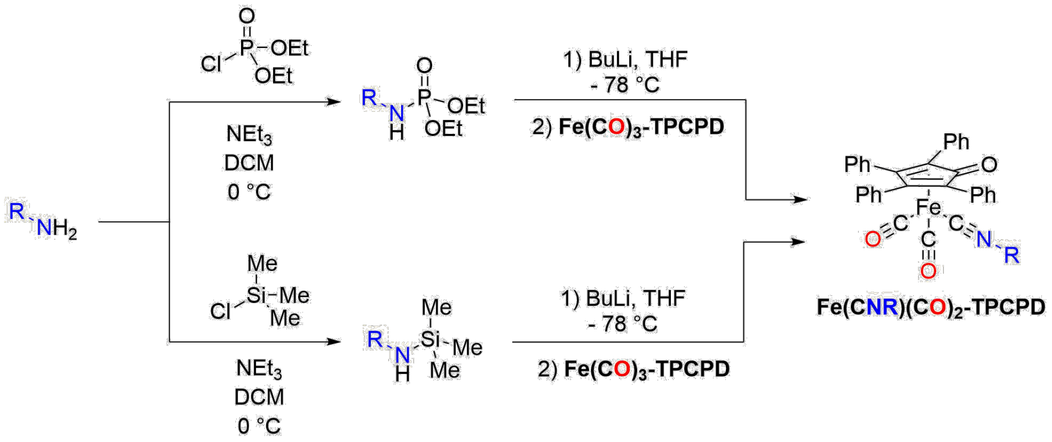
In this work, we report the synthesis, characterization and catalytic performance of several aliphatic and aromatic cyclopentadienone iron monoisocyanide complexes and extend on our previously published [1] and presented work. The previously reported method by Gibson et al. [2] involving phosphoramidates was found to efficiently yield aliphatic isocyanide complexes which do not possess electron withdrawing groups without the need to isolate the corresponding isocyanides themselves. The method employing isolated isocyanides was recently reported [3]. For aromatic isocyanides, it was found that the method reported by Sattler and Parkin [4], which employs silyl amines as substrates, allows the preparation of the corresponding aromatic isocyanide complexes. Both aliphatic and aromatic complexes were found to be active in transfer hydrogenation, albeit with conversions lower by an order of magnitude compared to the corresponding tricarbonyl complexes. Kinetic experiments indicate that the isocyanide complexes show very similar kinetic traces independent of the electronics of the isocyanide ligand. Furthermore, they indicate fast catalyst decomposition. Post-reaction ESI-MS analysis revealed the formation of catalytically inactive di- and triisocyanide complexes, indicating a possible catalyst decomposition pathway.



R = Me, ^{i}Pr, Cy, Bn, (*S*)-NaphthEt, (*R*)-PhEt, Ph, *p*-C_6H_4-Me, *p*-C_6H_4-Ph, *p*-C_6H_4-OMe, *p*-C_6H_4-$CO_2{}^t$Bu

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Towards Understanding Electrochemical Interfaces: An interplay of chemical interactions and electric fields

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Catalysis of thermal reactions can be enhanced through the aid of electric fields. This has been noted for enzyme catalysis and demonstrated in molecular catalysis as well as heterogeneous catalysis.[1-3] However, electric field effects on heterogeneous catalysis are not well understood due to the complexity of such effects on the solid-liquid interfaces, at which catalysis occurs. Electrified solid-liquid interfaces experience a complex interplay from the intrinsic properties of materials, effects from the interaction of the surface with electrolyte components, and the interfacial electric field.[4-6] In situ infrared spectro-electrochemical approaches have been employed to understand interfacial electric fields. However, recent work[7-8] has shown that observed vibrational shifts are influenced by both the electric field as well as electroinductive effects coming from specific binding of a probe to the surface. This highlights the need for a more quantitative understanding of such effects happening at electrified solid-liquid interfaces to improve electrocatalytic technologies.

Herein, we employ in situ surface-enhanced infrared absorption spectro-electrochemistry (SEIRAS). In our system, we incorporate two types of electrode films and a reporter probe capable of providing distinct signatures of electric field and chemical binding. We observed characteristic IR patterns as a function of applied potentials and the coexistence of multiple surface species. From this, we extracted quantitative information on surface population and vibrational shifts and discuss the contributions from electric fields and chemical binding effects to our observations on different surfaces. Our work enables disentangling various factors that influence interfacial interactions in an externally applied electric field. This is an important step towards the critically needed understanding of electrochemical interfaces.

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A palladium-based coordination cage for selective lithium binding

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Receptors for Li^+ are receiving a lot of interest as potential tools for Li^+ extraction, sensing, and isotope enrichment. One important challenge in the design of such receptors is the selectivity against competing ions, such as Na^+ and Mg^{2+}, for which the control of the cavity's size and rigidity is important. A lantern-shaped coordination cage with the formula $[Pd_2L_4]^{4+}$ was obtained by self-assembly using Pd^{2+} salts and ditopic N-donor ligands. In the presence of small anions, such as nitrate, the cage shows high affinity towards Li^+, whereas no interaction with Na^+ was observed, as determined by ^1H and ^7Li NMR spectroscopy. The association constant with Li^+ in acetonitrile measured by isothermal titration calorimetry (ITC) is $(4.8 \pm 0.8) \times 10^5$ M^{-1}.

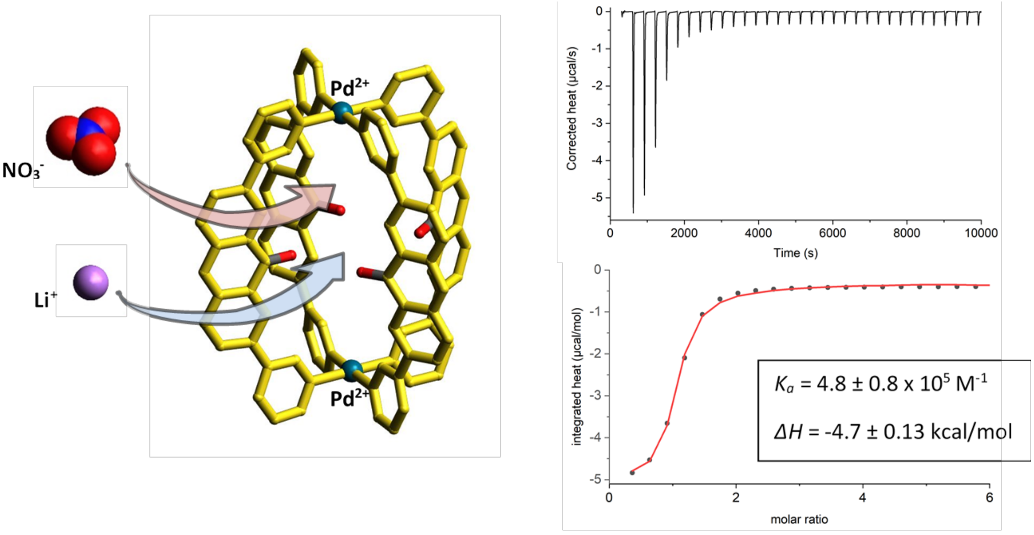

Figure 1. A Pd^{2+}-based coordination cage acts as a potent receptor for $LiNO_3$ as evidenced by isothermal titration calorimetry.

Aluminum Transfer at Zinc and Copper

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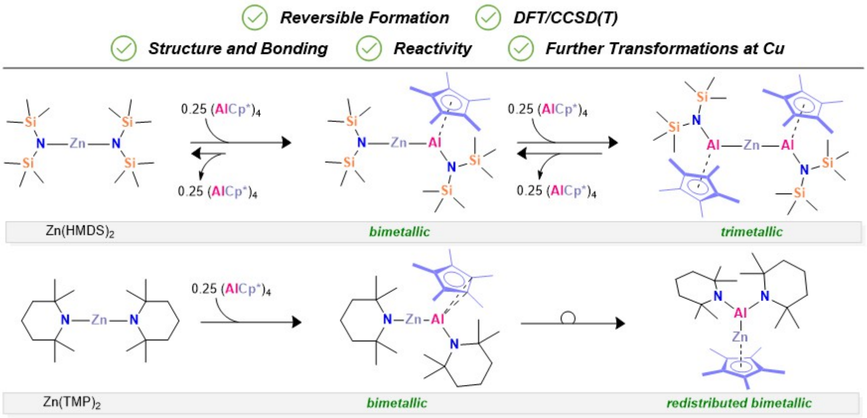
Recent advances on low valent main group metal chemistry have shown the excellent potential of heterobimetallic complexes derived from Al(I) to promote cooperative small molecule activation processes. A signature feature of these complexes is the use of bulky chelating ligands which act as spectators providing kinetic stabilization to their highly reactive Al−M bonds. Our recent advances in the field, however, render the acyclic utility amides HMDS and TMP (R=HMDS, hexamethyldisilazide; TMP, 2,2,6,6-tetramethylpiperidide) as excellent alternatives to facilitate the formation of such complexes. The use of these amides in combination with the simple and comparably easy to handle Al(I) source $(AlCp^*)_4$ serves as a platform for reversible formation of various heterometallics, ligand scrambling, insertion of heterocumulenes and counter-intuitive reaction pathways. Examples for Zn and Cu including the templated formation and deconstruction of low-valent Al-based ligands are presented throughout our contribution. See the concept for Zn in the attached scheme.



Palladium-based cages of low symmetry

J. de Montmollin[1], R. Li[1], A. B. Solea[1], D. W. Chen[1], P. Gorrea Acín[1], F. Fadaei-Tirani[1], R. Scopelliti[1], K. Severin[1]*

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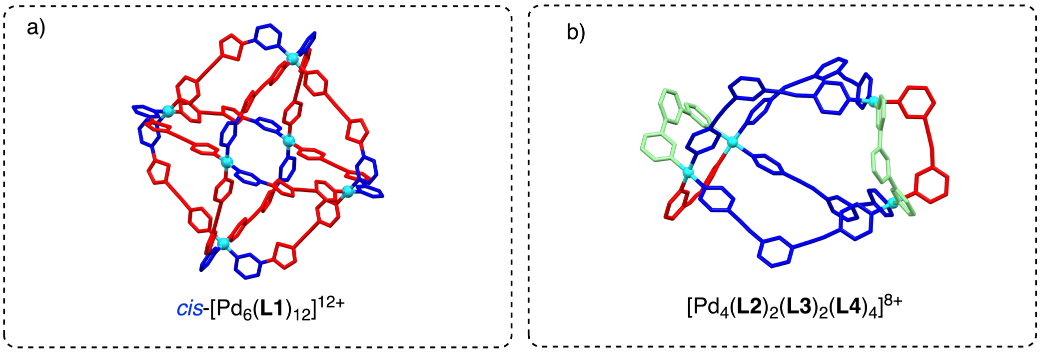
Palladium-based metal-organic cages (MOCs) have been widely studied and have applications in medicinal chemistry as well as in catalysis. Ditopic N-donor ligands L and Pd(II) precursors form a variety of MOCs of the general formula $[Pd_nL_{2n}]^{2n+}$. While the synthesis of high-symmetry palladium cages is fairly straightforward, the synthesis of low symmetry cages is usually more challenging. They can be obtained in several ways; either by using low-symmetry ligands, multiple different ligands to form heteroleptic cages, or different metal cations to form heterometallic cages. The associated challenges emerge from the great number of possible products that can be formed. It is therefore interesting when conditions are found which favor the selective formation of a single low-symmetry cage. Herein, we present our results on low-symmetry cages using low symmetry ligands (orientational self-sorting[1]) or multiple ligands simultaneously (heteroleptic cages[2]).



cis-$[Pd_6(\mathbf{L1})_{12}]^{12+}$

$[Pd_4(\mathbf{L2})_2(\mathbf{L3})_2(\mathbf{L4})_4]^{8+}$

Fig. 1 Different approaches to low symmetry cages. a) Orientational self-sorting in $[Pd_6L_{12}]^{12+}$ cages using low-symmetry ligands. b) Integrative self-assembly of heteroleptic cages.

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N–heterocyclic carbene tailoring allows tuning of iron-catalysed C–H amination

L. A. Hudson[1], M. Albrecht[1]*

[1]University of Bern, Department of Chemistry, Biochemistry and Pharmaceutical Sciences

Nitrogen-containing heterocycles are ubiquitous in nature and industry with C–N bonds being found in numerous natural products and pharmaceutically relevant molecules. Therefore, carbon-nitrogen bond formation is of utmost importance with catalytic and atom economical syntheses being particularly attractive. In this context, in 2013, Betley reported the first example of iron-catalysed direct C–H bond amination using an iron-dipyrrinato catalyst to yield a range of pyrrolidines. However, the activity was limited to only single-digit TONs requiring 20 mol% catalyst loading and an equivalent of Boc_2O to prevent product inhibition. More recently, Betley also reported the additive-free C–H amination of nickel-dipyrrin complexes. In 2021, our group disclosed a highly efficient iron(II) mesoionic carbene complex, which afforded a range of C–H aminated pyrrolidine products in excellent yield with no need for additives, generating only N_2 as the sole side product and achieving TONs exceeding the state of the art by an order of magnitude.[5] Herein, we aim to build better understanding of the influence of the ligand and to improve the catalytic performance of the iron complex by designing and synthesising novel ligands. Our data shows that appropriate ligand design can increase the selectivity of this challenging rection to >99%.

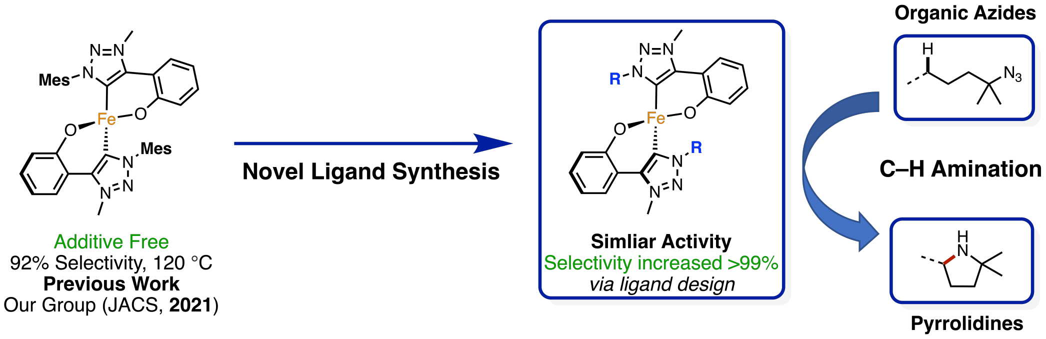

Figure 1. Utilizing novel ligand design for improving selectivity of the iron-catalysed C–H amination reaction of organic azides to afford pyrrolidines.

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Uncovering the Super Basic and Nucleophilic Reactivities of Co(II) Amide Co(TMP)$_2$

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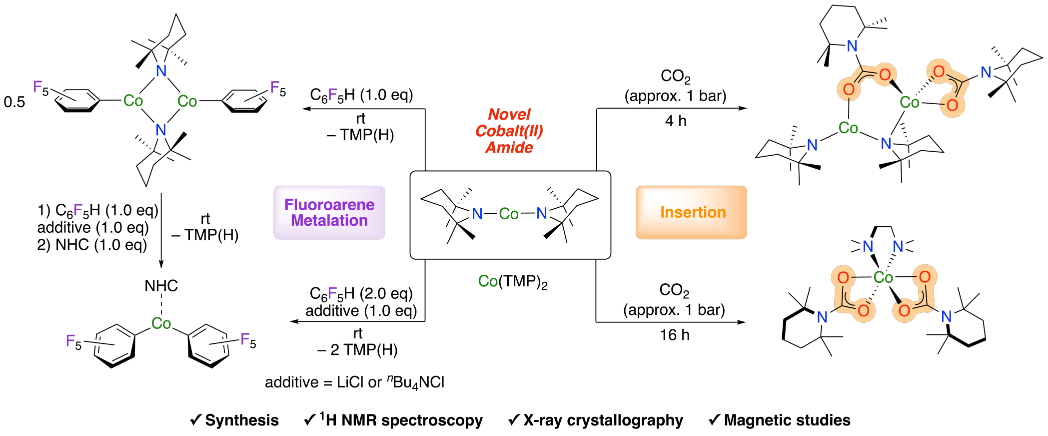
Low valent, earth abundant transition metal amides have found numerous applications in synthesis due to their ability to catalyse many transformations as well as their special magnetic properties.[1] Within Co(II) chemistry most studies have focused on the use of amide groups containing silyl substituents such as Co(HMDS)$_2$ [HMDS = N(SiMe$_3$)$_2$].[2] An area where these systems have shown no applications is arene metalation due to their reduced basicity in comparison with related s-block metal amides.[3]

Breaking new ground in this field, here we report the synthesis and characterisation of a novel cobalt(II) bis-amide Co(TMP)$_2$ (TMP = 2,2,6,6-tetramethylpiperidide).[4] Exhibiting a unique reactivity profile, this amide can selectively promote direct Co-H exchange reactions with a range of fluoroarenes.[4] Furthermore, despite its relative steric bulk, Co(TMP)$_2$ undergoes stepwise insertion of CO$_2$ in one or two of its Co–N bonds. This insertion study has been extended to other unsaturated organic electrophiles such as isocyanates, isothiocyanates and nitriles. Interestingly when assessing its reactivity towards amines the competition between insertion and metalation reaction can take place.



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Structure and reactivity of a rhenium(VII)-methylidyne complex

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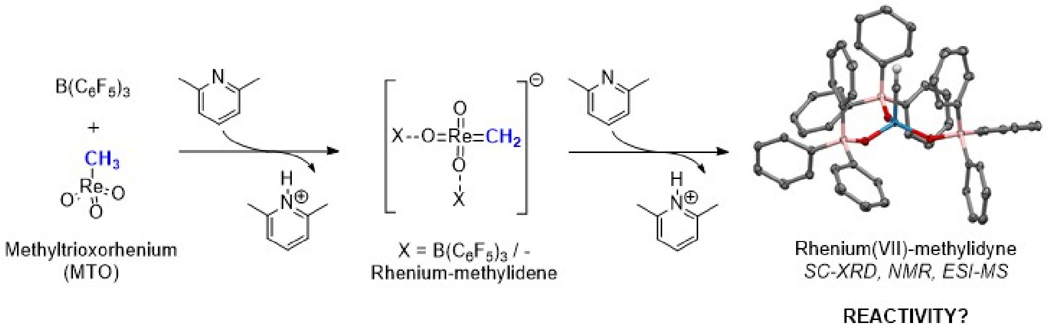
Methyltrioxorhenium (MTO) supported on Al_2O_3 or SiO_2-Al_2O_3 is an efficient heterogenous alkene metathesis catalyst.[1] Surface studies revealed that MTO interacts with highly Lewis-acidic tricoordinate aluminum centers on the support surface, and that its methyl group is C–H activated resulting in rhenium-methylidene species.[2,3] We have previously developed a homogeneous model system for the MTO/Al_2O_3 catalyst, consisting of a frustrated Lewis-pair ($B(C_6F_5)_3$/2,6-lutidine). The highly Lewis-acidic $B(C_6F_5)_3$ was shown to coordinate to MTO, which allowed for the deprotonation of the MTO methyl group by 2,6-lutidine. The resulting highly active rhenium-methylidene species was not observed. However, performing ESI-MS studies on reaction mixtures with different sterically hindered cyclic alkenes (e.g. norbornene), allowed for the detection of active rhenium-alkylidene species. While the activation mechanism and the nature of the active species was found to be similar to the heterogenous system, we have identified several catalyst deactivation pathways which are most likely unique for our model system. The second deprotonation of the catalytically active rhenium-methylidene species was shown to yield a rhenium-methylidyne complex, which was characterized by ESI-MS, NMR and SC-XRD.



In this work we explore the stability and reactivity of this rhenium(vii)-methylidyne species. We show that the 2,6-lutidinium cation of the doubly negatively charged methylidyne species can be readily exchanged with more innocent tetrabutylammonium cations. This simple modification significantly increases the thermal stability of the complex, which allowed us to explore its reactivity towards different substrates containing double and triple bonds. We also examine if the controlled re-protonation of the rhenium-methylidyne complex could provide a more convenient entry point towards the alkene-metathesis catalytic cycle.

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Metal template synthesis of aromatic tridentate ligand for studying the stability of lanthanide complexes in solution and solid state

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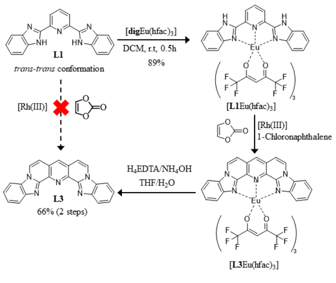
The *trans-trans* arrangement[1] of **L1** explains the failure of the rhodium-catalyzed cycloaddition of benzamides and alkynes via C-H/N-H activation to afford ultimately the ligand **L3** (red cross in Scheme 1).[2] A side-product [Cp*Rh**L1**][SbF$_6$]$_2$ reveals that the Cp*Rh unit can be encapsulated in the concave ligand **L1** acting as a bidentate chelate. Consequently, the bound Rh(III) catalyst cannot activate the CH-pyridine located on the opposite side of the bound ligands and no insertion occurs. In order to overcome the synthetic limitation, the complexation of **L1** to [Eu(hfac)$_3$] has been considered for (i) forcing the coordinated tridentate ligand to accommodate the *cis-cis* orientation required for the intermolecular rhodium-catalyzed reactions between vinylene carbonate and the NH and CH units of the bound ligand **L1** (Scheme 1), and (ii) pretending the molecular encapsulation of Rh(III) inside the **L1** cavity. As expected, the reaction of [**L1**Eu(hfac)$_3$] with vinylene carbonate, followed by decomplexation reaction with H$_4$EDTA, generates the target compound **L3** with a reaction yield of 66%.



Scheme 1. Metal template synthesis of the terdentate ligand **L3**.

In order to study the influence of the level of preorganization and the steric effect in lanthanide complexes, we prepared the *N*-substituted tridentate **L4-L6** and semi-rigid **L2** ligands. The increasing level of preorganization along the **L1?L2?L3** series leads to a duality where improved formation constants with lanthanides in CD$_2$Cl$_2$ are accompanied by decrease Ln-N affinity in solid state due to a limited match between the lanthanide size and the enlarged preorganized cavities. On the contrary, the connection of an additional methyl group at the 1-position of the benzimidazole moieties in **L4, L5** and **L6** implies a decreased stability with trivalent lanthanide and accompanied by variable coordination geometries, angular distortions and metal-nitrogen bond lengths.

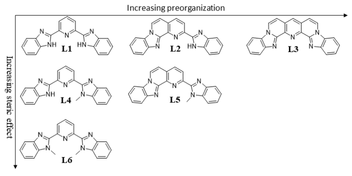


Figure 1. Chemical structures of ligands **L1-L6**.

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Bio-Inspired Molecular Oxygen Evolution Catalysts with $\{Co_4O_4\}$ Cubanes Embedded in a Conducting Polymer

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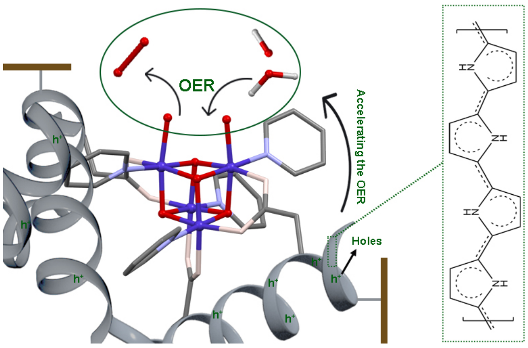
Exploration of efficient water oxidation catalysts based on polynuclear metal-oxo clusters for long-term application remains a key challenge and chance for the conversion of renewable energy sources into fuels. Cuboidal $\{Co_4O_4\}$ complexes keep attracting interest as molecular water oxidation catalysts as they combine features of both heterogeneous and homogeneous catalysis with bio-inspired motifs.[1-3] However, their application for the oxygen evolution reaction (OER) still requires stabilization strategies. Drawing inspiration from the structure of the oxygen-evolving complex of photosystem II (PSII),[4] we introduce a polymer-hybrid approach to immobilize $\{Co_4O_4\}$ cubane oxo clusters as OER catalysts. This strategy is based on asymmetric cubane design and their integration into conjugated polypyrrole, with the goals of enhancing the OER performance and preventing intermolecular aggregation during the OER. The asymmetric design not only reduces catalyst decomposition pathways, but also increases the catalytic efficiency by exposing a directed cofacial dihydroxide motif during catalysis. In addition to its protective function, polypyrrole is a p-type conducting polymer that promotes hole transfer during the OER process, resulting in higher turnover frequency (TOF) compared to the pristine $\{Co_4O_4\}$ oxo cluster and heterogeneous Co-oxide benchmarks. Based on the combination of our experimental and theoretical results, different oxygen evolution pathways, affected by intramolecular hydrogen bonding, are proposed. This study provides an elegant design concept for improving the efficiency of $\{Co_4O_4\}$ cubanes as easily accessible and very versatile OER catalysts.



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Design and characterization of new sensors based on functionalized organometallic cages for the selective detection of sugars and other analytes

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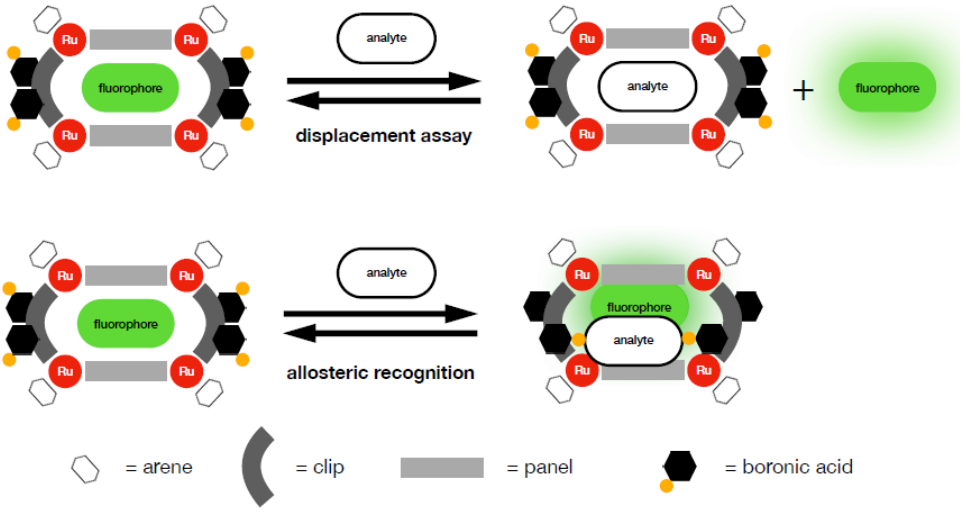
Mimicking nature, engineering of proteins, incorporation of intelligent systems, and robotization are four fundamental topologies driving our research in the development of advanced chemical sensors.[1] In recent years, the detection of biomolecules such as sugars and phosphorylated molecules, has garnered significant interest due to their crucial roles in biological processes and potential applications in medical diagnostics and environmental monitoring.[2] This project focuses on the synthesis of organometallic cages composed of transition metal nodes, such as Ru(II) and organic linkers, which are engineered to form stable assemblies.[3] These cages exhibit high surface area, tunable cavity sizes, and functional sites that can interact specifically with target biomolecules. By incorporating recognition elements, such as boronic acids, amine groups, pyridinium, sugars, and urea groups into the cage scaffold, we aim to enhance the selectivity towards analytes. The chemosensor is capable of selectively interacting with the analyte, as well as fluorophores, causing corresponding changes in the physical properties of the initial system (absorption spectra, fluorescence spectra, etc.). The complexity of the organometallic cages mimics proteins, and it shows an allosteric or displacement response to analytes. This project promotes the development of new metallacage-based sensors with potential applications in medical diagnostics, environmental monitoring, and beyond.



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Mechanistic Investigations of Metal-Oxo Cubane Formation

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Metal-oxo cubane complexes (of the formula $\{M_4L_4\}^{4+}$) based on cobalt and templated by the ligand 2-dipyridly ketone (dpk), have been shown to be effective photo-catalytic water-oxidation catalysts. The conformation of the dpk ligands in these metal-oxo cubane systems has also been observed to be affected by anion doping in the synthesis. In this work, the formation of these metal-oxo cubanes is investigated by synthetic parameter screening as well as through stopped-flow absorption methods. Investigation of a broad range of anions and reaction conditions gives insight into the interplay between metal ions and "innocent" anions in coordination complexes. Several novel structures are reported and their activity towards photo-catalytic water-oxidation are compared based on the ligand conformation in the metal-oxo cubane complexes.

Chemical and Redox Non-Innocence in Low□Valent Molybdenum □□Diketonate Complexes: Novel Pathways for CO_2 and CS_2 Activation

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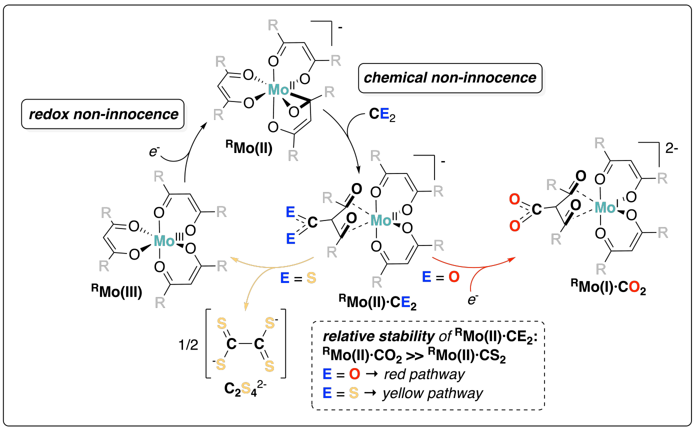
The investigation of fundamental properties of low□valent molybdenum complexes bearing anionic ligands is crucial for elucidating the molybdenum's role in critical enzymatic systems involved in the transformation of small molecules, including the nitrogenase's iron molybdenum cofactor, FeMoco.[1] The β-diketonate ligands in $[Mo(acac)_3]$ (acac = acetylacetonate), one of the earliest low□valent Mo complexes reported,[2] provide a robust anionic platform to stabilize Mo in its +III oxidation state. Surprisingly however, given the widespread use of β□diketonate ligands in coordination chemistry, only a very limited number of low-valent Mo β□diketonate complexes have been reported.[3] To address this gap, we explored the redox behavior of homoleptic molybdenum tris-β-diketonate complexes, employing a tertiary butyl substituted diketonate ligand (dipivaloylmethanate, ^{tBu}diket) to isolate and fully characterize the corresponding Mo complexes across three consecutive oxidation states (+IV, +III, +II). We observed marked reactivity of the most reduced congener with heterocumulenes CE_2 (E = O, S), yet with very distinct outcomes. Specifically, CO_2 stoichiometrically carboxylates one of the β-diketonate ligands, while in the presence of excess CS_2, catalytic reductive dimerization to tetrathiooxalate occurs. Through the isolation and characterization of reaction products and intermediates, we demonstrate that the observed reactivity results from the chemical non-innocence of the β□diketonate ligands, which facilitates the formation of a common ligand□bound intermediate, ^{tBu}**Mo(II)·CE$_2$** (E = O, S). The stability of this proposed intermediate dictates the specific reduction products observed, highlighting the relevance of the chemically non□innocent nature of β-diketonate ligands.



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Revisiting Early-Stage Coordination Chemistry: Exploring the Phosphorus Analogue of Hydroxylamine

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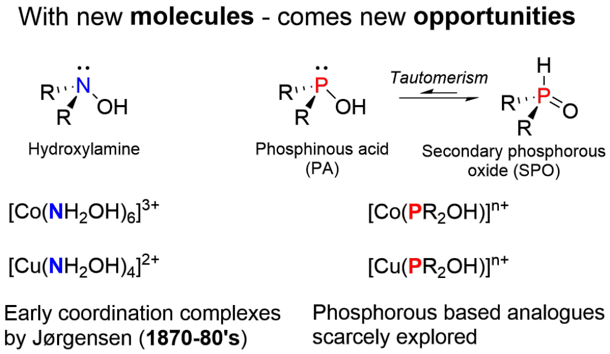
[1]ETH Zürich

One of the very first coordination complexes ever investigated was the hydroxylamine cobalt and copper complexes studied by the Danish professor Sophus Mads Jørgensen. He conducted his pioneering work 10-20 years before the Swiss chemist Alfred Werner established the foundational theory of coordination chemistry in 1893. In this study, we revisit the roots of coordination chemistry, but with a twist. We synthesized the periodic relative, the phosphorus analogue of hydroxylamine, namely a secondary phosphine oxide (SPO) / phosphinous acid (PA). We will demonstrate that it offers interesting and rich coordination chemistry, and we reiterate the importance of making and studying new molecules.



With new **molecules** - comes new **opportunities**

Hydroxylamine

Phosphinous acid (PA)

Secondary phosphorous oxide (SPO)

$[Co(\mathbf{N}H_2OH)_6]^{3+}$

$[Cu(\mathbf{N}H_2OH)_4]^{2+}$

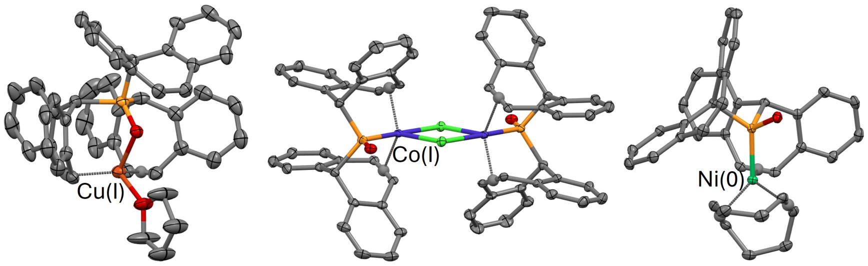
Early coordination complexes by Jørgensen (**1870-80's**)

$[Co(\mathbf{P}R_2OH)]^{n+}$

$[Cu(\mathbf{P}R_2OH)]^{n+}$

Phosphorous based analogues scarcely explored

The SPO-PA equilibrium results in a rich variety of bonding modes for the ligand: The way this ligand binds to metals—either through the hard oxygen donor atom or the soft phosphorus donor atom—strongly depends on the metal and the conditions [1]. This is why we have explored the synthesis and bonding of this specific tridentate olefin-based SPO ligand with metals across the periodic table, including: Cu, Co, Ni, Mn, Zn, Rh, etc. Opportunities and applications will be shown and discussed [2].



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Exploring New Methathesis Routes to Access Calcium Organometallics

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Since Victor Grignard's discovery of Grignard reagents (RMgX) in 1900 there has been significant utilisation in labs for synthesis due to their highly nucleophilic nature. People have often sought to expand this success to the use of heavier analogues. Calcium's high abundance (4.2% earth crust) along with its low toxicity has great promise for such function.[1] Yet unlike Grignard reagents organocalcium reagents are difficult to prepare, due to the low energy of atomization of calcium making direct synthesis from calcium metal impossible without prior activation [2,3](typically through addition of liquid ammonia). Routes to synthesise these reagents via salt metathesis routes using CaI_2 and organolithiums lead often to the formation of complex mixtures of calciates along with the desired product.[4] The origin of these calciates occurs due in part to the low solubility of CaI_2 leading to poor stoichiometrical control.[5]

In this work we showcase how by using highly soluble Ca amide $Ca(HMDS)_2$ (HMDS= Hexamethyldisilazane) along with N-donors such as PMDETA (N,N,N′,N″,N″-pentamethyldiethylentriamine) in combination with RM (M= Li, Na, R= alkyl, aryl), we can break the calciate intermediates formed from salt metathesis routes in order to form both alkyl and aryl calcium reagents in high yields with excellent selectivities (see Figure 1). These reactions are driven by the insolubility of the MHDMS byproduct. We also show the structural diversity of both alkyl and aryl calcium species along with contrasting the unique reactivity of organocalcium reagents.

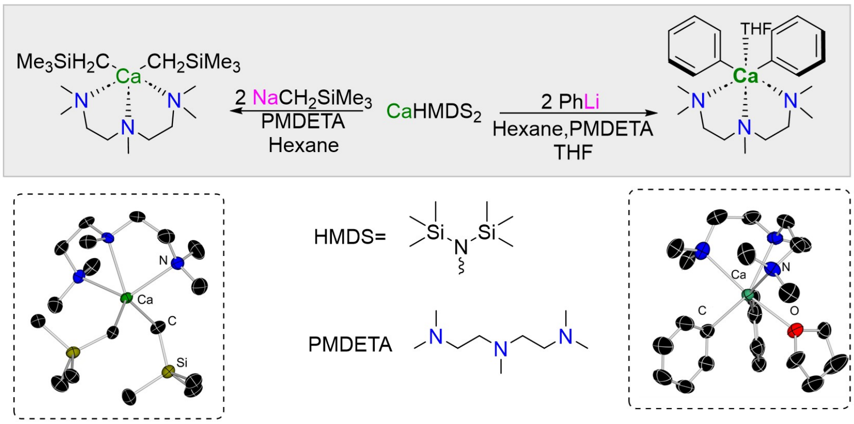

Figure 1 Synthesis of aryl and alkyl calcium from $CaHMDS_2$

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Probing of BDFEs of surface Pd-H across solvent environments and applications thereof

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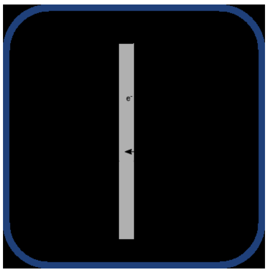
Common to many energy-relevant small molecules transformations, ranging from conversion of CO_2, H_2, N_2, etc., is the involvement of proton-coupled electron transfer (PCET) processes, i.e. the transfer of hydrogen atom equivalents (n(H^+ + e^-)) therein.[1] Mediators that transfer H atom equivalents have recently been shown to be promising catalysts for such transformations, prompting further development of mediators that promote different catalytic reactions.[2,3]

The thermodynamics of any PCET reactions is benchmarked by the bond dissociation free energy (BDFE) of the heteroatom-hydrogen (X-H) bonds involved therein. While BDFEs of molecular PCET mediators are well defined, tuning them remains challenging. On the other hand, surface metal hydrides (M-H's) have been shown to possess tuneable BDFEs, and could lead to new applications in heterogeneous catalysis.

Metallic Pd has been recently revisited as a hydrogen atom mediator[4,5]. Thanks to its permeability to hydrogen atoms, one could separate the generation and consumption/characterisation of surface metal hydrides (Pd-H), allowing transfer of H atoms obtained from aqueous Volmer reaction to organic media. Herein, we demonstrate that the characterisation of surface Pd-H BDFE via potentiometry, originally applied in aqueous media, can be extended to buffered and conductive organic solutions, allowing the construction of an RHE without use of H_2 gas cylinders or junctions, avoiding potential safety hazards and junction potential issues. This would 1) allow easier determination of med-H BDFE values and 2) pave way for further research to tune surface M-H BDFEs via e.g. doping of secondary metals. With another pH-independent redox couple, e.g. $Fc^{+/0}$, as pseudo-reference electrode, such device could also be used as a membrane-free pH meter not only in aqueous, but also organic media.



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Salen-derived heterometallic complexes

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Salen is one of the most studied ligands in chemistry, notably for its straightforward synthesis and its ability to coordinate to a variety of metal ions.[1] This Schiff Base compound has a N_2O_2 chelate site allowing the coordination of one metal ion. Salen is a versatile ligand that can be functionalized to create a wide range of new ligand structures, offering numerous possibilities for further functionalization.

In our studies, we aim at synthesizing heterometallic complexes with two or three different metal ions. To achieve this goal, salen can be functionalized with glycol chains creating e.g. a O_3O_3 recognition site for a second metal ion. The combination of different metal ions can provide enhanced chemical and biological properties.[2] For instance, the synthesized heterometallic complexes could be used as mixed metal oxides precursors or show potential synergic antibacterial properties.[3] In addition, functionalized salen with aromatic rings (e.g. naphthalene) can be used as fluorescent sensor.[4] We report the results for several antimicrobial tests, mixed metal oxide precursors, and fluorimetric sensing.

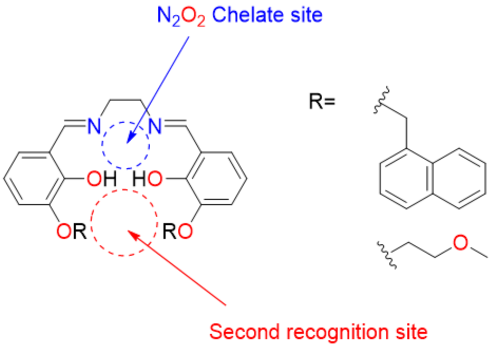

Fig. 1: Representation of salen-derived ligand with N_2O_2 chelate and second recognition sites.

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Synthesis and Understanding of Donor Flexible Thioamide Ligands

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Pyridylidene amides (PYAs) are nitrogen-based donor-flexible ligands offering properties that enhance their applicability in various catalytic transformations. PYAs exhibit the unique ability to adapt to different electronic environments by exhibiting neutral (L-type) and anionic (X-type) metal bonding.[1] Donor-flexible amides have demonstrated remarkable catalytic performance in transition metal-catalyzed reactions such as hydrogen transfer catalysis,[1] and oxidation of alcohols,[2] olefins[3] and water.[4] In this research endeavor, we expanded the donor-flexible family tree to include thioamides. We synthesized the first pyridylidene thioamide (PYT) and we performed investigations underscoring the similarities and differences between PYAs and PYTs. Using spectroscopy, cyclic voltammetry, and XRD, we established that PYTs can serve as robust ligands for catalytic reactions, possessing strong donor properties. These properties have been applied to develop transition metal catalysts that considerably outperform PYA-based systems in transfer hydrogenation.

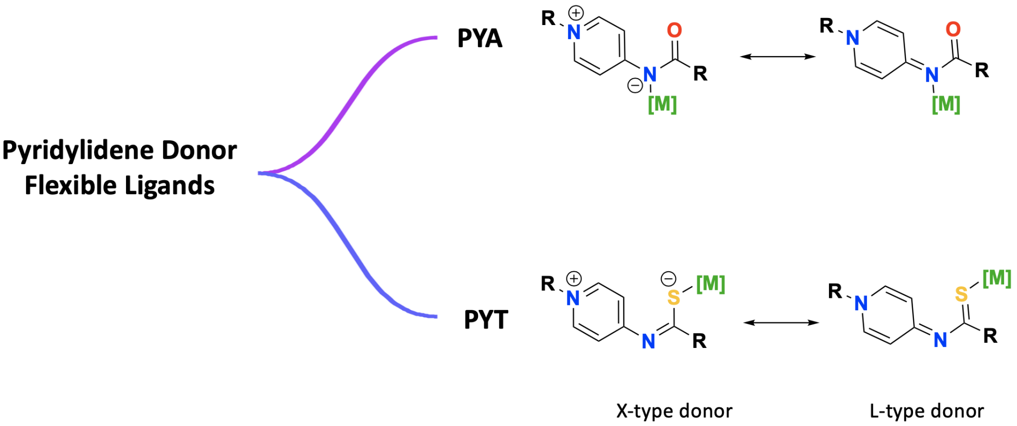

Figure 1: Zwitterionic X-type and quinoidal L type resonance structures of PYA and PYT ligands

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Hetero- and homometallic complexes based on (iso)-nicotinic acid

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Nicotinic acid is a well-known molecule in the biological and chemical fields. Also known as Niacin (or as Vitamin B3), it is an important molecule for our organism as it is the precursor of two coenzymes that are fundamental for our metabolism: NAD and NADP[1]. Because of its obvious biocompatibility, this molecule has always been a subject of study.[2] In addition, the presence of the N-donor pyridine (or iso-pyridine) makes this molecule an ideal candidate for the construction of MOFs based on the use of metal ions of medical interest, such as Zn, Cu, Ag, Pt or Mg. Studies conducted in our research group in the past have demonstrated good in vitro antimicrobial activity of silver (I) coordination compounds derived from isonicotinic or nicotinic acid.[3] Thus, building on the encouraging data previously obtained, this project also aims to investigate the anti-tumor properties of new coordination compounds derived from (iso)-nicotinic acid. In fact, metal based compounds have been the basis of important therapeutic strategies against cancer (e.g. Cisplatin).[4,5] Moreover, nicotinic acid derivatives are currently available as anti-cancer drugs.[6] The first step in this study is to synthesize ligands by functionalizing (iso)-nicotinic acid, and many synthesis strategies for that are adopted. Symmetric and asymmetric ligands were designed by exploiting the flexibility of polyglycol ethylene and polyamine chains. Their coordination to metal ions will be presented.

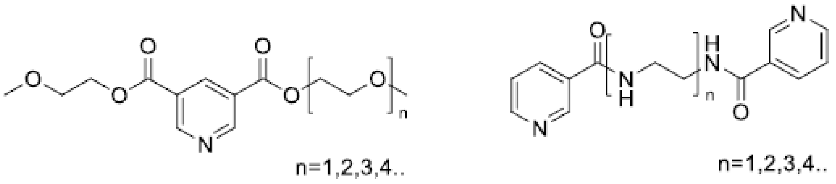

Figure 1 : Examples of new structures for (iso)-nicotinic acid-based ligands

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New Frontiers in Organocaesium Chemistry: Advances with Caesium Amides

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Despite the slow adoption by synthetic chemists of the first caesium amide, CsHMDS [$CsN(SiMe_3)_2$], reported by Stalke in 1992,[1] recent studies indicate a promising future for caesium amides. Guan recently reported using CsHMDS as a catalyst for benzylic hydrogen isotope exchange (HIE) with D_2 gas, although forceful reaction conditions (4 bar, 80 °C, 24 h) are required and the constitution of the organometallic intermediates involved in these reactions remain concealed.[2] Recently our group has reported that sodium amide NaTMP (TMP= 2,2,6,6-Tetramethylpiperidine) in combination with the tridentate ligand PMDETA (N,N,N',N'',N''-pentamethyl-diethylenetriamine) is a powerful metallating reagent that can outperform its lithium counterpart for the borylation of non-activated arenes[3] as well as promote the perdeuteration of arenes like naphthalene using C_6D_6 as deuterium source under mild reaction conditions.[4]

In this work, we report the exploration of the synthesis and reactivity of caesium amide reagent CsTMP, with the incorporation of several Lewis donor ligands such as PMDETA or Me6TREN (N,N-Bis[2-(dimethylamino)ethyl]-N',N'-dimethyl-1,2-ethanediamine) which has characterised by X-ray crystallography and NMR spectroscopy (Figure 1). The ability of [$\{CsTMP(PMDETA)\}_2$] **(1)** to metalate non-activated substrates such as toluene was examined by intercepting the metalated intermediates with a range of unsaturated organic electrophiles such as Weinreb amides, demonstrating its higher efficiency compared to other alkali metal analogues. In addition, **1** has demonstrated excellent catalytic abilities in promoting the perdeuteration of arenes using C_6D_6 as a deuterium source, as shown in Figure 1 for naphthalene.

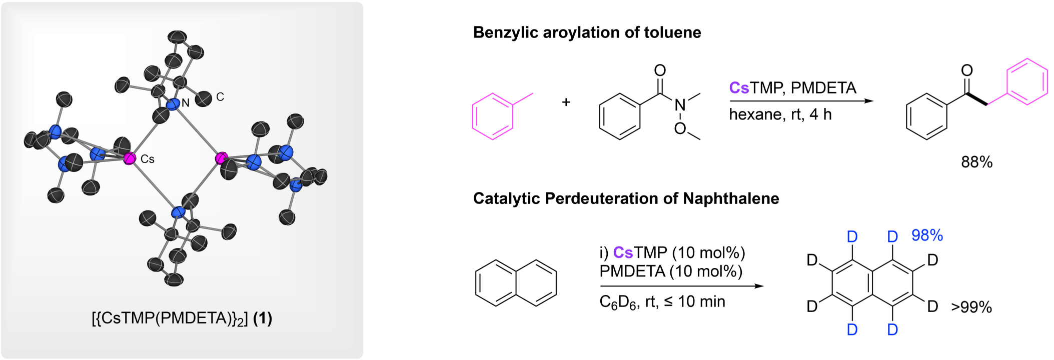

Figure 1: Reactivity studies with CsTMP.

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Speciation and Profiling of Bulky Chiral Cyclopentadienyl Cobalt Complexes

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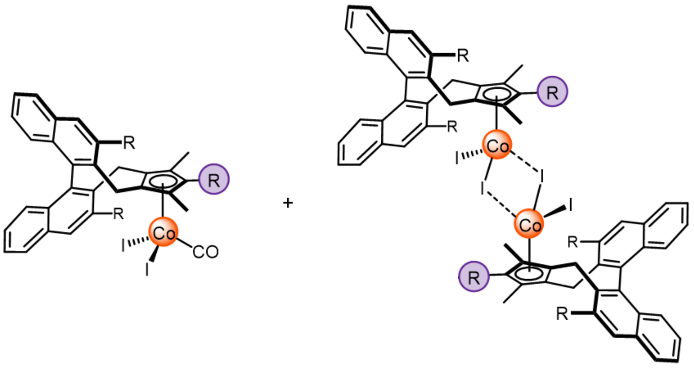
Answering the global call for sustainability, we aim to trade the use of precious noble metals in catalysis for Earth-abundant 3d-metals, such as cobalt, considering their vastly reduced environmental footprint, substantially lower cost, and significantly reduced toxicity.[1] Notably, it also holds tremendous potential, since they can display both similar as orthogonal reactivity patterns compared to their 4d- and 5d-congeners. The Cramer group endeavors to seize this opportunity by developing synthetic routes, that allow the construction of a diverse set of Earth-abundant cobalt(III) complexes, bearing tailored chiral cyclopentadienyl (Cp^x) ligands,[2] and subsequently employing them as effective catalytic agents in various enantioselective C-H functionalization reactions.

Herein, we disclose some exciting findings with regard to organometallic speciation, unveiled during our ongoing development of cobalt(III) complexes, that carry novel pentasubstituted Cp^x ligands. The increased steric encumbrance of the latter result in the formation of distinct species upon cobalt complexation, differing in the nature and number of auxiliary ligands. Aside from coordinatively saturated mono- and dimeric structures, the unexpected presence of an air-stable 16-electron Cp^xCo-complex was confirmed as well.



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Synthesis and Catalytic Applications of Highly Reduced Heterobimetallic Nickelates

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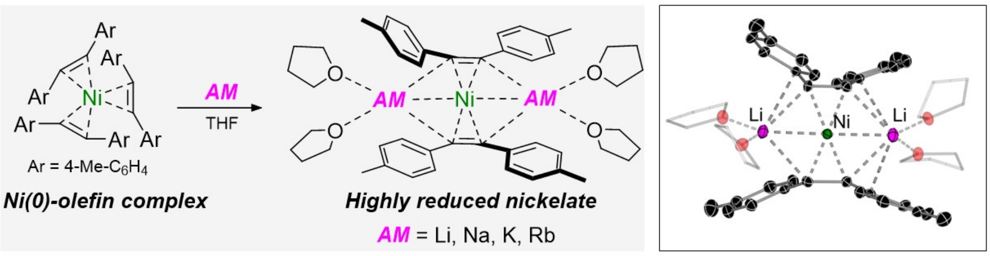
Nickel(0)-olefin complexes were first reported in the 1960s by Wilke[1] and continue to serve as ubiquitous and versatile Ni(0) sources with widespread use as reagents or in catalysis. Heterobimetallic nickelates derived from Ni(0)-olefin complexes and polar organometallics have recently witnessed a renaissance due to their involvement in challenging cross-coupling reactions,[2] whilst highly-reduced nickelates which can be accessed by direct reduction with alkali-metals are currently underexplored.[3]

Using air-stable [Ni(trans-stilbene)3] complex[4] as a Ni(0) precursor, this contribution will discuss the synthesis, structure, bonding and reactivity of highly reduced nickelates, obtained directly by reduction with the relevant alkali-metal (Li, Na, K and Rb). Profiting on their highly reducing nature, these compounds can promote challenging synthetic transformations, such as catalytic alkene isomerization, reductive couplings and hydrogenations.[5]



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Controlled Heteroelement-Transfer onto Transition Metal Phosphide Surfaces

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One big challenge in catalysis is the need for replacing noble metal catalysts with materials based on more earth-abundant elements. Transition metal phosphides have shown promising catalytic activity for hydroprocessing reactions as well as water splitting. [1-2] A positive effect on the catalysis by transition metal phosphides has been discovered upon incorporation of a range of heteroelements into the transition metal phosphides.[3-4] However, how the heteroelements influence catalysis is in many cases unclear, because the addition of the heteroelements to the phosphides is often not well controlled. Recently, we have reported a more controlled manner of adding sulfur to cobalt phosphide using molecular S-transfer reagents.[5] Our method enabled important insight into the effect of different number and types of sulfur on the surface on catalysis. Here, we show that our molecular methods can be easily extended to other heteroelement-transfers onto transition metal phosphide surfaces. The addition of such heteroelements is governed by thermodynamics and reversible. Our results provide key insight into the identity of different binding sites at the surface of transition metal phosphides and open new avenues for rational development of compositional engineering of catalytic phosphide surfaces.

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The coordination chemistry of di(2-pyridyl) ketone: Structural versatility and synthetic strategies of the Co^{2+}/Zn^{2+} chemistry with the ligand di(2-pyridyl) ketone

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Transition metal oxo clusters are highly valued for applications in single molecule magnets, water oxidation catalysis, and as photoluminescent materials.[1] The ligand di(2-pyridyl) ketone exhibits versatile binding modes, with its ketone group undergoing nucleophilic attack by solvent molecules in the presence of metal salts. This facilitates the formation of complex transition metal oxo species, including transition metal oxo cubanes, which are structurally similar to the oxygen-evolving complex (OEC) in Photosystem II (PSII).[2] Adjustments in reaction conditions, such as the use of different counterions like ClO_4^-, significantly impact the structural composition and catalytic performance of resulting complexes.[3] This poster will highlight the structural versatility of these cobalt or zinc oxo clusters and the various reaction conditions employed to synthesize them, providing insights into structure determining parameters.

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Reactivity of Diazoolefins

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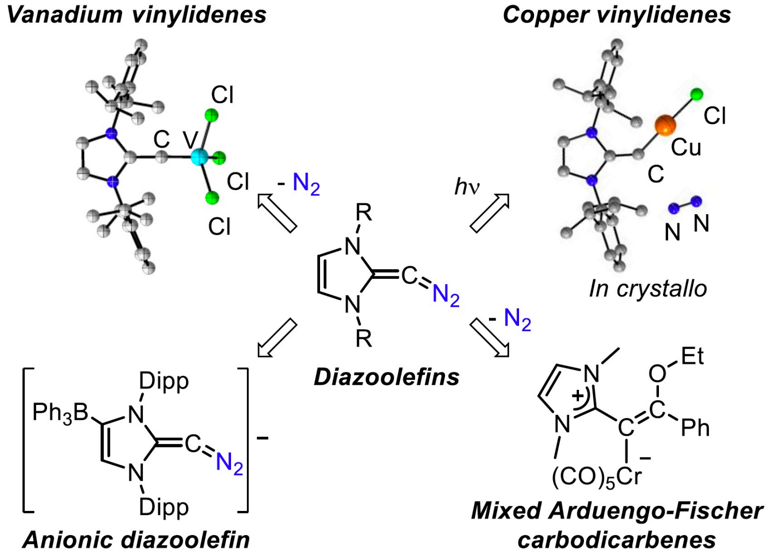
Diazo compounds of the type R^1R^2CN2 are widely used in organometallic catalysis and synthetic chemistry. Stable diazoolefins, $R^1R^2C=CN2$, have only been isolated recently. Diazoolefins undergo cycloaddition reactions and tend to be carbon donors when used as ligands. In diazoolefin coordination chemistry, the diazo group mostly staysintact. However, when combined with VCl3(THF)3, an N-heterocyclic alkenylidene complex was obtained after spontaneous dinitrogen extrusion.[1] The diazo moiety can also be removed photochemically. Irradiation of diazoolefinsgives triplet vinylidene carbene intermediates, which undergo intramolecular C-H activation. Irradiation of diazoolefincopper complexes gave a collection of complexes, including a bridged alkenylidene copper cluster and a C4-cumuleneligand.[2] In crystallo irradiation resulted in a monomeric copper alkenylidene, which likely acts as a reactive intermediate in solution-based reactions. A new type of diazoolefin was obtained after deprotonation and subsequent borylation.[3] The resulting anionic diazoolefin was used in salt metathesis reactions and showed distinct reactivity compared to neutraldiazoolefins. Stable carbene, germylene and multiple neutral diazonium compounds were reported. Combining diazoolefins with Fischer carbenes formed mixed Arduengo - Fischer carbodicarbene ligands via formal vinylideneinsertion into the metalbond.[4] The resulting complexes were able to undergo transmetallation reactions, and the free carbodicarbene could be isolated.



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