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Furan or tellurophene, which will the ruthenium ion choose? Reactivity of furan and tellurophene embedded in the porphyrin skeleton.

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Porphyrin analogues containing other atoms instead of the internal nitrogen atoms are called heteroporphyrins. Among them, oxa- and telluraporphyrins exhibit unusual reactivity. The reactivity of telluraporphyrins is focused on tellurium atoms. Examples include chlorination or oxidation of 21-telluraporphyrin [1, 2]. In the reaction of 21,23-ditelluraporphyrin with acid, each tellurium atom was exchanged for two hydrogen atoms, forming a porphyrin-annulene hybrid [3]. Furthermore, the tellurophene ring(s) of the 21-oxa-23-telluraporphyrin and 21,23-ditelluraporphyrin was/were transformed into metallacyclopentadiene unit(s) embedded within the macrocycle using metal salts (Pd, Pt, Rh) [4]. These organometallic compounds are called ***metallaporphyrins***.

The exchange of heteroatoms in the macrocyclic core has also been observed in tetraoxaporphyrinogen. Four oxygen atoms were replaced by selenium or sulphur atoms using appropriate acids [5]. For 21,23-dioxaporphyrin, the Achmatowicz rearrangement was observed, in which the furan unit was converted into a 3-pyranone ring [6].

Here, we will present the reactivity of 21,23-ditelluraporphyrin and 21-oxa-23-telluraporphyrin towards ruthenium(II) and rhodium(I) ions. In the reaction of 21,23-ditelluraporphyrin with a ruthenium(II), the tellurium atom was replaced by ruthenium atom to form 21-ruthena-23-telluraporphyrin. In contrast, the reaction of 21-oxa-23-telluraporphyrin with ruthenium(II) led to the insertion of the ruthenium(II) ion into the macrocyclic cavity and the breaking the C–O bond in the furan ring to form the oxo-triphyrin ruthenium(II) coordination compound. In the reaction of this compound with rhodium(I), the furan ring was mended, while the tellurium atom was replaced by rhodium to form 21-oxa-23-rhodaporphyrin.

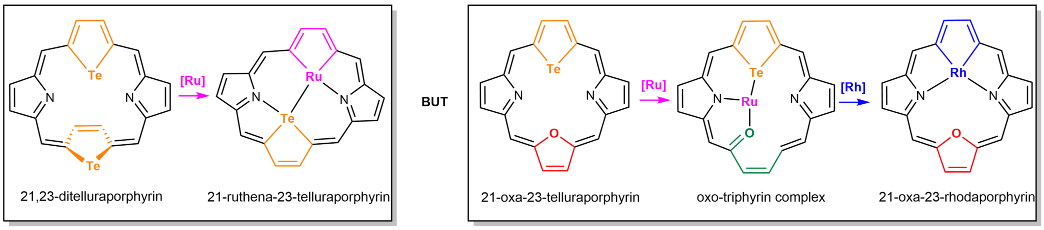

Figure 1. The reactivity of diheteroporphyrins towards ruthenium(II) and rhodium(I) ions. Additional substituents and ligands are omitted for clarity.

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Metalation of Aromatic Compounds with Sodium Ferrates

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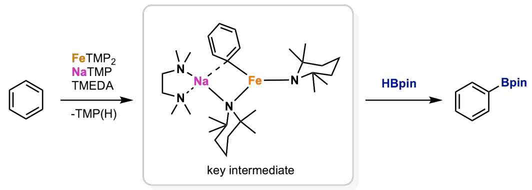
Deprotonative metalation constitutes one of the most utilized and important chemical reactions, facilitating the functionalization of molecules and the generation of novel reactive species. Traditionally these reactions are performed with monometallic organolithium or lithium amides, which are highly activated due to the large polarity of their Li-N or Li-C bonds. However, their high reactivity imposes challenges, which diminish the atom economy and synthetic processes that are far from sustainability. In particular, the metalation of most fundamental arenes such as benzene or other non-activated polyarenes remain challenging due to the lack of acidity based on the absence of functional groups. Herein, we represent the deprotonative mono- and multi-metalation of highly challenging substrates mediated by bimetallic cooperativity. The combination of earth abundant alkali metal sodium and iron in a bimetallic ate system allows a unique ability to promote direct Fe-H exchange on non-activated arenes at ambient conditions. With the isolation and characterization of the organometallic key intermediates, we were able to study the metalation process as well as the redox properties, leading to relevant arene species which can be valuable precursor to build more complex organic molecular scaffolds.



Anilido-aldimine group 4 complexes as catalysts for CO_2/epoxide cycloadditions

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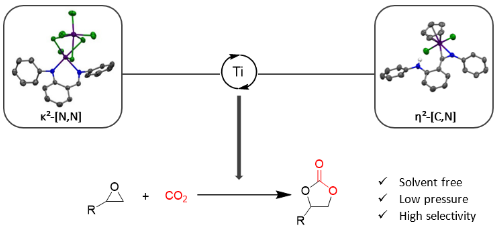
Anilido-aldimine ligands $[o\text{-}C_6H_4(NR_1)(CH{=}NR_2)]^-$ are homologues of the ubiquitous N-aryl β-diketiminate ($\{ArNC(R)\}_2CH^-$ or "nacnac") ligands. The benzannulated backbone of the anilido aldimine removes the notorious methine carbon on nacnacs, which is susceptible to nucleophilic behaviour in the presence of substrates like CO_2, all while retaining strong bidentate metal coordination and steric and electronic tunability.[1] Anilido-aldimine complexes of metals across the periodic table show unique reactivity and have been utilised as catalysts for a range of polymerisation reactions, as well as organic transformations.[2] Anilido-aldimine complexes possess two metal coordination modes: a κ^2 [N,N] mode and an η^2 [C,N] iminoacyl mode. The latter of which is highly uncommon in organometallic complexes, with just one previously reported structure.[3]

This work explores the versatility of anilido-aldimine ligands with group 4 metal centres, highlighting how the metal coordination mode can be influenced by the steric profile of the ligand and the metal fragment. Several anilido-aldimine ligands with a range of steric properties have been synthesised and further reacted *via* salt metathesis to form a series of titanium and zirconium complexes exhibiting both metal coordination modes.



✓ Solvent free
✓ Low pressure
✓ High selectivity

Towards the efficient capture and utilisation of carbon dioxide, a selection of titanium complexes have been taken forward as catalysts for CO_2/epoxide cycloaddition. The cyclic carbonate product formed is a key small molecule transformation in which CO_2 can be converted into useful chemical building blocks towards green solvents, lithium-ion battery electrolytes and bulk chemical processes.[4] Here we report the first use of η^2 titanium iminoacyl complexes as catalysts for the cycloaddition of CO_2 and a terminal epoxide under mild, solvent-free, conditions exclusively producing the corresponding cyclic carbonate with remarkable conversion.

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Synthesis and Structural Elucidation of New 5-atomic Heterocumulenes Anions [NCC-L] (L = CO, N_2, CS)

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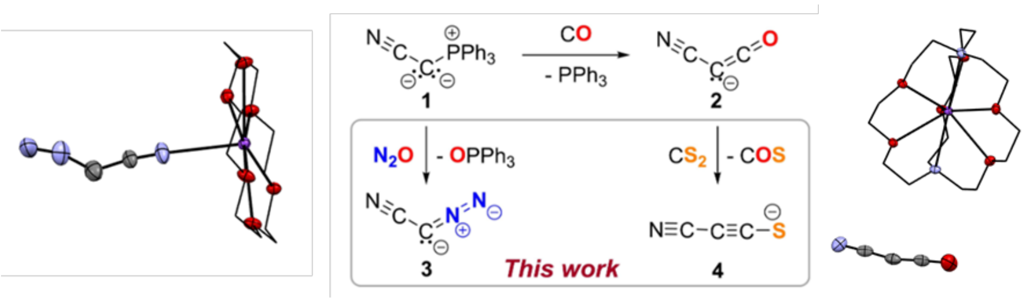
Cumulenes and heterocumulenes are very valuable intermediates in synthetic chemistry, but they are very reactive compounds, which makes their isolation difficult.[1] Some stable heterocumulenes are known, such as CO_2 or N_2O, but isolation of longer ones is very rare. Isolable heteroallenes such as ketenes, ketenimines or diazomethanes are versatile reagents in organic synthesis, exhibiting a wide range of reactivity. The reactivity of heterocumulenes increases with the number of double bonds, resulting in a higher propensity for oligomerization.

Recently, our group demonstrated that α-metalated ylides can undergo exchange of the phosphine ligand by CO.[2],[3] This process allowed the isolation of alkali metal ketenyl anions, which are viable precursors for various carbonyl-containing compounds based on CO as a sustainable C1 source. Building on this strategy, we published the synthesis of anionic diazomethanes by the reaction between an α-metalated ylide and N_2O.[4]

In this presentation we describe the synthesis and isolation of the anionic 5-atom heterocumulenes $[NCCCO]^-$, $[NCCNN]^-$ and $[NCCCS]^-$ and their reactivity towards other small molecules. Crystallography, spectroscopy and theoretical studies will be presented to discuss the geometry of these new heterocumulene compounds.[5]



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Development of heterobimetallic precursor molecules for atomic layer deposition

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The continual demand for new highly functional materials in the microelectronic industry will necessitate synthetic access to atomically precise thin films with novel and diverse elemental compositions. Molecular precursors have a key role in the process of atomic layer deposition (ALD), and new precursors are constantly being developed for improving the ALD process.[1] For the synthesis of heterometal oxide films, multiple ALD steps have to be carried out, where each metal atom is individually delivered. Consequently, the ratio of two individually delivered metals is difficult to control, leading to low atomic precision.[2] Heterobimetallic precursor molecules could circumvent that problem because the metals can already be preassembled in a ligand scaffold so that a single precursor delivers two different metals simultaneously during an ALD process.

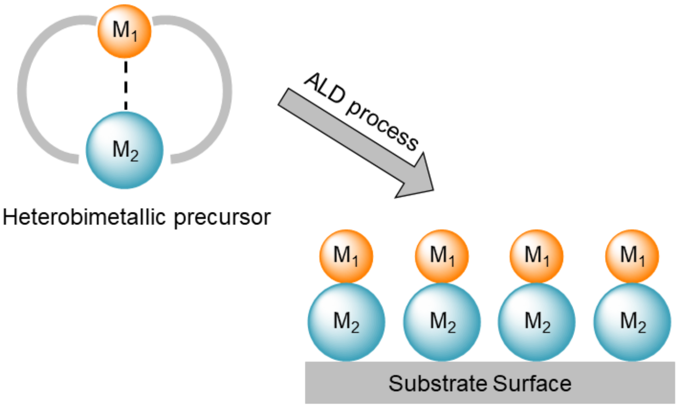

Figure 1. Schematic representation of an ALD process using a heterobimetallic precursor.

We present a variety of Al complexes with different aminopyridinato ligands. To evaluate the potential applications of the monometallic complexes as ALD precursors, and study the effect of different substituents on the volatility of the resulting complex, the thermal properties were investigated by thermogravimetric measurements. Furthermore, the first Co-Al heterobimetallic aminopyridinato complex was synthesized and the thermal properties of the complex were analyzed.

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Iron-based N-Heterocyclic Carbene complexes as emerging catalysts for Water Oxidation

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Water splitting is a key reaction in the advancement of innovative green energy technologies, enabling the production of molecular oxygen (O_2) and molecular hydrogen (H_2). For the oxygen evolution reaction (OER), water oxidation catalysts (WOCs) are essential to overcome the high overpotential associated with this process.[1] While traditional catalysts often rely on rare and expensive metals, iron-based alternatives have been explored in electrocatalysis due to their cost-effectiveness. However, these systems typically suffer from high overpotentials and low catalytic activity.

To address these challenges, our research group has designed and synthesized an iron N-heterocyclic carbene (NHC) complex that demonstrates competitive catalytic performance with reduced overpotential under basic conditions.[2] Our primary objective is to develop novel and efficient synthetic strategies to obtain iron complexes featuring variously substituted cyclopentadienone (CpO) and NHC ligands, which hold promise as heterogeneous catalysts for the water oxidation reaction (WOR). Specifically, NHC ligands incorporating a pyrene moiety have been designed to facilitate immobilization onto a glassy carbon working electrode.[3]

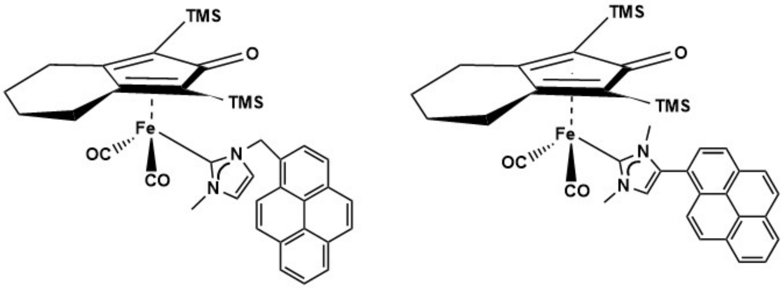

Figure 1: Synthesized Fe^0 complexes with CpO and NHC ligands

These complexes have been extensively characterized by NMR, IR, UV-vis absorption spectroscopy, ESI-MS, and cyclic voltammetry, and their electrocatalytic behavior is investigated in both homogeneous and immobilized forms through cyclic voltammetry analysis.

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Bimetallic Complexes with New Pyridine-based Ligands for Oxidative Transformation

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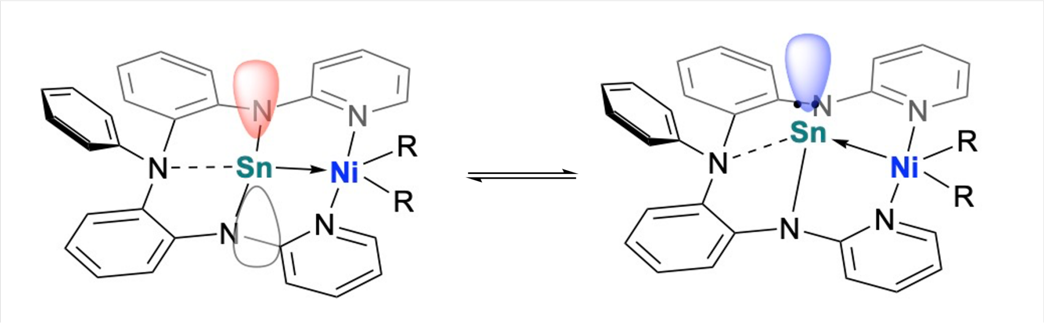
Heterobimetallic complexes with two metal atoms in close proximity can exhibit diverse metal-metal interactions and cooperative reactivity.[1] Pairing a divalent heavier group 14 element with a transition metal center can capitalize on the ambiphilic nature of group 14 carbenoids to simultaneously tune the electronics of the transition metal center and act as a secondary site for binding substrates.[2]

To date, phosphine donors have been strongly featured in main-group-based metalloligands for their favored coordination to low-valent transition metal centers. However, phosphines cannot support oxidative reactivity due to their tendency to become oxidized. We set out to explore metalloligands featuring pendant pyridine groups, which would withstand oxidizing conditions and also stabilize high oxidation states.[3] This enables us to explore transformations that are challenging with lower-valent metal counterparts.



Scheme 1 Ambiphilic character of group 14 metalloligands

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Alkynyl Nanoclusters of 3d Transition Metals: Synthesis, Characterization and Catalysis

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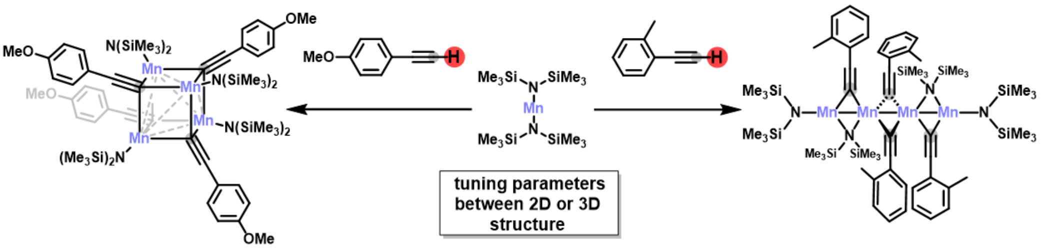
Polynuclear metal clusters composed of 3d transition metals such as manganese, iron and cobalt stabilized by organic ligands represent a unique class of materials that bridge the gap between molecular compounds and bulk nanoparticles. The clusters exhibit metal-metal or metal-nonmetal bond interactions, which contribute to their distinctive magnetic and catalytic properties.[1] Recently, our group has reported the synthesis of three-dimensional Mn_4-nanoclusters featuring μ_3-bridged organyl ligands.[2]

The cluster formation depends on the pK_a driven reactivity of metal amide precursors with moderately acidic compounds such as terminal alkynes. The heteroleptic clusters contain amide and acetylide ligands in equimolar ratios. The cluster architecture depends on the steric demand of both amide and phenylacetylide substituents where steric hindrance leads to a linear Mn_4-alignment or a dimeric configuration.



The current research focuses on elucidating the influence on the manganese arrangement. DFT calculations show that the energy difference between Mn_4-chains or cubane cores is less pronounce for bulkier substituents, thereby increasing the tendency to form chain structures or dimers. Ongoing studies are exploring the doping of the manganese cubane with other 3d transition metals such as iron, as well as the incorporation of linker motifs like 4,4'-bipyridine to rearrange the cubane structure to form 2D architectures.

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Development of new non-coordinating borate anions for lithium-ion batteries

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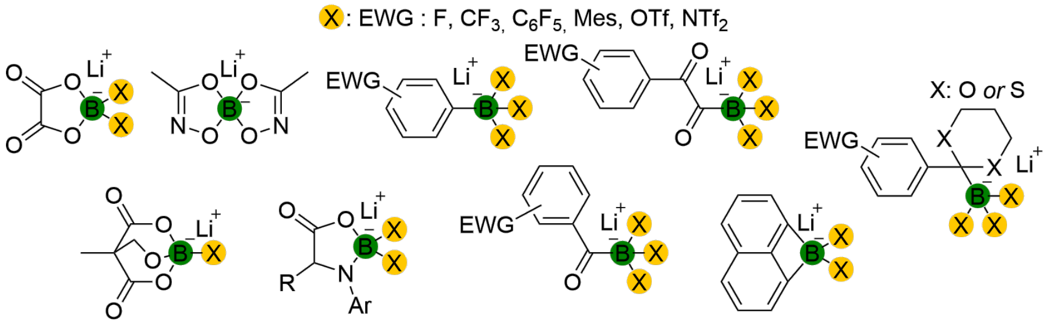
The development of advanced lithium-ion batteries (LIBs) is crucial to meet the increasing demand for high-performance energy storage systems.[1] This study focuses on the synthesis and characterization of novels non-coordinating boronated lithium ions aimed at enhancing the electrochemical properties of LIBs. By introducing boron into the lithium-ion framework, we aim to improve ion transport and stability, which are critical for battery efficiency and longevity.[2]

The new boronated lithium compounds were synthesized using a combination of organoboron reagents and lithium salts under controlled conditions. The synthesis process was optimized to achieve high yields and purity. Comprehensive structural analysis was conducted using NMR spectroscopy, X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR).



Electrochemical performance was evaluated through cyclic voltammetry, electrochemical impedance spectroscopy, and charge-discharge cycling tests in a standard button cell configuration.[3] Preliminary results indicate that these boronated lithium ions exhibit improved ionic conductivity and thermal stability compared to traditional lithium salts such as BF_4^-, leading to enhanced battery performance, particularly in terms of higher charge capacity and longer cycle life.[4]

The promising electrochemical performance of the synthesized borate lithium salts not only paves the way for enhanced lithium-ion battery technologies but also highlights the versatile potential of boron chemistry. Beyond their application in energy storage, these boronated non-coordinating anions exhibit unique properties that can be leveraged in the design of advanced ionic liquids, which are crucial for green chemistry and sustainable processes. Additionally, their role as non-coordinating anions opens new avenues in organic catalysis, where they can improve reaction selectivity and efficiency by stabilizing reactive intermediates. These findings suggest that boronated compounds could serve as multifunctional materials, driving innovations not only in energy storage but also in broader chemical applications.

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Aurophilic interaction in d^8 complexes or enforced short contact? Investigation of diiminoisoindole coinage metal complexes...

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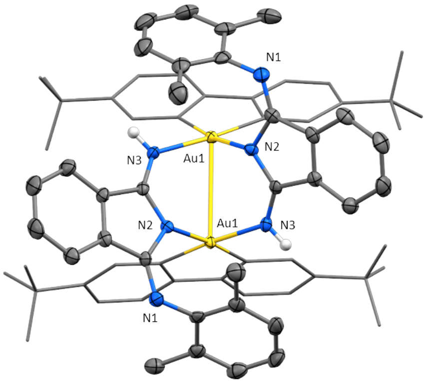
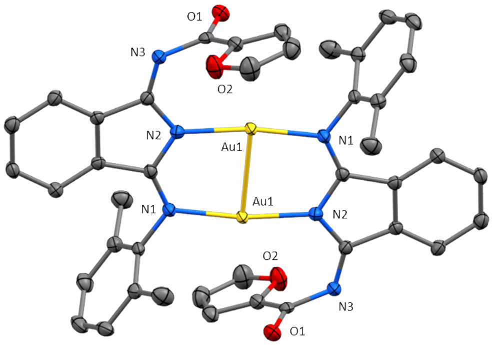
Isoindole and its derivatives already found application in multiple fields of chemistry. Among others, its use as pharmaceuticals or resistant pigments can be mentioned.[1]

A group of unsymmetrically substituted diiminoisoindoles was prepared and the coordination abilities of these ligands were systematically investigated. A significant group of prepared compounds are coinage metal complexes. These dimeric complexes contain unusually short metallophilic interactions between metal atoms in solid structure, as confirmed by X-ray crystallography. Their structure, properties and possible uses were investigated.

Counterintuitively, unusually short metal-metal distances have also been reported in the case of gold(III) complexes. We can therefore assume that, even in these complexes a weak aurophilic interaction can occur within the metallacycle. This phenomenon has already been described and discussed several times in the literature[2], but not fully proven or understood. That is why our work aims to further explore and explain this interaction based on experimental and computational research.





This work was supported by Czech Science Foundation (reg. No. 25-17434S).

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Synthesis of Quinazolinone Scaffolds *via* Zinc(II) Stabilized Amidyl Radical Promoted Deaminative Approach

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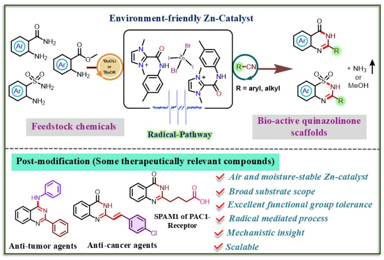
The C-N bond is one of the most important and prevalent bonds in nature, hence, development of better ways to generate C-N bonds has become one of the vital research objectives in synthetic chemistry.[1] In this context, N-heterocyclic scaffolds like quinazolinone indeed hold a significant position due to their versatile presence in several fields such as agrochemicals, pharmaceuticals, natural products etc.[2] In this line, herein, we report a solely ligand-based redox controlled effective deaminative protocol for the coupling of *o*-amino amides/esters with nitriles to afford quinazolin-4(3*H*)-ones, for the first time, utilizing C2-amidated imidazolium salt supported Zn-complex. This readily scalable solvent-free protocol works proficiently under low catalyst loading for a broad range of *o*-amino amides including sulfonamides and nitriles, ranging from benzonitrile to benzyl cyanide and also the aliphatic nitriles, with high level of functional group tolerance to provide the desired products possessing medicinally relevant scaffold in high yields Importantly, detailed mechanistic probes established the reaction pathway that proceeds *via* aminyl radical formation.[3] Further, synthetic utility of the obtained products was showcased by their post-modification to access therapeutically relevant complex organic molecules.

Keywords: Cyclization, Zn-Catalyst, C-N bond formation, bioactive molecule synthesis, nitriles



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Sodium Mediated Zincation of Dihydrogen and it's Applications on Imine Hydrogenation

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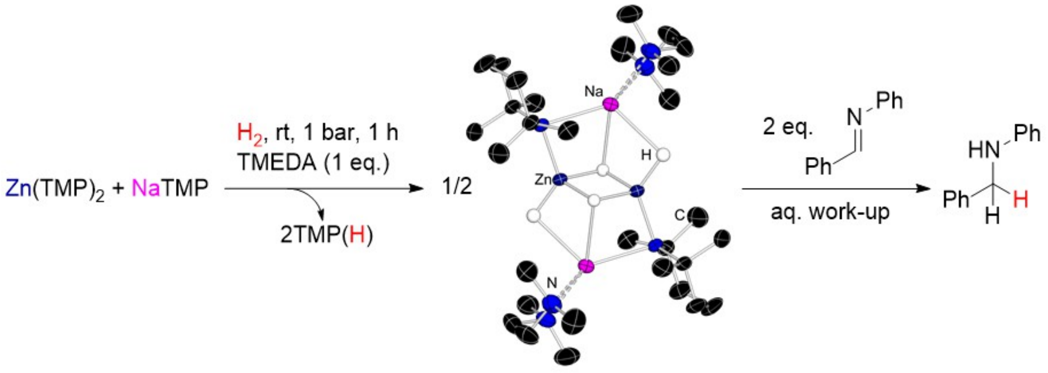
The hydrogenation of unsaturated substrates via molecular hydrogen activation is one of the most extensively utilized chemical reactions.[1] Although H_2 activation is typically induced by precious transition metals, growing societal emphasis on sustainability has driven efforts for alternatives to these often expensive, toxic, and scarce elements.[2] Recently main group metal systems have shown great promise using s-block metal amides,[3] and zinc complexes.[4] While these studies give high conversions, they often require harsh conditions, i.e. high temperatures, pressures, and long reaction times. Thus, efficient precious metal-free hydrogenation of unsaturated substrates via H_2 activation at ambient conditions would provide a breakthrough in this field.

Herein, we report the synthesis and characterisation of a novel well-defined sodium dihydride zincates species: $NaZnH_2(TMP)(TMEDA)$ (TMEDA= tetramethylethylenediamine), accessed through activation of H_2 by the combination of $Zn(TMP)_2$ and NaTMP (TMP = 2,2,6,6-tetramethylpiperidine) at ambient pressure and temperature. Both metal species show a synergistic effect for this process, being unable to activate and transfer H_2 efficiently on their own. Our studies have shown that both hydrides are active, as seen through hydrogenation of a model imine substrate at room temperature. These investigations are being extended towards other unsaturated substrates, examining the role of the alkali metal and the amide ligand.



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Unraveling the Mechanism of Reversible NAD^+/NADH Interconversion Catalyzed by Cp*Ir(Pyrazine-2-Amidate) Complexes

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Reversible electrocatalysis refers to an electrochemical process where an electrocatalyst facilitates a reaction in both the forward and reverse directions with minimal energy loss.[1] Electrocatalysts possessing such capability are termed “reversible” and play a crucial role in energy storage, conversion, and sustainable chemistry. However, the design of a reversible electrocatalyst is an extremely difficult task. As a matter of fact, only a handful of molecular systems have been reported so far exhibiting such an extraordinary property. Among them, we recently reported the reversible electrocatalytic NAD^+/NADH interconversion mediated by [Cp*Ir(pyza)Cl] (pyza = pyrazineamidate).[2] The latter catalyzes both NAD^+ reduction and NADH oxidation with high selectivity in response to even a small departure from equilibrium potential.

In this study, another member of the [Cp*Ir(pyza)Cl] (pyza = pyrazine amidate) family of complexes is reported exhibiting NAD^+/NADH electrocatalytic reversibility, *i.e.* Cp*Ir(*N*-Methyl-2-pyrazineamidate)Cl. Moreover, detailed mechanistic investigations using electrochemical methods and NMR studies are described. The experimental findings are interpreted based on the mechanism illustrated in Figure 1. Specifically, ligand centered $2e^-$, 1 H^+ proton coupled electron transfer (PCET) of the redox active form of the catalyst (**I**) leads to the formation of intermediate **II**. A subsequent metal/ligand proton tautomerism (MLPT) generates intermediate **III**, which then transfer a hydride to NAD^+, yielding the reduced cofactor NADH and regenerating the starting complex.

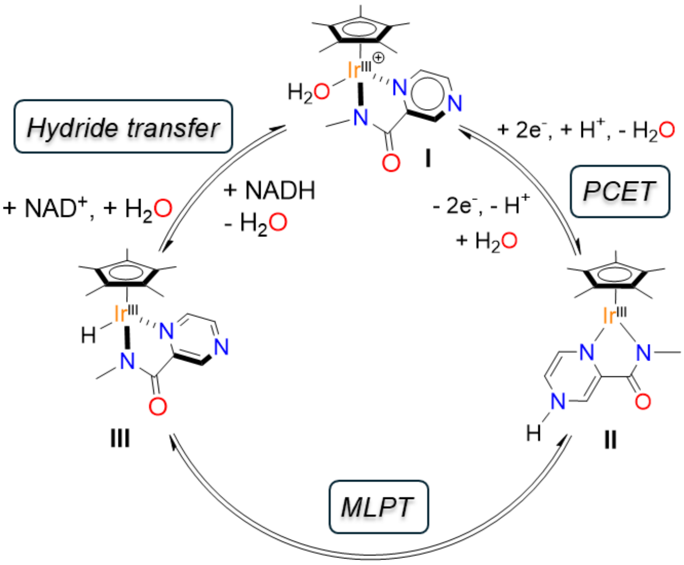

Figure 1. Proposed mechanism for the electrocatalytic NAD^+/NADH interconversion.

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(Electro)chemical N_2-splitting with MoX_3 complexes supported by PPP ligands: Towards the application fo arylphosphine donor groups

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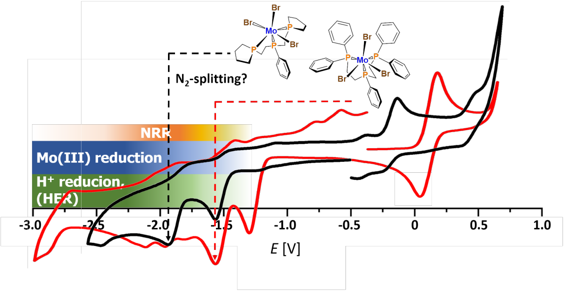
The production of ammonia and other N-containing building blocks from elemental N_2 is considered one of the more prestigious research fields in chemistry. To date, two main approaches towards NRR proved successful: 1) single site Chatt-type catalyst designs[1] and 2) pincer type metal nitrides, being superior in terms of raw output of ammonia with up to 60000 equivalents.[2] These impressive numbers are achieved by *in situ* formation of a (L)M-N≡N-M(L) intermediate, facilitating N_2-scission into (L)M≡N nitrides that are readily protonated to yield NH_3. One necessary condition for this is the correct number of electrons within the M-N≡N-M moiety.[3] With the field moving towards electrification of the NRR[4–6], the focus shifts onto reduction potentials facilitating the necessary electron count.[7,8] However, since most ligand designs employed are based on a PNP or PCP backbone with PR_2-donors (R = alkyl), reduction potentials for electrochemical N_2 scission are inside of the proton reduction (HER) window. Still, a study by the Peters group showed the feasibility of this approach, producing 11.7 eq NH_3 at -1.89 V vs Fc/Fc^+.[9] This inspired us to revisit N_2-splitting chemistry of PPP pincer type, since reported catalytic NRR seems to be based on separate electron- and proton-transfer steps[10] - similar to heterogeneous electron transfer on an electrode - compared to other catalyst/PCET reagent mixtures.[11] Additionally, we are investigating the need for terminal alkyl-substituents to shift reduction potentials outside the HER window. We will report on the synthesis of updated PPP designs featuring a varying number of aryl-substituents in the ligand backbone, their coordination chemistry and electrochemical reactivity under different conditions.



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Chemistry of Chromium σ-Borane/Borate Complexes

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Transition-metal σ complexes, in which an E–H σ bond (E = main group element) serves as a two-electron donor, have been extensively studied. Over the past decades, these complexes have been of significant interest due to their contributions in catalytic hydroboration, dehydrogenation, and CH functionalization reactions.[1,2] The family of σ-borane complexes is less explored than those of σ-silane and σ-dihydrogen complexes, mainly because of the scarcity of simple and convenient synthetic methods. Despite having catalytic applications, the number of early TM σ-borane complexes is relatively limited as compared to those containing late transition metals (chart).[3-5] During our research on early and late transition metal complexes with low boron contents, we have isolated some σ-borane/borate molybdenum complexes.[6] Subsequently, we have synthesized various chromium σ borane complexes, from the reaction of $[Cp^*Cr(CO)_3Me]$ with borane/borate reagents such as $BH_3{\cdot}SMe_2$ and $Li[BH_3(EPh)]$ (E = S, Se, Te). The key results of this work will be presented.

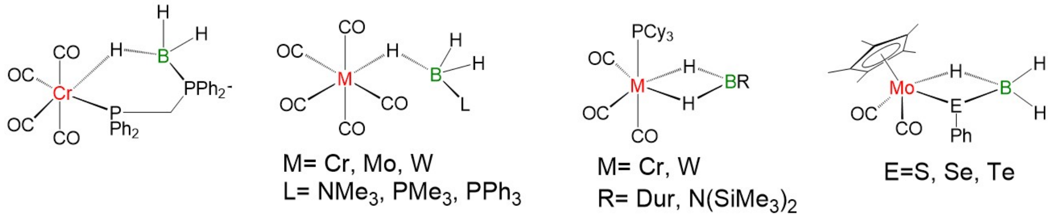

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Chart: Examples of group 6 transition metal stabilized σ-borane/borate complexes.

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PPh$_3$/Isocyanide and N$_2$/Isocyanide Exchange: Pathways to Isolable Alkali Metal Keteniminyl Anions

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Ketenimines ($R_2C{=}C{=}NR$), the nitrogen analogs of ketenes, are versatile reagents that can participate in nucleophilic, electrophilic, and pericyclic reactions, making them excellent precursors for synthesizing complex molecules.[1] Alkali metal keteniminyl anions represent promising reagents to access ketenimines via simple nucleophilic substitution reactions, yet their isolation has remained elusive until now. Drawing inspiration from recent advances in ligand exchange reactions at carbon,[2] herein, we report the successful synthesis and isolation of a series of keteniminyl anions in good to excellent yields by exchange of the phosphine ligand in the metalated ylide and the N_2 ligand in the diazomethanide with isocyanides.[3]

The keteniminyl anions exhibit a bent geometry in the solid state, with the bending angle decreasing as the electron-donating capacity of the nitrogen substituent increases. Density functional theory calculations revealed an intermediate bonding situation in the anions, falling between that of an ynamine ($RC{\equiv}C\text{-}NR_2$) and ketenimine ($R_2C{=}C{=}NR$), with electron-withdrawing groups at the nitrogen favouring the ynamine structure and a larger R-C-CNR angle. The keteniminyl anions react efficiently with unsaturated compounds to form a diverse array of heterocycles, highlighting their potential as versatile building blocks in synthetic chemistry.

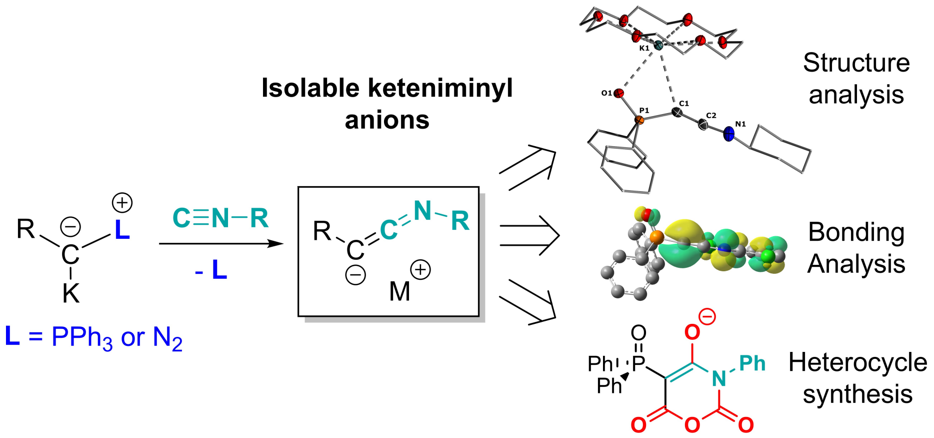

Fig 1. Accessing keteniminyl anion via ligand exchange reaction at carbon

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Zirconium Trielyl Complexes: Synthesis and Reactivity

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Anionic compounds of group 13 elements (E) in the +1 oxidation state can act as X-type ligands, allowing the formation of M-E bonds from electrophilic metal complexes.[1-3] Very few examples of group 4-group 13 metal bonds have previously been reported, with the majority of examples being of a donor-acceptor nature.[4-5] Exploration of the synthesis and geometric/electronic structure of covalent group 13-group 4 bonds is therefore of significant interest. The synthesis of bimetallic trielyl complexes is potentially hindered by the reducing power of the trielyl anion. As such, drawing inspiration from the recent synthesis of a beryllium aluminyl complex[1], π-donating cyclopentadienyl ligands/leaving groups were chosen to increase electron density at the transition metal centre, and favour metathesis over reduction. A range of trielyl (Al, Ga, In) complexes of zirconium were synthesised, using NON (4,5-bis(2,6-diisopropylanilido)-2,7- ditert-butyl-9,9-dimethylxanthene) ligated trielyl anions and $ZrCp_4$. The geometry of these complexes is significantly distorted compared to other bimetallic trielyl species, preferring an equatorial bonding mode within the TBP geometry at E instead of the more typical axial geometry.[1,2] The thermolytic and photolytic reactivity of the synthesised complexes was also explored, revealing trends relating to stability of the +1 oxidation state of E, the energies of the Zr-E bonding orbital and the orbital symmetry.

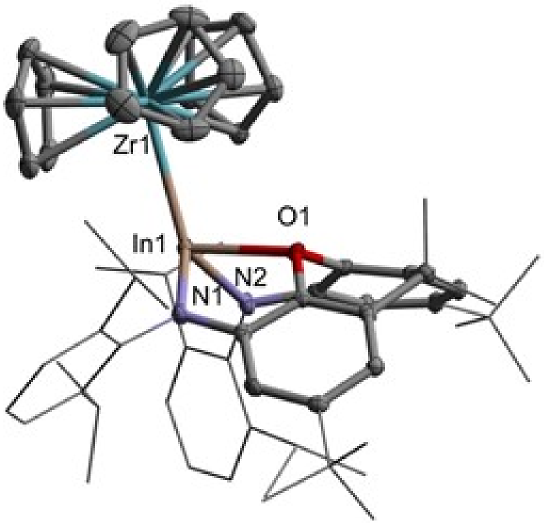

Figure 1: Molecular structure of $(NON)InZrCp_3$ in the solid state determined by X-ray crystallography

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E(0) cubane $Si_8\{N(SiMe_3)_2\}_6$: Insights into the formation and its diverse reactions

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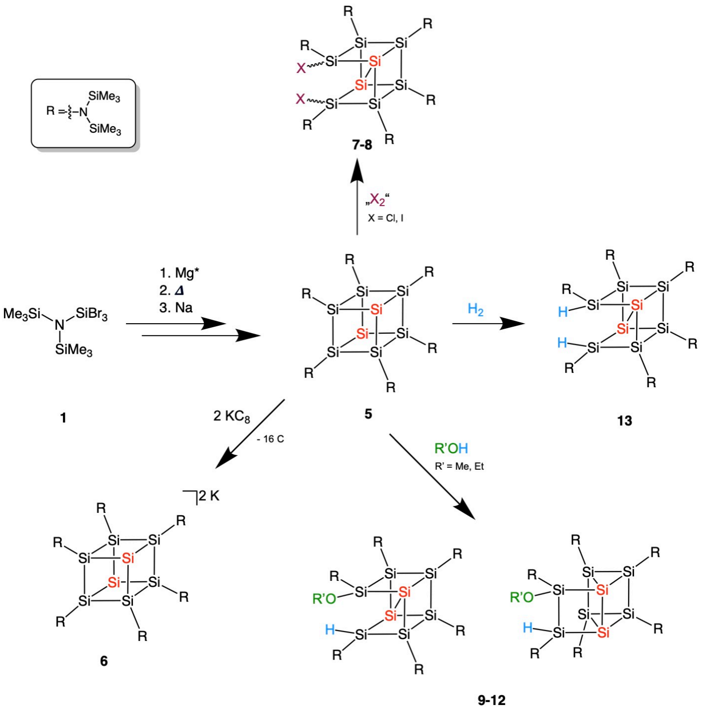
Reductive dehalogenation is a method for the synthesis of ligand-substituted clusters of group 14 elements. This includes “metalloid” and “siliconoid” clusters.[1,2] Due to the lack of commercially available Si(II)-precursors, the resulting synthetic strategies for silicon clusters with unsubstituted vertices is not always straightforward. Herein, we present the stepwise formation of the siliconoid octasilacubane **5**. This cluster was synthesized starting from the amido-substituted tribromosilane **1**[3] in several steps. Octasilacubane **5** shows interesting reactivities with halogens, alcohols and is able to activate dihydrogen under mild conditions. These reactions occur under retention of the unsubstituted silicon atoms.



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Hexaphenyl-1,2-Diphosphonium Dication $[Ph_3P–PPh_3]^{2+}$: Superacid, Superoxidant, or Super Reagent?

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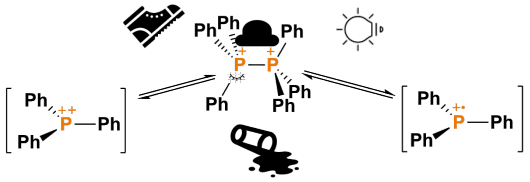
The long known trityl radical prefers to dimerize to Gomberg's dimer,[1][2] rationalizing the elusive nature of hexaphenylethane[3] in respect to its heavier and isolable congeners. Herein we present the characterization and reactivity of the isoelectronic group 15 analogue, namely the hexaphenyl-1,2-diphosphonium dication. Ambiphilic reactivity is demonstrated by its strong Lewis acidity, validated by fluoride abstraction from SbF_6, oxygen abstraction from $OPEt_3$, and Lewis donor substitution with DMAP and $^tBu_3P$. Under UV irradiation, it engages in H-atom abstraction from dihydroanthracene and CH phosphoranylation of difluorobenzene. Further, we describe the oxidation of trimethylphosphine, and addition to multiple bonds.[4]



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Synthesis and Characterisation of Cationic Gold Complexes Based on a 1,2,3-Triazolium Alkyne for Hydroamination Catalysis

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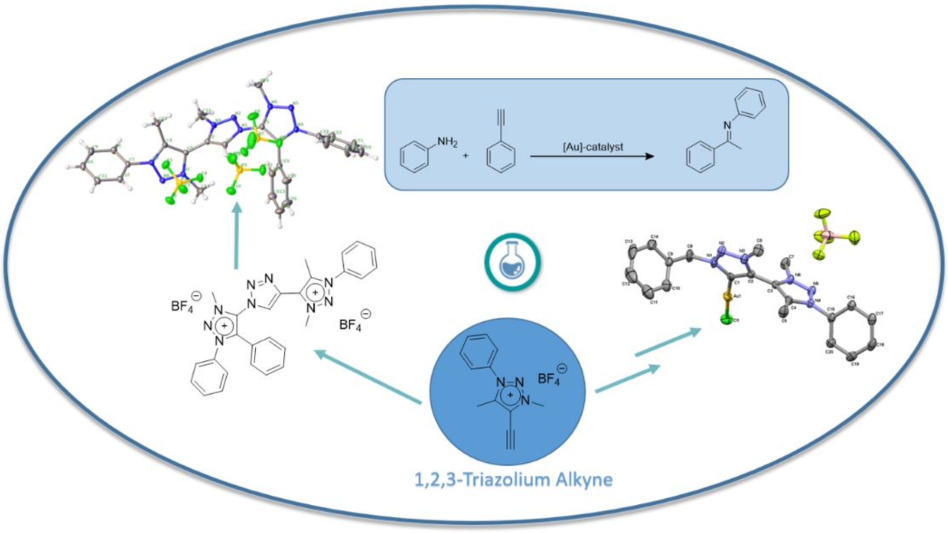
The catalytic properties of gold complexes are considered one of the most remarkable characteristics of the metal. In particular, tuning catalytic activity through ligand design and redox-switchable activation represents a highly valuable approach.[1][2][3] Herein, we present a strategy for the synthesis of cationic gold(I) complexes based on a 1,2,3-triazolium alkyne. The cationic alkyne undergoes cycloaddition reactions with both a cationic and a neutral azide, resulting in the formation of electron-poor ligands. The reaction of the 1,2,3-triazolium alkyne with the cationic azide is distinguished by an exceptionally short reaction time, representing an ultrafast copper-catalyzed cycloaddition. The effect of the ultrafast copper-catalyzed cycloaddition of positively charged alkynes was first reported by Aizupurua's group, who demonstrated that the reaction time is significantly reduced due to the stabilization of the transition state resulting from the positive charge.[4] Subsequent methylation of the ligand synthesized from the 1,2,3-triazolium alkyne and cationic azide resulted in the formation of a tricationic ligand system, confirmed by NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction. Gold(I) complexes obtained through transmetallation were investigated in terms of their electrochemical properties and demonstrated catalytic activity in the hydroamination of terminal alkynes. Ongoing efforts in our laboratories focus on enhancing catalytic activity by establishing a redox-switchable catalytic system.



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Probing structural diversity in a series of heterobimetallic complexes associating tantalum and 3*d* transition metals

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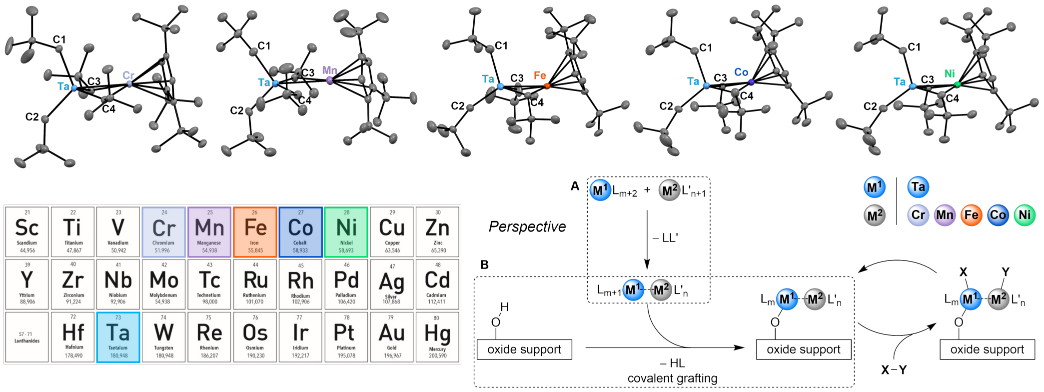
Over recent years, chemists have sought to tackle the challenging activation of kinetically inert bonds by developing catalysts combining two different metal centers in a single molecule.[1–3] Heterobimetallic systems relying on a cooperative interaction between early and late transition-metal centers which feature diverging electronegativities and Lewis acidities are highly promising because the strongly polarized metal pair is expected to enable concerted heterolytic bond cleavage via unusual pathways, as highlighted for Hf-Ir and Ta-Ir complexes by Camp and co-workers at the CP2M laboratory.[4,5]

Salt metathesis between an alkali-stabilized tantalate complex, $[Li(thf)_2][Ta(CtBu)(CH_2tBu)_3]$, and a series of alkylcyclopentadienyl 3*d* transition metal halide dimers, $[Cp'M(\mu\text{-}X)]_2$ (Cp' = 1,2,4-*t*BuC_5H_2, X = Cl, Br or I), was developed as a powerful strategy towards novel perhydrocarbyl-stabilized heterobimetallic Ta-M complexes in which the expensive, heavy 5*d* transition metal (M = Ir) is replaced by less expensive and chemically potentially more interesting first-row transition metal ions (M = Cr, Mn, Fe, Co, Ni) that may promote unprecedented bond activation mechanisms involving open-shell intermediates, as shown recently for iron.[6,7] In this communication, we will compare the unusual structural features of this series of compounds, including an atypical alkyl / alkylidene / alkylidyne tautomerism, and discuss their utility as precursors for Surface OrganoMetallic Chemistry (SOMC).



*Crystal structures of a series of novel tantalum-3*d *transition metal complexes and project perspectives*

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Organometallic porphyrins with metallacyclopentadiene units replacing pyrrole rings

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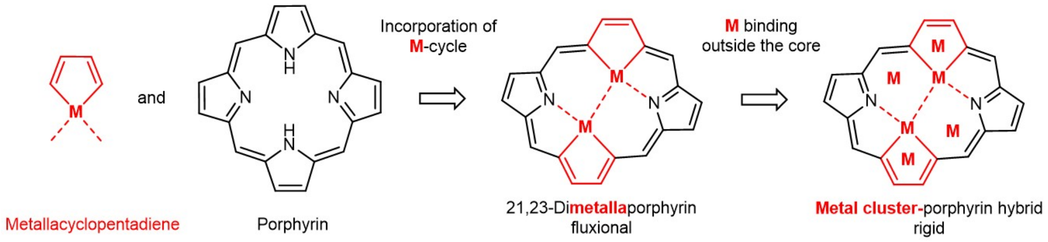
Porphyrins, versatile macrocyclic ligands, were designed by nature to bind metal ions inside a four-nitrogen coordination core. The idea of replacing the pyrrole ring of a porphyrin with a metallacyclopentadiene, containing a transition metal atom, has led us to the creation of a family of organometallic molecules, named metallaporphyrins in analogy to known heteroporphyrins. These macrocycles exhibit macrocyclic aromaticity, with an 18-π-electron circuit playing a crucial role in the stabilization of the molecule. Replacement of two opposing pyrrole rings with metallacyclopentadienes allowed the accommodation of two transition metal ions in the porphyrinoid core, and imposed the proximity of the two metal ions. Different degrees of metal-metal interaction were observed for three metal ion pairs, $Rh^{III}Rh^{III}$, $Rh^{III}Pt^{II}$, and $Rh^{III}Pt^{IV}$[1-4].



The specific coordination preferences of two metallic centers and their relatively large ionic radii impose a strong in-plane deformation of dimetallaporphyrin from the rectangular shape typical for diheteroporphyrins with nonmetallic heteroatoms. The interplay between the macrocyclic constraints and the ion coordination preferences is reflected in the fluxional behaviour of 21,23-dimetallaporphyrins, involving alteration in the metal ion coordination sphere accompanied by changes in the macrocyclic skeletal conformation, studied in solution by ^{1}H NMR. The introduction of additional metal centers above and below the macrocyclic plane, bound by metal-metal and/or metal-p system interactions, leads to much more rigid and less aromatic, however, still very robust, multinuclear porphyrin-metal cluster hybrids.

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C−C Bond Cleavage and Carbonylation Enabled by an NNN-Pincer Uranium Scaffold via Metal-Arene Interaction

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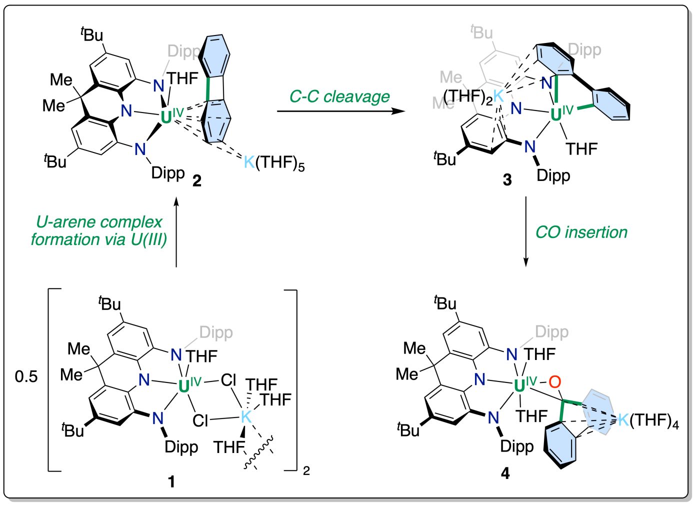
Uranium-arene interactions were found to enable unique stoichiometric and catalytic redox reactivities.[1,2] In contrast, functionalization of arenes mediated by uranium-arene interactions is limited to a single example. Here, we report a new uranium-biphenylene complex supported by a bulky, rigid trianionic NNN-pincer ligand in which the uranium-arene interaction can promote C−C bond cleavage and functionalization with CO under mild conditions to yield a U-bound 9-fluorenone. Reduction of the U(IV)-pincer complex [NNN-U(THF)Cl_2K$(THF)_3]_2$ (**1**) with KC_8, in the presence of biphenylene, results in the terminal arene complex [NNN-U(THF)(biphenylene)][K$(THF)_5$] (**2**) that undergoes C_{aryl}−C_{aryl} bond cleavage in biphenylene, affording [NNN-U(THF)(2,2'-biphenyl)][K$(THF)_2$] (**3**) via a concerted mechanism. Complex **3** undergoes facile CO insertion into the U−C_{aryl} bond, followed by the C_{aryl}−$C_{carbonyl}$ bond formation, yielding [NNN-U$(THF)_2$(fluorenone)][K$(THF)_4$] (**4**). This work demonstrates the tremendous potential of uranium-arene interactions to promote arene activation and functionalization.[3]



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Organometallic Osmium Compounds in High Oxidation States

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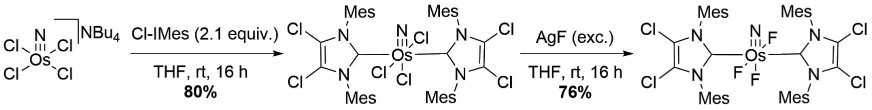
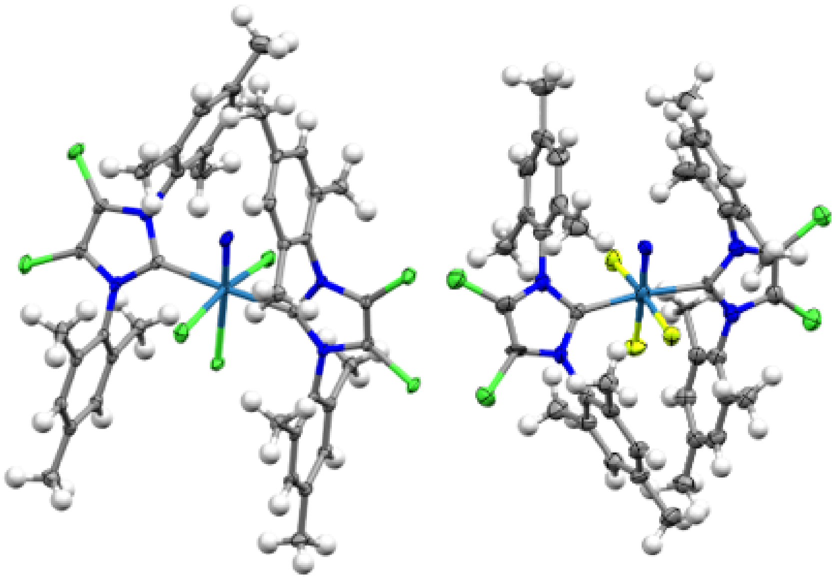
Isolatable organometallic compounds in the oxidation state +VIII are not yet known. Osmium seems to be the element of choice, as it forms the most stable compounds in this high oxidation state, e.g. in OsO_4. However, the synthesis of the corresponding organometallic complexes is accompanied by several obstacles, such as insertion reactions of oxo ligands into M-C bonds or reduction of the Os(VIII) center. In order to avoid side reactions suitable Os(VI) precursors are being investigated, which carry a nitrido ligand to stabilize the high oxidation state and the IMes carbene with a chlorinated backbone (Cl-IMes) as carbon-based ligand, due to its increased oxidative stability.

The direct reaction between the readily accessible Os(VI) precursor $[NBu_4][OsNCl_4]$ and the corresponding carbene was therefore investigated, leading to the formation of the neutral 18-electron complex $[OsN(Cl)_3(Cl\text{-}IMes)_2]$ by substitution of one chlorido ligand. Although the resulting complex proved to be unstable under oxidative conditions which would lead to an Os(VIII) complex, its reaction with an excess of AgF led to the exchange of all three chlorido ligands yielding $[OsN(F)_3(Cl\text{-}IMes)_2]$ as the more stable Os(VI) precursor. Both complexes were identified by NMR-spectroscopy and X-ray diffraction.

We are currently investigating the direct oxidation of $[OsN(F)_3(Cl\text{-}IMes)_2]$ as well as chemical transformations, in order to obtain the first isolatable organometallic Os(VIII) complex.





Molecular structure in solid state of $[OsN(Cl)_3(Cl\text{-}IMes)_2]$ (left) and $[OsN(F)_3(Cl\text{-}IMes)_2]$ (right). Solvent molecules are omitted for clarity. Color code: light-blue osmium, green chlorine, yellow fluorine, blue nitrogen, grey carbon, white hydrogen.

Synthesis of Chalcogenated Alkylboronates *via* Diboration of Carbonyl Compounds and Boronate Shift

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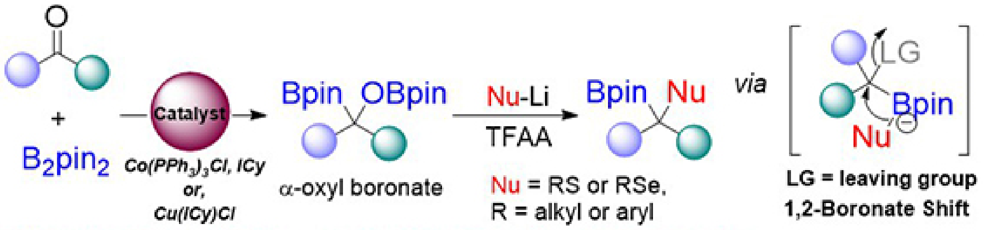
Alkylboronates are valuable reagents as they can be converted into a plethora of biologically important molecules, drug molecules, or natural products through versatile coupling reactions and transformations.[1] Introducing diverse functionality into the alkyl boronates will enhance their use as synthetic handles in target-directed synthesis. Herein, a new method has been described for the sequential thioborylation and selenoborylation of readily available aldehydes and ketones *via* diboration reaction.[2,3] NHC-Cobalt complex has been used as a catalyst for the diboration of aldehydes to generate a-oxyl boronates, which then react with lithium thiolates/selenolates as S/Se nucleophiles to form a tetracoordinate boronate species, which undergoes 1,2-metallate rearrangement in the presence of trifluoroacetic anhydride (TFAA). It is noteworthy to mention that the Matteson type 1,2-metallate rearrangement is well known only with carbon nucleophiles and recently with nitrogen and oxygen nucleophiles.[4] This is the first example of Matteson rearrangement involving chalcogen (S, Se) nucleophiles, which can be used to synthesize various organosulfides and organoselenium compounds. The orthogonal functionalization of boryl and sulfide moiety also enriches the chemical toolbox of diverse organic synthesis. Various substrates were compatible with this protocol to provide difunctionalized products from simple starting materials efficiently. The presence of the boronic ester in the resulting organosulfur and organoselenium compounds serves as a versatile synthetic handle for various functionalizations.



- ♦ Facile synthesis of α-thio and α-seleno boronates ♦ Mild reaction conditions
- ♦ Deoxygenative difunctionalization of carbonyls ♦ Good functional group tolerance
- ♦ 1,2-metallate rearrangement involving sulfur and selenium nucleophiles

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Pincer-type CNC- and CCC-MIC ligands in early and late transition metal chemistry

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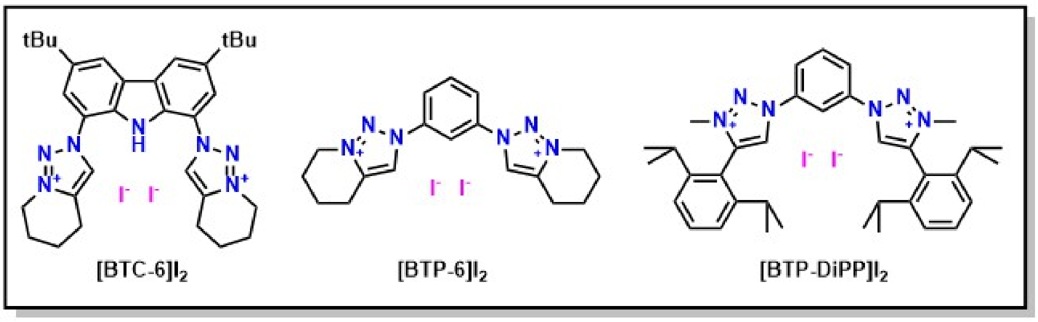
Pincer-type ligands were first reported by Shaw in 1976 and have been extensively studied over the past decades due to their rigid coordination mode combined with their modular design. [1][2] Over the years, a plethora of NHC-based pincer-type ligands have been reported. However, carbazole-based CNC pincer-type ligands as well as CCC pincer-type ligands with a phenyl linker are still rare, and common motifs feature imidazolylidene donors, while 1,2,3-triazolylidene substituted pincers are still scarce. [3][4a-d]



In this work we report the synthesis of two phenyl-based pincer-type ligands **[BTP-6]I$_2$** and **[BTP-DiPP]I$_2$**. Both ligands were prepared in a three step synthesis, analoguous to the previously reported ligand **[BTC-6]I$_2$**. [5a-d] The application of the ligands **[BTP-6]I$_2$** and **[BTP-DiPP]I$_2$** in the coordination chemistry of both, late and early transition metals, is investigated. [4c][5c][6] The spectroscopic, electrochemical and structural properties of the resulting complexes are compared to the corresponding complexes of **[BTC-6]I$_2$**.

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Application of NHC-Based Iridium Pincer Complexes in Borrowing Hydrogen Catalysis: Mechanistic Studies on Precatalyst Activation

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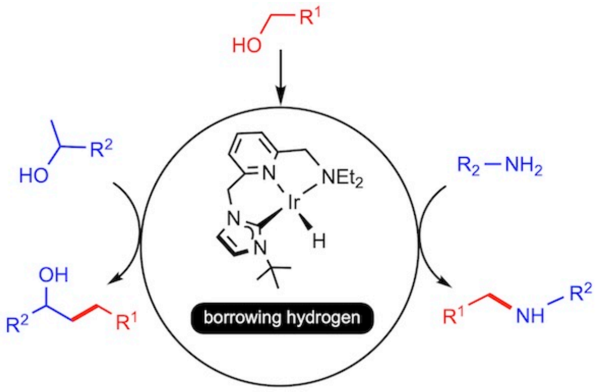
The borrowing hydrogen (BH) methodology, also known as hydrogen autotransfer, enables the use of commodity alcohols as alkylating agents in a wide range of C-N and C-C bond formation processes. This methodology has received considerable research attention due to their environmental sustainability and high atomic efficiency, producing only water as a by-product.[1] Well-established processes using the BH methodology are the β-alkylation of secondary alcohols with primary alcohols to produce branched long-chain alcohols, and the *N*-alkylation of amines with alcohols to prepare *N*-substituted amines. In this regard, great efforts have been made in catalyst design, resulting in a number of homogeneous catalytic systems based on both noble metals and earth-abundant first-row transition metals. However, mechanistic studies involving the precatalyst activation to the catalytically active species are lacking.

Transition metal complexes based on non-symmetric lutidine-derived CNZ ligands combining an NHC moiety with a different donor function have been shown to be efficient catalysts in a number of transformations. In fact, we have shown that iridium(I) complexes based on a CNO (Z = OMe) ligand exhibit excellent catalytic activity in the *N*-methylation of nitroarenes and amines using methanol as reducing agent and C1 source.[2] We report herein on the synthesis of iridium (I) and pincer iridium(III) dihydrido complexes derived from CNN (Z = NR_2) ligands and their application in borrowing hydrogen catalysis, namely β-alkylation of alcohols and *N*-alkylation of amines. Interestingly, both type of compounds exhibit similar catalytic performance in model reactions. A detailed mechanistic study, supported by DFT calculations, has shown that activation of both catalytic precursors lead to the common pincer iridium(I) hydrido species [IrH(k^3*C*,*N*,*N*-^{t}BuImCH$_2$PyCH$_2$NEt$_2$)] which is thought to be the active species responsible for reducing the intermediate unsaturated condensation products in the borrowing hydrogen catalytic cycle.



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Development of murgocil derivatives and their Re(I) and Ru(II) complexes for overcoming multridrug-resistant bacterial infections

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Despite significant advances in the development of more effective and better-tolerated antibiotics, multidrug-resistant bacteria continue to spread and are responsible for 50% of all nosocomial infections in Europe [1,2]. Moreover, secondary bacterial infections that appeared during viral epidemics such as the recent COVID-19, have increased mortality by ca. 50% [3,4]. These infections originated from *Streptococcus pneumoniae*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* bacterial strains; the latter is responsible for most of the nosocomial and community-acquired infections with broad spectrum of diseases from simple skin and soft tissue infections to more serious conditions such as meningitis and pneumonia [5]. Patients infected with this Gram-positive bacterium were treated successfully for long time by β-lactam antibiotics (*e.g.* penicillin) until the emergence of its drug-resistant counterpart impeded effective therapy [5]. This form is known as methicillin-resistant Staphylococcus aureus (MRSA), which has acquired resistance to β-lactam antibiotics. The WHO recognized the appearance of antibiotic resistance as one of the biggest global health threats and research is in progress to overcome the problem [6]. Herein, steroid-like compounds like murgocil (Fig. 1) and their metal complexes were prepared. The focus was on bidentate sterane-based compounds with (N,N) donor set as co-ligands in the complexes of Re(I) and Ru(II). The antibacterial activity of the compounds was further tested, with a particular focus on its effectiveness against multidrug-resistant bacterial strains as highly selective inhibitors of the cell-wall synthesis of bacteria.

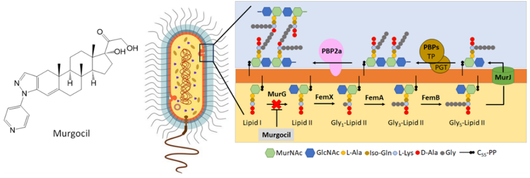

Figure 1. Left: Chemical structure of murgocil. Right: Schematic representation of peptidoglycan (PG) biosynthesis in MRSA and mechanism of action of murgocil.

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Tuning Ruthenium(II) Complexes: Impact of Mesoionic Carbene Units on Structural and (Spectro)Electrochemical Properties

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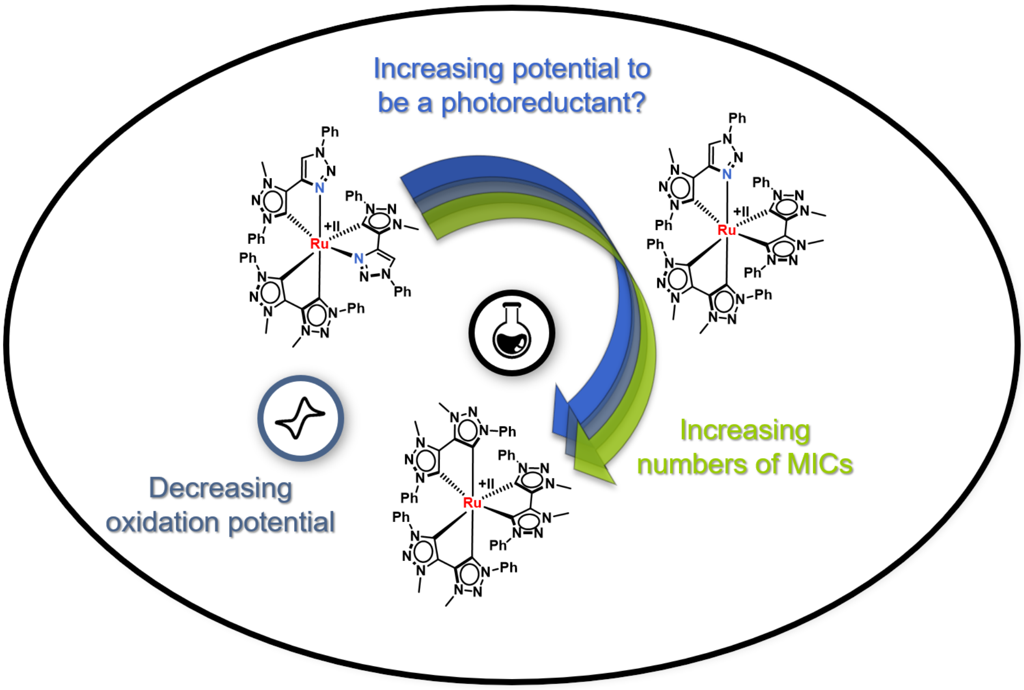
Ru complexes of pyridyl-mesoionic carbenes (MICs) were investigated for their intriguing electrochemical and photophysical properties.[1] T. Bens *et al.* investigated the electrochemical properties of Ru(II) complexes bearing pyridyl-MIC ligands, with up to three MIC units, and observed notable characteristics.[2] The MICs are based on the 1,2,3-triazole-5-ylidene unit. In comparison to the well-established Ru(II) tris(bipyridine) complex, each additional MIC unit induced a stepwise cathodic shift in the oxidation potential. These findings suggested a further stepwise increase in MIC units until a point where the oxidation potential might reach a range where the corresponding Ru(III) complex could exhibit stability. Thus, the synthetic route established earlier by our group was further employed to synthesize novel Ru(II) complexes containing up to six MIC units. Herein, we present a thorough study of these complexes, including the isolation, crystallographic analysis, (spectro-)electrochemical, and theoretical investigations. To validate the initial hypothesis, cyclic voltammetry (CV) was employed to examine the electrochemical behaviour of these complexes. Further insights into the oxidation properties were gained through UV/vis/NIR and EPR spectroelectrochemical techniques, alongside (TD)DFT calculations for both the native and oxidized species. Since $[Ru(bpy)_3]^{3+}$ exhibits intriguing photophysical properties, the potential photophysical behaviour of the Ru(II) complexes synthesized in this work may also be of interest in the future.[3]



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Setting the gram scale synthesis of BHMF catalysed by Ru and Fe-complexes, and its use as a building block for innovative, sustainable polymers

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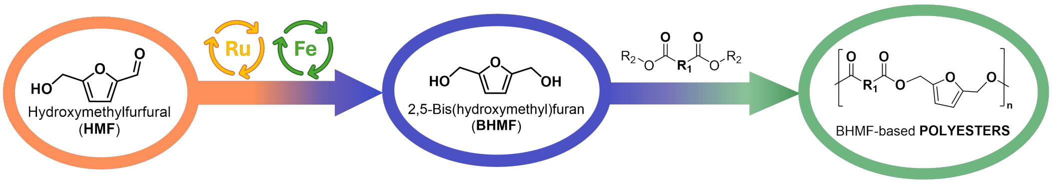
The concept of biorefinery focuses on generating chemical building blocks from biomasses instead of fossil oil. Generally, the complex composition of biomasses makes it possible to obtain a wide variety of molecules, which can then be further processed. Among these chemicals, 5-hydroxymethylfurfural (HMF) stands out due to its significant potential. One of the most promising HMF derivatives, 2,5-bishydroxymethylfuran (BHMF), has numerous possible applications, including as a biodiesel additive, non-ionic surfactant, monomer, or substrate in the flavour industry.[1] The homogeneous catalytic reduction of HMF to BHMF was investigated using Shvo's catalyst, achieving over 99% yield and selectivity for BHMF under mild conditions and hydrogen atmosphere.[2] A novel iron-based catalyst was also tested for the same reaction obtaining complete HMF conversion in less than 20 minutes (toluene, 90°C, 5 bar H_2).[3] Now, a robust procedure for scaling up this process was successfully developed, obtaining good catalyst recyclability and using green solvents such as anisole. The resulting BHMF was then used as a bio-derived diol to create innovative polyesters. First polymerization experiments, following literature mechanisms,[4] yielded good results. The reaction conditions were optimized, by selecting the best solvent and the most efficient reacting time. The use of different reagents, such as aliphatic dicarboxylic acid, is currently under study, with promising results.



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Acknowledgments: This work was carried out within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4D.D. 1032 17/06/2022, CN00000022).

Ir vs. Co fragments as counterparts in silica-supported Ta-M heterobimetallic complexes: a catalytic H/D exchange study

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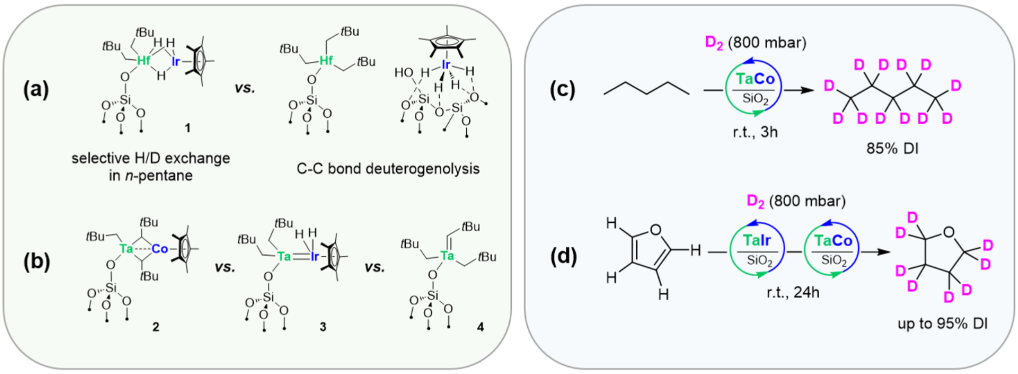
Promotional cooperative effects arising from metal-metal interactions in heterobimetallic complexes have been found to facilitate direct activation of C-H bonds [1]. In our group, we have recently illustrated this concept with silica-supported M/Ir (M = Hf, Ta) complexes, possessing enhanced catalytic performance in the C(sp^2)–H/D exchange in arenes [2, 3]. In parallel, we achieved efficient and selective C(sp^3)–H/D exchange in alkanes using D_2 as deuterium source and Hf/Ir complex **1** as a catalyst [4], in contrast with monometallic species, promoting undesired C-C bond cleavage (Figure 1, a). Next, aiming to replace noble Ir with more sustainable and earth-abundant metals, we prepared novel silica-supported Ta/Co species, **2**, which was characterized by IR, EA, TEM and EPR (Figure 1, b). This material outperformed both Ta/Ir (**3**) and monometallic Ta (**4**) catalysts, promoting fast and selective deuteration of *n*-pentane already at room temperature (Figure 1, c). However, with coordinating substrates such as furan, the Ta/Co system demonstrated only minimal H/D exchange activity, while being very efficient in C=C bond deuterogenation. This result is notable in the context of catalytic hydrogenation of furans, often requiring harsher conditions and use of noble metals. At the same time, the Ta/Ir catalyst efficiently promoted H/D exchange in furan, in agreement with previous results [2]. Thus, we took advantage of the complementary activity of the Ta/Ir and Ta/Co species to develop an unprecedented tandem catalytic strategy for the preparation of perdeuterated THF – a valuable and expensive chemical – directly from furan and in mild conditions (Figure 1, d).



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Antimicrobial application of cyclometalated gold(III) complexes

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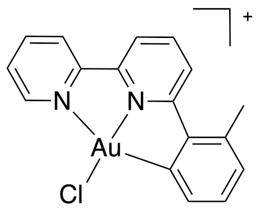
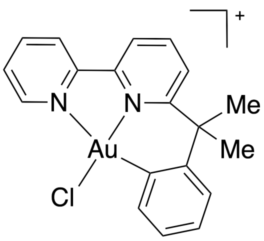
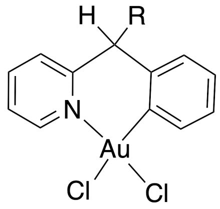
The urgent issue of Antimicrobial Resistance (AMR), which is on track to become the leading cause of death worldwide in the coming years, needs the development of a new generation of antibiotics. The escalation of AMR, in addition to multidrug resistance, requires new strategies to combat disease-causing bacteria and yeasts. For this reason, new approaches to develop the next generation of antimicrobials have become imperative. Metal-based compounds have emerged as a potential alternative to traditional antimicrobial drugs, generating the new class of metalloantibiotics.[1] In particular, cyclometalated gold(III) complexes appear particularly promising.[2] Following our longstanding interest in the investigation of cyclometalated complexes[3,4] we report here a series of Au(III) cyclometalated complexes with substituted pyridines and 2,2'-bipyridines, which were synthesized and characterized by means, *inter alia*, of 1D and 2D NMR spectroscopy, Cyclic Voltammetry and, in some cases, X-ray diffraction.







The complexes were tested on Gram-positive (*Streptococcus pyogenes* DSM 20565, *Staphylococcus aureus* DSM 1104), Gram-negative (*Klebsiella pneumoniae* DSM 681, *Escherichia coli* DSM 1103 and *Pseudomonas aeruginosa* DSM 1117) and yeast (*Candida albicans* DSM 1386) strains, revealing promising antibacterial and antibiofilm properties. Antibiofilm activity of the complexes was also evaluated.

The work was carried out under the framework of the project ""Noble metal complexes with heterocyclic nitrogen ligands: application as antimicrobials" Financed by the European Union - NextGenerationEU - mission 4, component 2, investment 1.1. Project code MUR P2022PZ8JE

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Coordinative properties of phospha-crown ethers in platinum and palladium complexes

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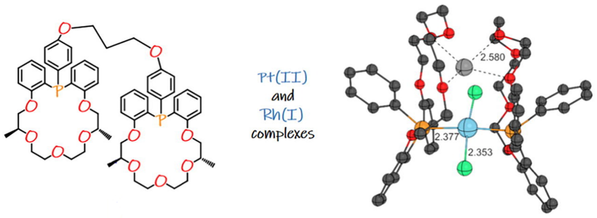
Since the first report on crown ethers in 1967, numerous studies have focused on the synthesis of new derivatives and the detailed investigation of the exceptional coordinative properties of these compounds.[1] Analogously, various macrocyclic phosphine ligands – phosphacrown ethers – were also synthesised,[2] having much different behaviour on metal binding.[3-5]

Coordination properties of recently synthesised chiral phospha-modified crown ethers were studied in the presence of platinum(II) and rhodium(I) precursors. The prepared and *in situ* formed complexes were characterised by ^{1}H and ^{31}P NMR spectroscopies. Platinum(II)-complexes were dominantly formed as *trans* arrangements, even in the case of diphosphines, possessing large bite angles, enabling them to act as *trans*-chelating ligands. Isomers of *trans*-complexes were identified and explained by ligand-backbone interactions, supported by DFT calculations. Basically different complexes were formed in the presence of rhodium(I) precursors, since only one of the two phosphorus donor atoms was coordinated to the metal centre. The addition of Na[BPh$_4$] was also examined, showing dramatically different effects: sodium ion coordination to the crown ether moiety can be supposed in the case of platinum complexes, while the use of rhodium(I) precursors brought about the formation of ionic complexes.

The synthesised complexes were used as catalyst precursors in the asymmetric hydroformylation of styrene. Chemoselectivities of up to 90% toward aldehydes were obtained. The branched aldehyde was slightly favoured for the reaction, and e.e-s of up to 52% were obtained. Similar selectivities and higher activities were obtained in the presence of rhodium–monophospha–crown ether catalysts formed *in situ*.



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Intramolecular C–H arylation in the synthesis of helical naphthochrysenes

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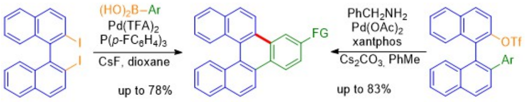
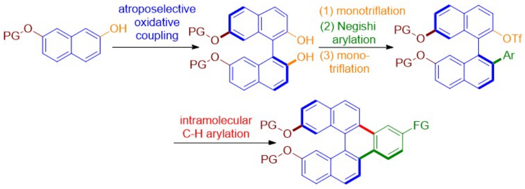
Helicenes are *ortho*-fused polycyclic aromatic hydrocarbons that form a twisted three dimensional helical structure. The helicene derivatives can be applied in nonlinear optic materials, optoelectronic devices and as chiral ligands for asymmetric synthesis or supramolecular building blocks.[1] However, [5]helicene itself has limited configurational stability with an atropisomerization barrier of 98 kJ/mol.[2] This can be increased by substitution at positions 10 and 11.[3] Enantiopure 9,12-substituted [5]helicenes have so far been prepared only by separation of racemic products using analytical or semipreparative HPLC.[4,5]

We found that tandem arylation of binaphthyl-2,2'-diiodide by Suzuki cross-coupling and C–H activation results in formation of naphtho[1,2-*g*]chrysenes containing [5]helicene scaffold (Scheme 1, left).[6] Some of these derivatives were also prepared by intramolecular C–H arylation of arylbinaphthyl triflate (Scheme 1, right).[7]



Based on this, we proposed the preparation of 9,12-substituted [5]helicenes according to the scheme below. The results obtained in its realization will be presented.

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00141.



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Alkene Promoted NHC Ligand Substitution in Orthometalated Ru-NHC Complexes via σ-bond metathesis: A Mechanistic Insight

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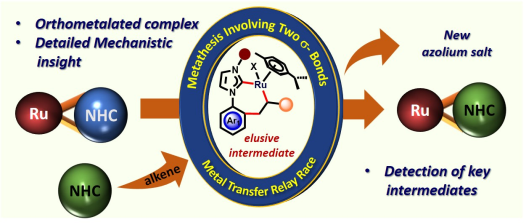
Metathesis reaction has evolved as an important protocol, that involves swapping of atoms or functional groups between two reacting species, to generate new compounds. In this context, the pioneering work by Yves Chauvin on alkene metathesis has had a remarkable impact on various domains of chemistry starting form polymer synthesis to biomass valorization and even drug synthesis.[1] Similarly, metathesis of other important bonds including the single bonds, which is conceptually similar to alkene metathesis however, represents a simpler molecular dance involving σ-bonds, has also garnered ample interest among the chemists.[2] In this context, an unprecedented NHC ligand substitution around ruthenium center, involving σ-bond metatheses has been developed.[3] Captivatingly, the employed metal complex here undergoes a unique σ-bond metathesis in presence of an alkene and azolium salt leading to facile exchange of ancillary NHC ligands at the Ru-center, which is even possible several times in presence of different azolium salts (akin to a relay race of NHC ligands), not known to the extent of our knowledge. Comprehensive mechanistic insight via active-intermediate-capture and various control experiments including deuterium labelling studies unequivocally established the reaction pathway via σ-bond metatheses.



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Non-Phosgene Synthesis of Aromatic Isocyanates Through Direct Catalyzed Reductive Carbonylation of Nitroaryls

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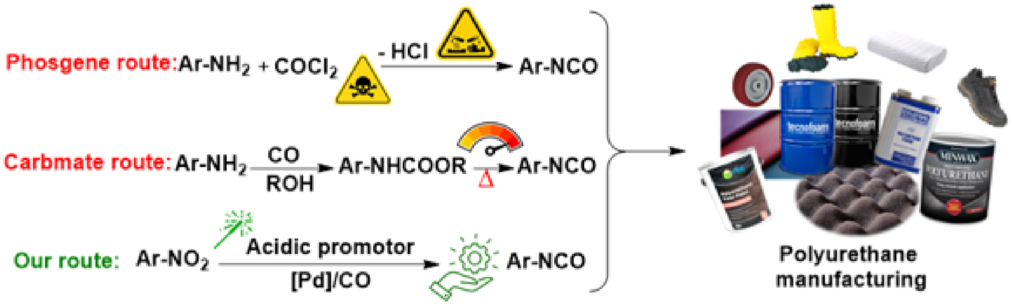
style="text-align: justify;">Isocyanates are key precursors in the industrial production of a wide variety of materials.[1] Aromatic isocyanates, such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) are extensively used to produce polyurethanes foams, adhesives, elastomers and coatings. Furthermore, these compounds are vital intermediates in the synthesis of various pharmaceuticals.[1] Isocyanates are almost predominantly produced through phosgenation of amines.[2] However, this popular ''phosgene route'' possess serious environmental concerns arising from the toxicity of the phosgene reagent and the corrosiveness of hydrogen chloride. Alternative methods, such as thermal cracking of carbamates, require drastic reaction conditions.[3] Thereby, there is a pressing need to develop sustainable non-phosgene processes for isocyanates production. The most direct and atom efficient alternative pathway is transition-metal catalyzed reductive carbonylation of nitroaryls, though this approach remains largely unexplored. Motivated by our expertise in the reductive carbonylation of nitroarenes,[4-6] we have initiated efforts to develop a direct and efficient technique for aryl isocyanates synthesis by palladium catalyzed carbonylation of nitroaryls, exploring different solvents, ligands and acidic promotors (**Scheme 1**). Promising selectivites (**up to 76%**) have been achieved, and further optimization trials are underway.

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



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The Flexibitlity and Versatility of Pyrazole Mono-Ligand Systems on the Inert *fac*-$[RE(CO)_3]^+$ Synthon

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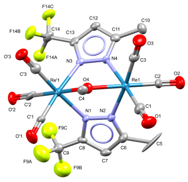
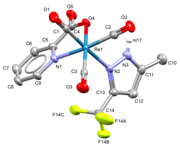
The use of organic chelators in developing transition metal complexes has been extensively explored for various applications, including nuclear imaging, cancer therapy, and photodynamic therapy (PDT), among others. Despite the positive aspects of stable rhenium (I) complexes, their ideal nuclear properties, including the emission of high-energy beta particles, make them suitable candidates for radiochemistry.[1-3]Moreover, the versatility of the inert tricarbonyl synthon (*fac*-$[Re(OH_2)_3(CO)_3]^+$) allows for the accommodation of a wide range of ligand systems through a [2 + 1] mixed ligand approach, based on Roger's model.[4] This model aims to saturate the metal's coordination sphere while creating stable complexes.[4] Additionally, bimetallic complexes are often favored alongside certain organic conjugates, as illustrated in Figure 1. In this study, we present a variety of pyrazole ligands in conjunction with the inert Re(I) synthon for pharmacological evaluations.





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Metal- *vs* Ligand-Bound Hydride Storage on Iridium–PYA Complexes

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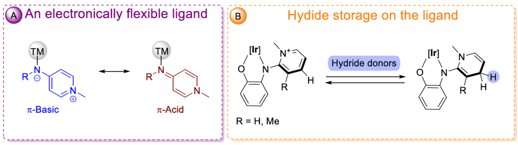
Our group recently reported a highly active catalyst towards formic acid dehydrogenation.1 The complex bears a O-functionalized pyridinium-amidate (PYA) moiety, which exhibits a unique donor flexibility, known to impart high catalytic activity (Fig. 1a).2 Further modifications of this complex enabled us to observe unique reactivity, namely the reversible storage of a hydride on the PYA moiety upon reaction with formate (Fig. 1b).3 Similar to nature's NAD+/NADH hydride storage and transfer system, the complex reversibly dearomatizes upon addition of the hydride.4 The hydride-bearing complex exhibits remarkable stability in air and moisture, however reacts towards electrophiles such as acids and carbonyl compounds. This property enabled efficient hydrogenation catalysis and deuterium isotope labeling without notable scrambling in the presence of air and moisture. In this work we will interrogate the reactivity of the Ir-PYA complexes towards different hydride sources in order to establish factors that distinguish hydride storage on the ligand through dearomatization, or on the iridium as classic metal-hydride species. Moreover, stability and reactivity features emerging from the different hydride storage modes will be presented.



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Ambiphilic Ferrocene Ligands

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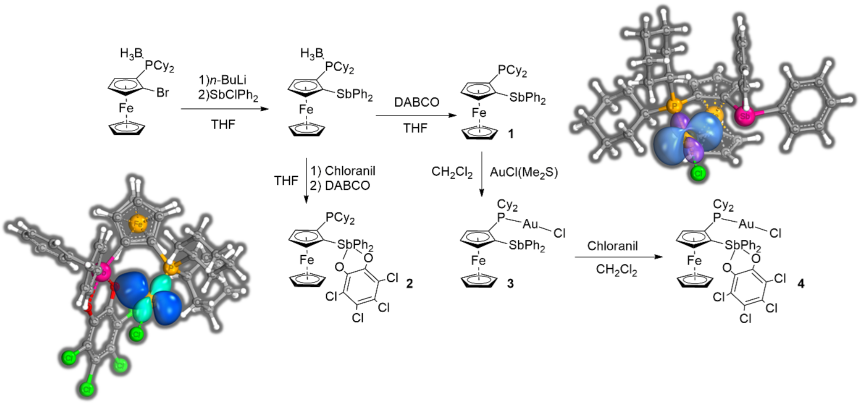
Ambiphilic ligands, which can act as σ-donors or acceptors depending on their electron richness, have garnered significant interest in recent years due to their applications in catalysis. Moreover, these compounds exhibit an unusual electronic structure, offering new insights into coordination chemistry.

To investigate this class of compounds, ligand **1**, its oxidized form **2**, and their gold complexes **3** and **4** were prepared. Quantum chemical calculations were performed to assess whether a bonding interaction **Au→Sb** occurs. This interaction was indeed observed in both complexes.



To further investigate the electron-acceptor properties of antimony a series of corresponding chalcogenides was prepared. The E–Sb distance was examined and compared to the sum of WdV radii. Additionally, quantum chemical calculations were performed to determine the bond orders of the **E→Sb** interaction, and an IBO analysis was carried out to identify the orbitals involved in this interaction. In compounds **1E**, a significantly shorter E–Sb distance than expected based on the sum of WdV radii was observed, along with a notable bond order value with a decreasing trend within the group. In the case of stiboranes **2E**, the E-Sb bond distances were not only significantly shortened, but bond orders also increased. Unlike in the previous group, bond order values followed an opposite trend, increasing from **O** to **Se**.

Complexes **3** and **4** were further applied in gold-catalyzed cyclization of propargylbenzamide. The measurements showed that complex **4**, with antimony in a higher oxidation state, is over 30% more catalytically active than complex **3**. Further oxidation at the ferrocene moiety enhances catalytical performance of both complexes.

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Base-free highly active transfer hydrogenation catalysts based on Ru complex with acyclic diamino carbene ligands

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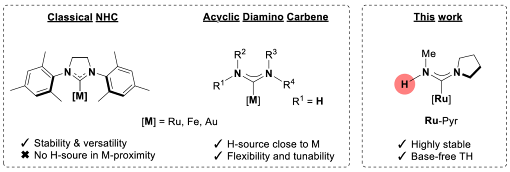
N-heterocyclic carbenes (NHCs) are key ligands in homogeneous catalysis due to their strong donor ability and thermal/oxidative stability.[1] Typically, bulky R-groups (e.g., mesityl, adamantyl) stabilize the metal complex and offer steric protection, though lack a proximal proton source for assisting hydrogen transfer.[1] To address these issues, acyclic diamino carbene (ADC) analogues have been developed. These ligands exhibit increased flexibility due to their open-chain geometry, exceptional donor strength, and localized steric bulk around the metal centre.[1–3]



Our design of a transfer hydrogenation catalyst thus involved the use of a protic ADC. We therefore synthesized Ru-ADC analogues such as Ru-Pyr from a Ru-isocyanide precursor and an amine source. We will present the synthesis as well as the excellent catalytic activity of these Ru-ADC variants in the transfer hydrogenation (TH) of ketones under base-free conditions, which is still fairly rare despite the many Ru-based catalysts known for this reaction.[4] Our studies show excellent reactivity across a diverse range of substrates with high catalyst stability and attractively low catalyst loading.

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Carbene-supported dinickel complexes for efficient hydroxylation of benzene to phenol

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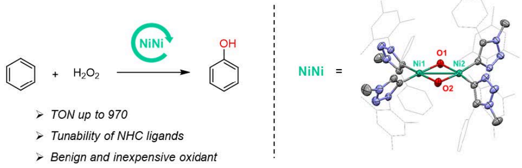
Phenol is a valuable base chemical applied in resin and dye industry. However, it is still largely synthesized through the Hock oxidation of cumene, which suffers from harsh conditions and a low 5% overall yield.1 Metal-catalyzed direct hydroxylation of benzene recently emerged as a more profitable synthetic approach, but only a few systems reach acceptable conversion and selectivity.2 Herein, we will present a series of bimetallic hydroxo-bridged NiII complexes supported by classical and mesoionic N-heterocyclic carbene ligands3 which catalytically oxidize benzene to phenol using H2O2 as benign oxidant with competitive efficiency. Spectroscopic and electrochemical studies suggest an electrophilic aromatic substitution pathway involving a [NiIII(μ-O)2NiIII]2+ species, an elusive compound detected for the first time starting from a pre-formed dinuclear Ni catalyst.



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Late transition metal PN^{H}N complexes for the dehydrocoupling of amine borane adducts

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Amine borane adducts ($H_3B{\cdot}NMe_nH_{3-n}$, n = 1, 2) are valence isoelectronic to alkanes and can undergo a dehydrocoupling reaction to form poly- or oligomers which are discussed as precursors for B-N-based ceramics and single-layer hexagonal BN thin films.[1] Transition metal complexes with cooperative PNP ligands with an NH-functionality are among the most active catalysts for these reactions, showing excellent selectivities for linear poly(aminboranes).[2] We were interested whether this behaviour is exclusive to PNP ligands or can be transferred to other cooperative PNN systems. In a previous study, we investigated the coordination chemistry of pyrazole-based Rh(I) PNN^H complexes and the catalytic dehydrocoupling of $H_3B{\cdot}NMeH_2$.[3] We found an increased activity upon addition of base, likely forming a Rh hydride complex as the active catalyst.

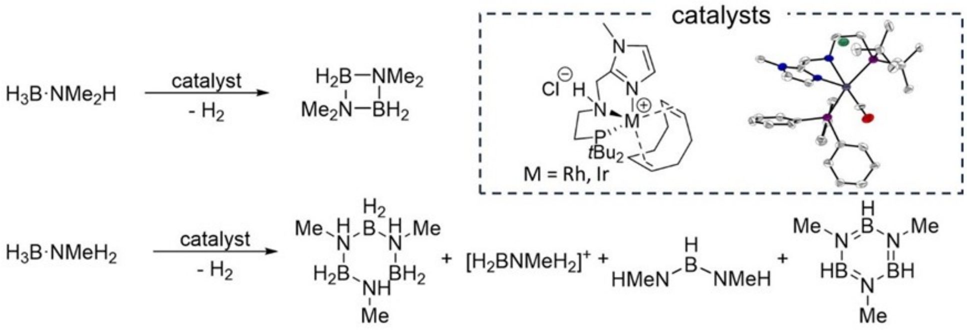

Figure 1: Dehydrocoupling of $H_3B \cdot NMe_2H$ and $H_3B \cdot NMeH_2$ and structures of some of the studied late transition metal complexes with imidazole-based PN^{H}N ligands.

To further understand the activity of cooperative ligands we extended our studies to systems with imidazole-based PN^{H}N ligands which resemble the above-mentioned PN^{H}P systems more closely. We synthesised complexes with the late transition metals rhodium, iridium and ruthenium. These new complexes showed a similar coordination chemistry, were fully characterised and tested for the dehydrocoupling of $H_3B{\cdot}NMe_2H$ and $H_3B{\cdot}NMeH_2$. We compared the hydrogen evolution of the different complexes and found unexpected results for the different substrates.

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Computational Exploration of Cyclic Bisphosphine Ligands for Applications in Catalysis

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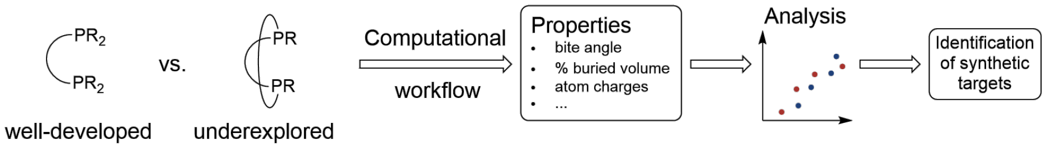
Bidentate phosphines are an important class of ligands for transition metal catalysis. Over time, many different ligand structures have been developed to enable a wealth of reactions. The structural modifications mostly concentrate on the ligand backbone between the two phosphino moieties. In contrast, cyclic bisphosphines, in which the two phosphorus atoms are connected by two backbone chains, have rarely been described,[1] and only few examples of their use in catalysis exist.[2]

We developed a computational workflow that allows to rapidly evaluate properties of cyclic bidentate ligands *in silico* and compare them to those of the corresponding acyclic congeners.



Based on our analysis, we identified structures with interesting properties for experimental evaluation, and synthetic strategies to access them are presented.

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Direct Access to Bridged Ni(I)-Imido Complexes from Amines: Synthesis and Reactivity

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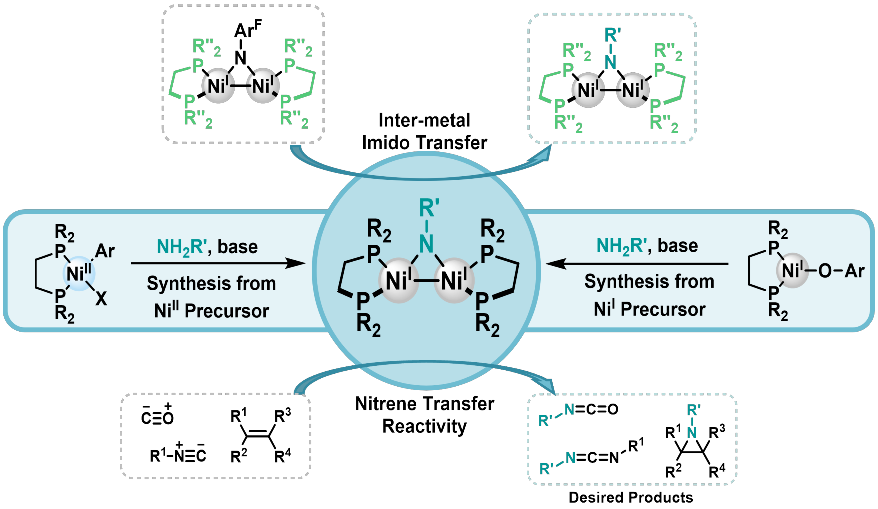
Nickel imido complexes have demonstrated potential in transferring nitrene groups to small unsaturated molecules, including olefins, CO, and isocyanides, yielding valuable and often challenging-to-synthesize products such as aziridines, isocyanates, and carbodiimides.[1-4] Ni-imido species are traditionally generated from azides, which pose safety concerns and have poor commercial availability.[1-6] In contrast, amines offer a safer and more readily available alternative, making them well-suited as non-activated nitrogen atom precursors. We have recently discovered that bimetallic Ni(I) imido complexes can be formed from deprotonated amines, starting from both Ni(I) and Ni(II) complex precursors. In this work, we explore this approach as a modular, one-step synthesis of Ni-imido complexes from amines, and are investigating the robustness of this synthetic method towards both aryl and alkyl amines. The reactivity of these imido complexes towards olefins, isocyanides and CO is assessed. In addition to nitrene transfer to small molecules, preliminary results show that these complexes can exchange aryl-nitrogen fragments between metal centers—a rare phenomenon among transition metals, particularly those of the first row.[7] The mechanism and scope of this inter-metal imido transfer is currently under investigation.



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Synthesis, characterization, and application of gold(I) complexes bearing thiol and thioacetate-functionalized NHC

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In the last few decades, N-heterocyclic carbene ligands (NHCs) have been widely used in organometallic chemistry for the synthesis of late transition metal complexes. This success is due to their strong donating capabilities, which allow to stabilize metal complexes, and to the possibility of modifying their electronic and steric properties by changing the backbone and nitrogen substituents.[1] Moreover, it is possible to develop bidentate ligands by adding another donating atom to the nitrogen-substituent (tipically N, P, O).[2] Also the sulfur atom has been evaluated as second coordinating moiety in NHC pendant substituents. Indeed, thanks to its weak σ-donor capabilities, it can establish an hemilabile equilibrium as chelating agent. This property is really useful both in homogeneous catalysis and in biological activity. Actually, gold(I) and gold(III) complexes bearing NHC-thioether ligands have been synthesized and studied as anticancer agents.[3] In this contribution, we discuss the synthesis of gold(I) complexes bearing alkyl chains of different lenghts with terminal thioacetate or thiol moiety. These new ligands, unlike those with the thioether pendant group, allow to move to other chemical areas, for example the coordination of gold complexes on gold surface and the possibility to favour the oxidative addition to gold(I) centers. Some preliminary results in homogeneous catalysis and biological environment will be reported.

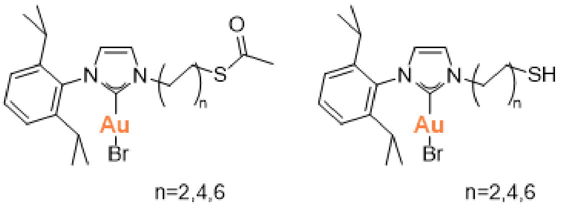

Fig. 1. Gold(I) complexes with NHC ligand bearing an alkyl chain and a sulfur-based terminal group.

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Theoretical Investigation of Carboborane Reaction Mechanisms Stabilized by Different Carbenes

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Polyhedral boranes and heteroboranes are known primarily as neutral or anionic species, while the cationic variants often being unstable or protonated at exoskeletal heteroatoms. In 2021, we reported the first thermally stable cationic carboranes stabilized by bulky *N*-heterocyclic carbenes.[1] Further studies revealed various unique chemical properties and rearrangements within this class of compounds. Our recent findings indicate that this approach is also applicable to chalcogenaboranes.[2] This work provides insight into the possible reaction pathways and mechanisms of carboboranes stabilized by different carbenes.

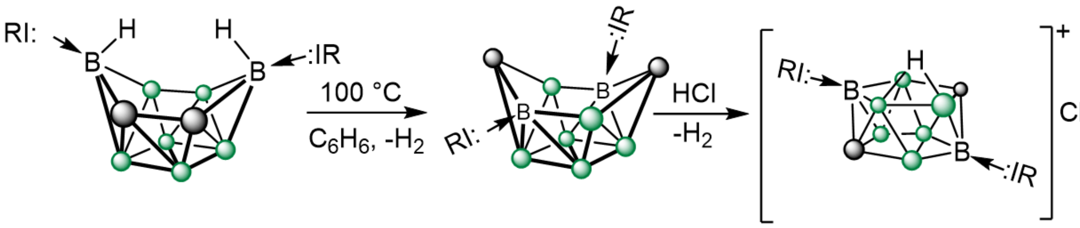

Figure 1. Intramolecular rearrangement and followed reaction with HCl. IR = 1,3-(2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$)-imidazole-2-ylidene and 1,3-diisopropyl-1H-imidazol-3-ium-2-ylidene.

The corresponding DFT calculations were carried out at the B3LYP-D3(BJ)/def2-TZVP level, incorporating the PCM(Toluene) solvation model. We examined possible mechanistic pathways for two types of carbenes differing in steric bulk. This work was supported by ERC-CZ project number LL2309.

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Insights into the deprotonative C–H silylation of (hetero)arenes mediated by a highly basic sodium amide

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Organosilicon compounds have become a versatile building block in organic synthesis and represent an important motif in drug discovery and materials science.[1] To incorporate new C–Si bonds into different molecular architectures, direct C–H silylation allows to bypass prefunctionalization steps and offers an improvement in the atom-economy of the process. Typically, this transformation has been accessed by the use of either precious transition metals (Ir, Rh, Ru)[2] or strong main group Brønsted bases, for instance, organolithium reagents or bimetallic systems (*n*BuLi/KO*t*Bu).[3] In both cases, different limitations can be found, such as lack of selectivity without strong directing groups or restriction to a single type of substrate (e.g. electron-rich heterocycles).

Herein, we present an alternative strategy for the deprotonative C–H silylation of (hetero)arenes mediated by a highly basic sodium amide, namely NaTMP (TMP = 2,2,6,6-tetramethylpiperidide). By using toluene as a model substrate, we have demonstrated the superior capacity of NaTMP towards this transformation, including a strong alkali metal effect (Na>K>Li) and a close dependence on the nature of the electrophilic chlorosilane. We have investigated the metalation process, isolating the sodiated intermediates and examining their nature in solution and in the solid state. Furthermore, our studies has been extended to a broad range of substrates, such as arenes and pyridines, and the multisilylation of different scaffolds.

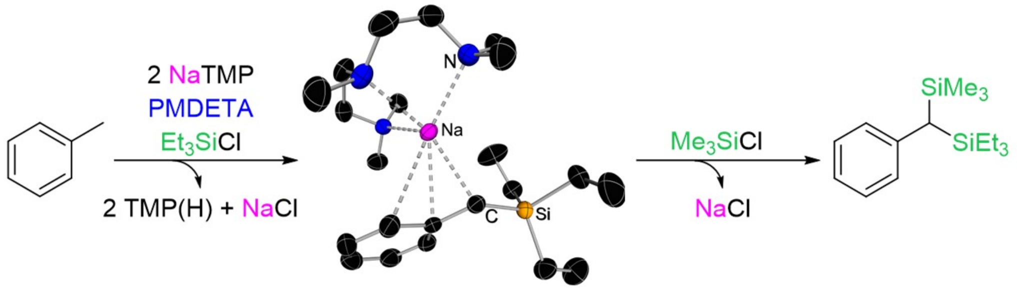

Figure 1. *Disilylation of toluene mediated by NaTMP.*

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Ethylene hydrogenation mediated by rhodium(I)-hydride: mechanistic insights

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In the field of homogeneous catalysis, alkene hydrogenation is one of the most impactful transformations with applications in pharmaceutical, agrochemical and commodity chemical industries.[1] Wilkinson's catalyst, the best known catatyst for this transformation, was first reported in the late 1960s, surpassing other systems due to its good performance under mild conditions.[2] Since its discovery, many other hydrogenation catalysts have been developed; however, Wilkinson's catalyst remains one of the most extensively studied systems with studies often focusing on the underlying mechanistics. The classical proposed mechanism involves oxidative addition of H_2 to Rh(I), forming an octahedral Rh(III)-dihydride intermediate that subsequently undergoes olefin insertion and releases the product by reductive elimination. If a superbase is present during this reaction, H_2 activation proceeds instead via heterolytic cleavage yielding a Rh(I)-monohydride species as shown by the Repo group.[3] This complex has shown extraordinary high reactivity towards otherwise inaccessible olefines, therefore broadening the scope of Rh-catalyzed hydrogenation.

In the presented work, we used experimental and computational methods to investigate the reactivity of the Rh(I)-monohydride complex toward the simplest alkene, ethylene, in the presence of Barton's base. Multinuclear NMR experiments at room temperature revealed the formation of two novel rhodium complexes, alongside the generation of ethane. While one of the complexes, a Rh(I)-ethylene species, was isolated and characterized, the second rhodium species remained elusive. Using density functional theory (DFT) calculations (M06-def2SVP/TZVP/SMD) and ^{31}P NMR simulations (4c-KT2), we could show that the herein studied reaction deviates from the classical mechanism. An almost barrierless insertion of ethylene into the Rh-H bond is proposed from the calculated free energies, and this step is taking place at the square planar Rh(I) species instead of an octahedral Rh(III) species. We could furthermore elucidate from our mechanistic studies that the second observed Rh species is an unexpected cyclometalated Rh(I) complex. To support this proposal, ^{31}P NMR chemical shift calculations were carried out which were in good agreement with the experimentally obtained values. Overall this study contributes to the mechanistic understanding of hydrogenation reactions which opens new pathways for enhancement thereof.

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New Rh-phosphine carbonyl clusters: synthesis, characterization, and catalytic activity

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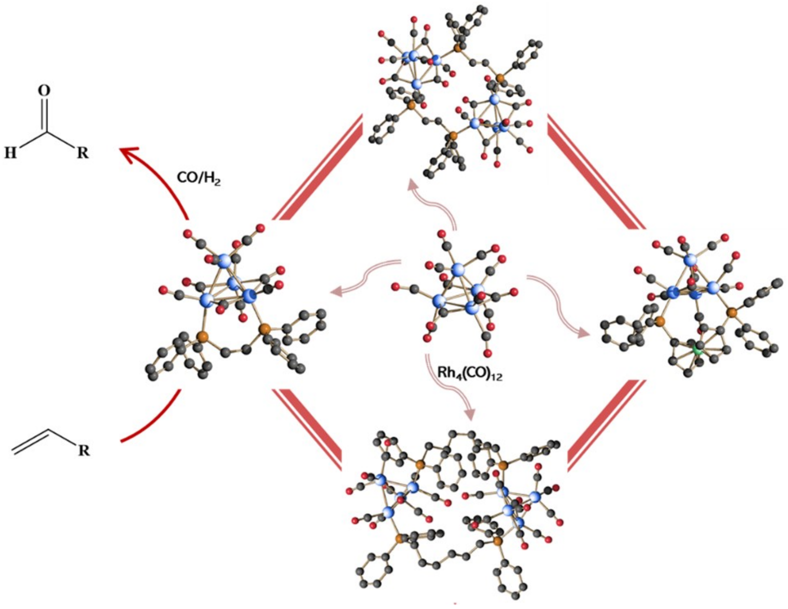
[2]Center for Chemical Catalysis “C3”, University of Bologna, Bologna, Italy

Rhodium is a transition metal known for its versatility in catalyzing a range of reactions, and the addition of phosphine ligands can further enhance its reactivity and selectivity. [1] The phosphine-substituted $Rh_4(CO)_{12-x}L_x$ and $Rh_6(CO)_{16-x}L_x$ clusters have demonstrated catalytic abilities in various reactions, such as hydrogenation, hydroformylation, and carbonylation, owing to the synergistic effects of the ligands and the metal core. [2]

This work investigated the reactivity of $Rh_4(CO)_{12}$ as a precursor in the presence of different bidentate phosphines, performing the reactions under a nitrogen atmosphere. New species of phosphine-substituted rhodium clusters have been characterized by IR, $^{31}P\{^1H\}$ NMR, and SC-XRD, and isolated with good selectivity and yield.

To compare the catalytic activity of these clusters with those known in the literature, the new species $Rh_4(CO)_{10}$(dppe) was investigated as a catalyst for the homogeneous hydroformylation of model substrates (*i.e.*, 1-octene). Under the same conditions, the cluster $Rh_4(CO)_{10}$(dppe) has shown better selectivity in the aldehydes products than $Rh_4(CO)_{12}$.



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Towards a pyramidalized silylium ion Lewis superacid from a sila-triptycene

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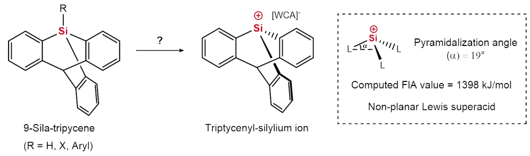
[1]University of Namur, [2]Technical University of Berlin

style="text-align: justify;">Geometric tuning, alongside steric and electronic tuning, has emerged as a means of controlling chemical outcomes. In recent years, strategies to distort main-group compounds from their predicted geometries have gained considerable attention due to the rise of unique structural features, spectroscopic properties and reactivity patterns as a consequence of the distortion.[1] The silylium ions, one of the highly reactive trigonal planar Lewis acids, find applications in bond activation reactions, catalysis, polymer chemistry and material science.[2] However, the pyramidalized silylium ions[3] have been less explored despite their potential to uncover new reactivities. One strategy to access such silylium ions involves the incorporation of a cationic silicon center within a geometrically constrained scaffold such as triptycene[4] that possess a unique three-dimensional rigid structure.



Within this context, we focused on the reactivity of sila-triptycenes as direct precursors to pyramidalized silylium ions. This contribution highlights the synthesis and characterization of a family of 9-sila-triptycene derivatives. Our recent progress in the generation of a pyramidalized triptycenyl-silylium ion will be presented. Additionally, theoretical investigations on the steric and electronic properties of these cage-shaped silylium ions will be discussed.

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Intermediates and Mechanism in Enantioselective Iron-Catalysed 3-Component Cross-Couplings

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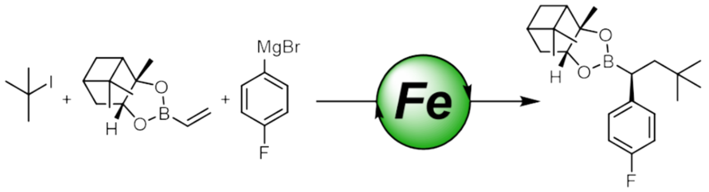
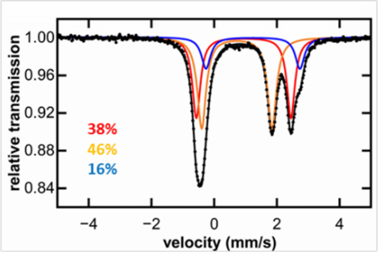
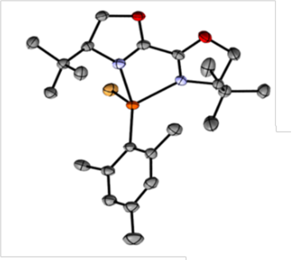
Historically, there has been a lack of mechanistic understanding of iron-catalysed organic transformations[1]. Recent mechanistic studies by our group have begun to elucidate the unique reaction profiles of iron catalysts including in traditional 2-component cross-coupling[2]. These insights offer the opportunity to pursue rational design of bespoke ligands and iron pre-catalysts that specifically target the active species and reaction pathways critical to effective catalysis.

In collaboration with the Gutierrez lab at UCLA, we have been extending our mechanistic studies to enantioselective iron catalysed 3 component cross-couplings. Initially developing a methodology utilizing a bisphosphine supported catalyst[4], further enantioselective methodologies have been developed utilizing ligand-induced and chiral auxiliary induced enantioselectivity. We endeavored to determine how these differing strategies would alter the mechanism of these cross-couplings, and continue to strive towards a deeper understanding of why these methods work. In the ligand supported system, a range of reactive intermediates involved in the reaction have been identified which, when tied to reactivity through kinetic studies and product analysis, present a mechanistic pathway. In the chiral auxiliary system, a handful of catalytically competent iron species have been identified and their assignment being pursued. The mechanistic insights gained from these systems provide explanations for procedural requirements during the reactions, insight into how the catalytic conditions target the active catalytic species, and may even pave the way for more efficient, powerful and unique methodologies.



- ✓ Mössbauer Spectroscopy
- ✓ SC-XRD
- ✓ EPR
- ✓ Kinetic Studies
- ✓ Product Analysis





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New carborane-based aggregation-induced emission luminogens

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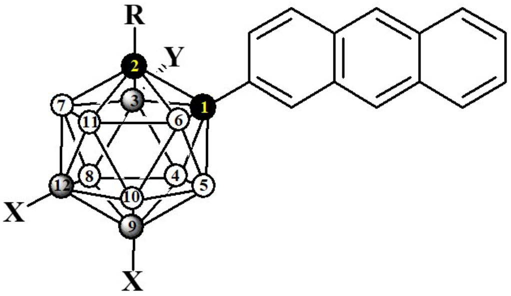
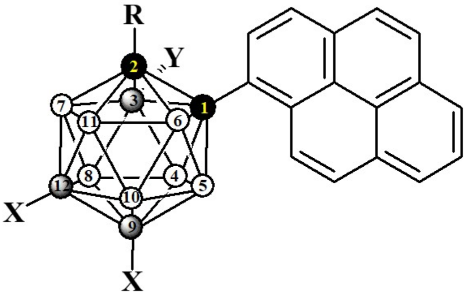
The *ortho*-carborane derivatives containing luminophoric polycyclic aryl groups are known to demonstrate intense solid-state emission due to the suppression of luminescence quenching caused by the restriction of intramolecular rotation of the aryl groups in the aggregate state [1]. In turn, the electron-acceptor effect of the carborane fragment can be regulated by introducing substituents of various natures [2], which makes it possible to control the luminescence wavelength and opens up good prospects for the development of stimuli-responsive luminochromic materials.

A series of *ortho*-carborane derivatives containing luminophoric anthracenyl and pyrenyl substituents at carbon atoms and various substituents of electron-releasing and electron-withdrawing nature at boron atoms $1\text{-L-2-R-9,12-X}_2\text{-1,2-C}_2\text{B}_{10}\text{H}_8$, $1,2\text{-L}_2\text{-9,12-X}_2\text{-1,2-C}_2\text{B}_{10}\text{H}_8$, $1\text{-L-3-X-1,2-C}_2\text{B}_{10}\text{H}_{10}$ and $1\text{-L-3,6-X}_2\text{-1,2-C}_2\text{B}_{10}\text{H}_9$ were synthesized by Ni-catalysed microwave-assisted cross-coupling of the carboranyl Grignard reagents with the corresponding aryl bromides. The luminescent properties of the synthesized compounds were studied and the relationship between their structure (the presence of additional substituents of various natures and their position) and luminescent properties was established.





For comparison, derivatives with anthracenyl and pyrenyl substituents at the boron atoms in positions 6 and 9 of the *ortho*-carborane cage were synthesized by Pd-catalyzed cross-coupling of the corresponding carboranyl iodides with the *in situ* prepared aryl zinc bromides, similar to that described previously for the synthesis of functionalized phenyl derivatives [3,4].

This research was supported by Russian Science Foundation (25-43-00072).

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Photophysical and catalytic properties of arylpyridine-based borenium salts

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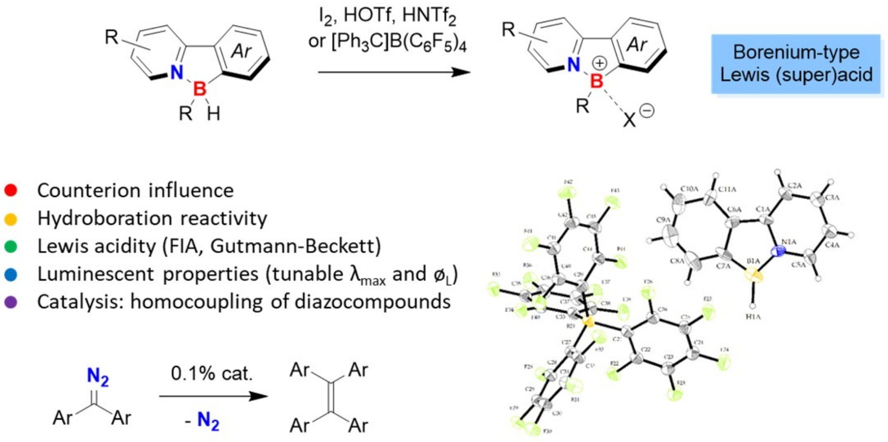
Tricoordinated boranes represents an archetypal class of Lewis acids and as such these are widely used as reagents or catalysts in organic synthesis. Particularly attractive strategy to increase electrophilic properties of boron-based Lewis acid is to introduce positive charge to boron by formal replacement of one σ-substituent R by neutral dative ligand L and formation of so called borenium specie.[1]

We present a simple cationic boron chelate synthesis via electrophilic borylation of arylpyridine,[2] followed by reduction to a BH_2-containing boron species. Hydride abstraction using Brønsted acids (TfOH, Tf_2NH) or trityl borate generates a cationic Lewis acid with a highly reactive B–H bond.[3] Several of the prepared compounds exhibit exceptional luminescent properties (PLQY up to 93%)[4] and have proven to be highly effective catalysts for the synthesis of tetraarylethenes via homocoupling of various diaryldiazomethanes.



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Synthesis, spectroscopic and electrochemical properties of 4-ferrocenylpyrimidine derivatives

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Due to its good stability, reversible redox properties [1] and easy chemical modification of the cyclopentadienyl rings, ferrocene has found wide application in diverse fields of chemistry, medicine and materials science [2]. Ferrocene derivatives can be excellent building blocks in sensors where the ferrocene moiety serves as a mediator. Substituents on the cyclopentadienyl rings can form host-guest complexes with ions or neutral molecules. These non-covalent interactions may induce a shift in the redox potential of the ferrocene-ferrocenium redox couple and the changes can be followed by electrochemical methods.

Recently, a series of 2-ureido- or 2-amino-4-ferrocenylpyrimidine derivatives with different substituents on C6 have been synthesised in our group [3]. The side chain of the ferrocene core of the first group of compounds offers an acceptor–donor–acceptor (ADA) hydrogen bonding pattern for neutral guests, while the 2-amino derivatives may bind different metal ions. In this presentation, the efficiency of some synthetic methodologies towards these compounds will be discussed. In addition to the analysis of their spectroscopic and electrochemical properties, investigations of their solution phase host-guest interactions by NMR- and UV-Vis spectroscopy as well as by cyclic voltammetry will be presented.

The support of the National Research, Develoment and Innovation Office is acknowledged (Project: ADVANCED 149644)

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Air-Tolerant Nickel-Catalyzed Suzuki-Miyaura, Hiyama, and Heck Reactions via Tridentate Ligands

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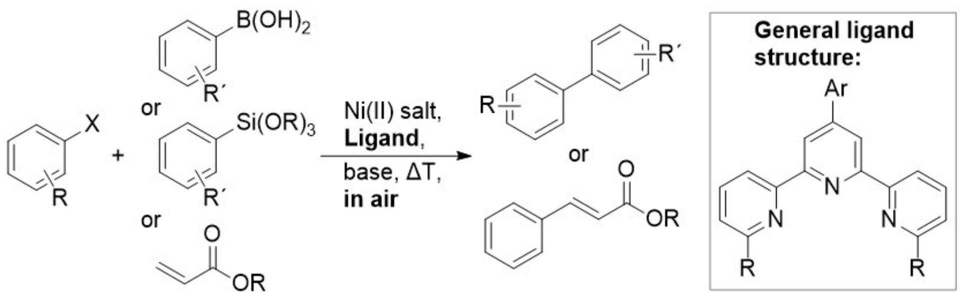
Transition metal catalyzed-cross coupling reactions have become an indispensable and powerful tool in organic synthesis. Among these, palladium- catalysts have been extensively studied and are currently still the most prominent players in the field [1]. Nonetheless, efforts to explore more economical and environmentally friendly metal alternatives have drawn significant attention, with nickel-based systems emerging as the most promising candidates [2-3].The main focus of this work is the development of an air-tolerant nickel catalyst system that can be modified for a variety of cross-coupling reactions. A tridentate terpyridine was identified as the most promising ligand platform. Suzuki-Miyaura, Hiyama and Heck coupling reactions were studied under air, demonstrating both promising reactivity and stability.



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Synthesis, Characterization and Biological Activity of New Pd(II), Pt(II) and Au(III) Complexes with 3-Aryl-1-(2-Pyridyl)Imidazo[1,5-*a*]Pyridine Ligands

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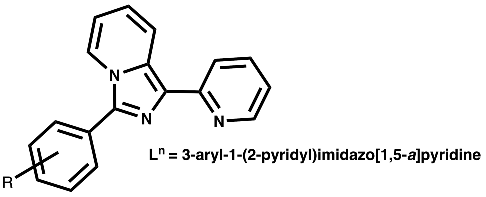
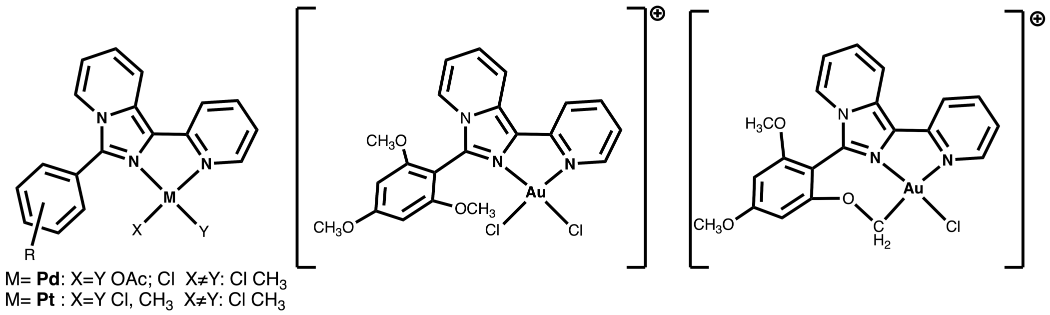
In the last time a particular class of heterocyclic aromatic nitrogen ligands 1-(2-pyridyl)imidazo-[1,5-*a*]pyridine 3-aryl substituted, containing the impy scaffold, has aroused great interest for the applications of their metal complexes in different fields.[1]





Following our interest in this field,[2] we report here the synthesis and characterization of new complexes of Pd(II), Pt(II) and Au(III) of the type $[(L^n)MXY]$ (M = Pd, Pt; X = Y = OAc, Cl, Me; X ≠ Y = Cl, Me), and $[(L^n)AuCl_2][PF_6]$ adducts, where the impy ligands $\mathbf{L^n}$ (3-aryl: **n=1** C_6F_5; **n=2** $C_6(CH_3)_5$; **n=3** 2,4,6-$C_6H_2(OCH_3)_3$) act as classic chelating N^N ligands. Given their great interest, various experimental conditions are being studied aimed at obtaining new derivatives such as the classic cyclometallates,[3] particularly with the metal ion Au(III), $[(L^n\text{-}H)AuCl][PF_6]$, as was already the case with ligands such as bipyridines.[4] Some of the complexes have been tested against Gram-positive (*S. aureus, S. pyogenes*) and Gramnegative bacteria (*P. aeruginosa, E. coli and K. pneumoniae*), as well as Yeast (*C. albicans*). An initial evaluation using the Kirby-Bauer procedure showed activity of several complexes: the promising preliminary results will be reported. *The work was carried out under the framework of the project ""Noble metal complexes with heterocyclic nitrogen ligands: application as antimicrobials" Financed by the European Union - NextGenerationEU - mission 4, component 2, investment 1.1. Project code MUR P2022PZ8JE.*

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Revisiting CNC_6F_5: Harnessing the power of perfluorination

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The carbonyl ligand (CO) is one of the gold standard organometallic ligands enabling the stabilization of homoleptic metal complexes across oxidation states ranging from –IV to +III, its disadvantage being no possibility for further modification. Alkyl- and arylisocyanides (CNR) have been extensively studied as these ligands offer the potential to fine-tune the electronic and steric properties as well as introducing possible chelating designs through the modification of the organic backbone. $CNCF_3$ and CNC_6F_5 had first been investigated in 1980s and 90s. Unfortunately, both of these ligands are synthetically difficult to access and similarly difficult to store. Lentz *et al.* published optimized syntheses of these ligands but only conducted limited studies. Thus, interest in these ligands subsided shortly after, with only limited insight and estimations on ligand donor properties.[1][2]

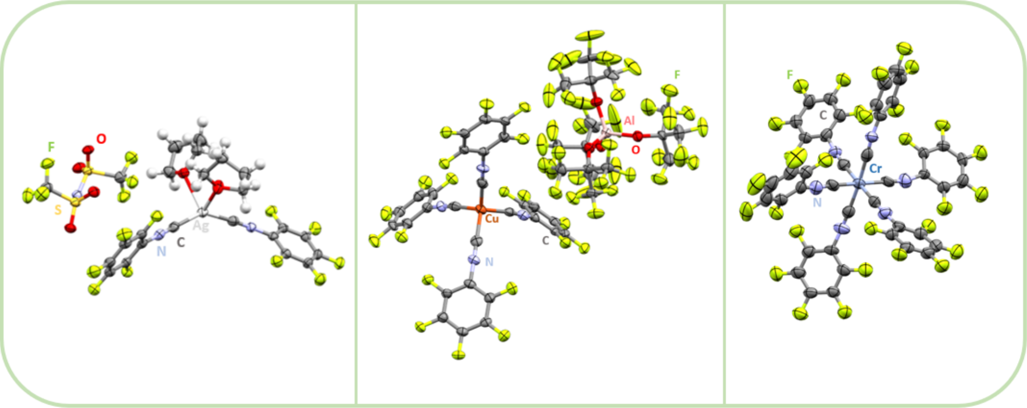

Figure 1. Molecular structure in solid state of $[Ag(CNC_6F_5)_2(THF)_2][NTf_2]$ (left), $[Cu(CNC_6F_5)][Al(OR^F)_4]$ (middle) and $[Cr(CNC_6F_5)]$.

Aiming to revitalize this chemistry, our computational analysis of $CNCF_3$ and CNC_6F_5 have revealed strong π-acceptor qualities comparable to that of CO, while not forfeiting significant σ-donor strength, making them feasible candidates for stabilizing electron rich metal centers.[3] We discuss the synthesis of homoleptic d^{10} isocyanide complexes, through the displacement of COD ligands by CNC_6F_5. Homoleptic isocyanide complexes of nickel and copper along with others, have recently been suspected as potent photosensitizer candidates with extended excited state lifetimes.[4] We believe that perfluorination of the arylisocyanide ligands may influence the excited state life times through to the absence of C–H bonds. We present CNC_6F_5 transfer reagents as well as several CNC_6F_5 homo and heteroleptic complexes. Photophysical properties of $[Ni(CNC_6F_5)_4]$ and $[Cu(CNC_6F_5)_4][Al(OR^F)_4]$ are currently under investigation by the Wenger group.

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Terminal monomeric calcium mono- and difluorides as fluoride shuttles?

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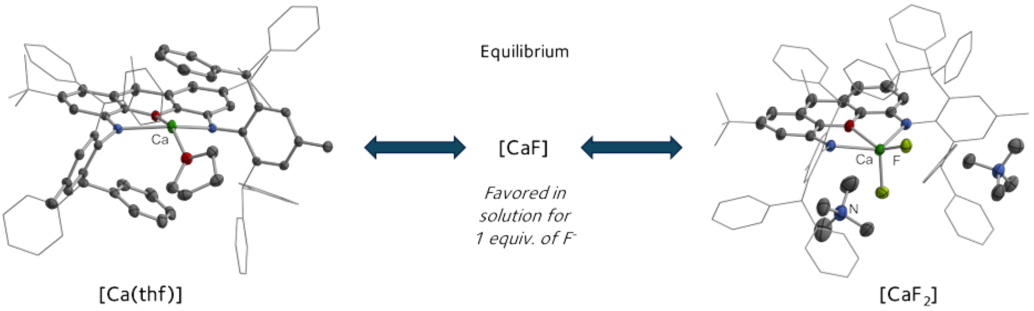
Calcium fluoride is the ultimate source of all fluorochemicals [1,2]. Current synthetic approaches rely on the use of HF, generated from naturally occurring fluorspar and sulfuric acid. Methods for constructing E–F bonds directly from CaF_2 have long been frustrated by its high lattice energy, low solubility, and impaired fluoride ion nucleophilicity. Little fundamental understanding of the reactivity of Ca–F moieties is available to guide methodology development; well-defined molecular species containing Ca–F bonds are extremely rare, and existing examples are strongly aggregated and evidence no nucleophilic fluoride delivery [3,4]. Building on our previous work [5] in which we showcase the synthesis, characterization and nucleophilic fluoride delivery of a range of well-defined complexes with structurally diverse Ca-F units, we now focus on the synthesis of true terminal Ca–F_x (x = 1,2) moieties. We show that these monomeric, terminal Ca–F complexes display interesting dynamic properties, with equilibria in solution that are not always reflected in the solid state. The terminal nature of the Ca–F motifs, in combination with the dynamic properties of the fluoride ligands, allows for reversible fluoride shuttling and enables their reactivity in nucleophilic fluoride delivery.



Structures in the solid state and interplay between Ca–F_x complexes with x = 0-2. Structures as determined by X-ray crystallography are displayed with thermal ellipsoids set at the 50% level. Hydrogen atoms, second disorder components and solvate molecules omitted, and selected fragments shown in wireframe format for clarity.

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Redox-Active Ligands Can Enable the Electrocatalytic Generation of Weak Bonds via Mediated PCET

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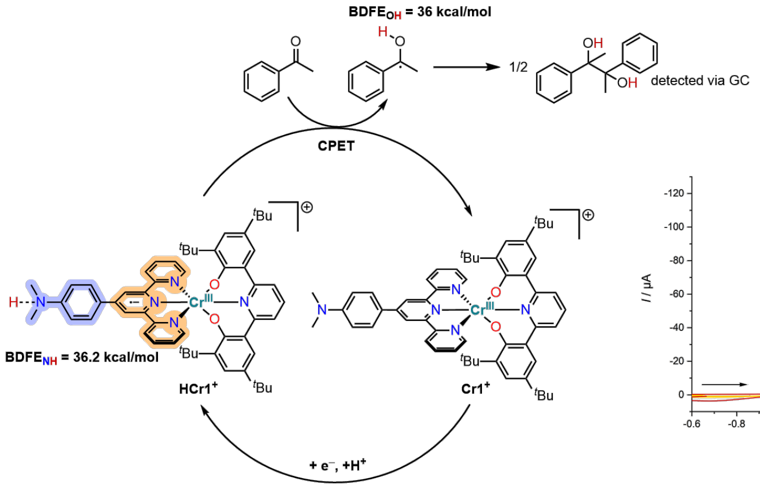
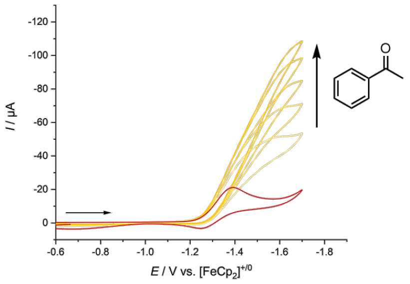
Proton-Coupled Electron Transfer (PCET) is of fundamental importance for the electrocatalytic transformation of small, unsaturated molecules into fuels and other value-added chemicals.[1] A persistent challenge in these reactions is the formation of dihydrogen under the cathodic potentials required to activate small molecules. Electrochemical PCET mediators can circumvent this issue: they serve as molecular shuttles that deliver protons and electrons in a controlled fashion to substrates and thus allow increased selectivity at lower overpotentials.[2,3] However, only very few molecular systems that effectively mediate the electrocatalytic reduction of unsaturated substrates are known to date. We now present a modular design for PCET mediators based on redox-active terpyridine ligands equipped with Brønsted-basic substituents. These complexes enable the electrocatalytic formation of weak -CH, -NH and -OH bonds, thus allowing electrochemical access to a variety of reduced products at low overpotentials.





The terpyridine scaffolds offers easy access to synthetic variations, which allows tuning the thermodynamic properties of the mediators. We use this approach to investigate which factors determine the rate of electrocatalytic PCET. This shows how the synthetic malleability of redox-active ligands can potentially be harnessed to steer the selectivity in challenging electrocatalytic reductions. Our work highlights how the use of redox-active ligands as electron reservoirs can be expanded to PCET reactivity for the activation of challenging unsaturated substrates.

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The synthesis and reactivity of borazine: benzene's inorganic sibling

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Despite extensive research into the reactivity of benzene and its derivatives, its so-called 'inorganic sibling', borazine, has received comparatively little attention.[1] Although borazine is isostructural to benzene, the lack of uniformity of the p-system leads to decreased aromaticity.[2] This results in notably different reactivity, including its susceptibility to both air and moisture. Furthermore, this can make its manipulation challenging, with the synthesis of borazine and its derivatives remaining non-trivial.

Whilst borazine holds potential as a versatile ligand in coordination and organometallic chemistry, the reactivity with both *d*- and *p*-block metals remains largely unexplored. To date, reported complexes primarily involve halogenated borazine derivatives and transition metal systems, with the addition of the B–H bond to any element in the periodic table yet to be reported.[3,4]

Here, we describe the B–H bond activation of borazine by means of main-group metal complexes, including an acyclic aluminyl compound and a bis(boryl)stannylene (Figure 1).[5,6] NMR spectroscopy studies, in combination with single-crystal X-ray diffraction of the novel complexes allowed for unambiguous structural determination, clearly demonstrating addition of the B–H bonds to the metal centers.

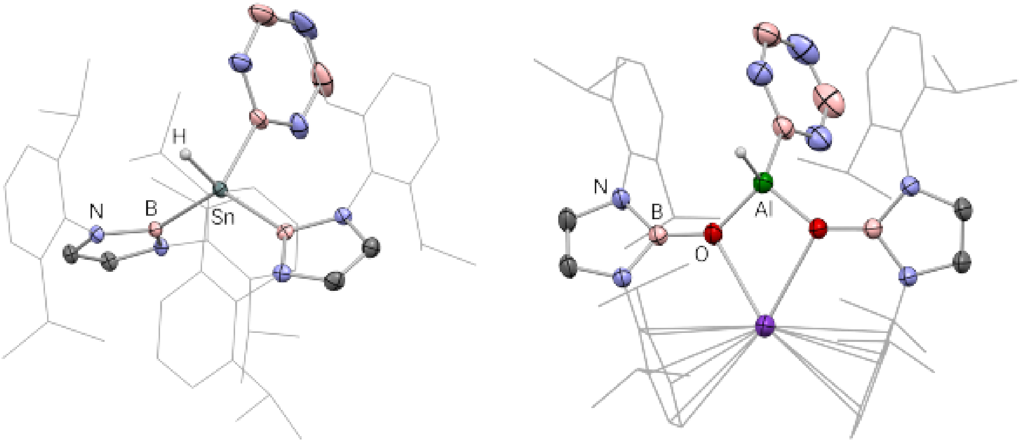

Figure 1. Solid-state structures of the B–H bond activation products $[B]_2Sn(Bz)H$ (left) and $AlK[BO]_2(Bz)H$ (right) ($[B] = B(NDippCH)_2$, $[BO] = OB(NDippCH)_2$ Dipp = 2,6-$^iPr_2C_6H_3$, Bz = $B_3N_3H_5$). Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

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Hydrogen Production from the Dehydrogenation of Formic Acid using Water-soluble Pyridylimine Ru(II) Complexes

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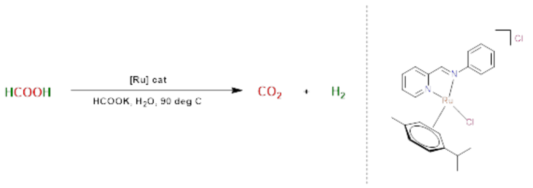
Liquid Organic Hydrogen Carriers (LOHCs) have been identified as promising energy vectors necessary for the implementation of the hydrogen economy. These molecules undergo reversible hydrogenation and dehydrogenation cycles which enable hydrogen storage and release [1]. Formic acid (FA, HCOOH) is one of the most attractive LOHCs due to its favorable properties such as a high hydrogen content (4.4 wt%) and a high energy density (1.77 kWh/L) [2]. We report the preparation of a panel of cationic, half-sandwich iminopyridine ruthenium(II) complexes of the type [(**L1**)RuCl(*p*-cymene)]Cl (**C1** – **C11**) where **L** = substituted N-Phenyl-1-(2-pyridinyl)methanimine ligand derivates (**L1-L9**) and their efficiency in catalytic dehydrogenation of formic acid (FA). The observed activity correlated with the nature of the substituent on the imine nitrogen and the solubility of the complexes in water, with **C1** exhibiting the highest initial turnover frequency (TOF) of 281 hr^{-1} at 90 °C. Kinetic and mechanistic investigations were undertaken in DMSO and H_2O, revealing that the proton source in the hydrogen production step is solvent-dependent. FA was found to be responsible for H_2 formation in DMSO and H_3O^+ ions were involved in generating H_2 in water. Complex **C1** was more stable in water, as it maintained efficient gas evolution for > 10 cycles without any deactivation, reaching a turnover number (TON) of > 13000.



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From 18- to 20-electron ferrocene derivatives via a ligand coordination

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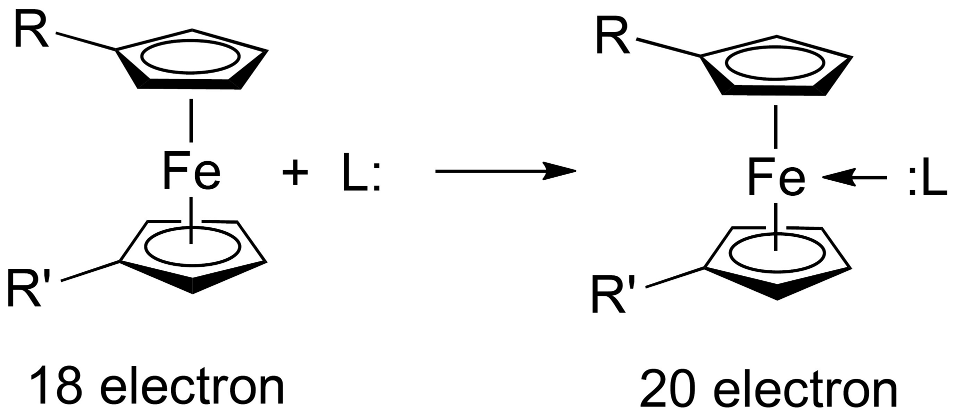
The 18-electron rule is a fundamental rule in coordination chemistry on which several revolutionary discoveries in catalysis and material science are founded. This rule has classes of exceptions; however, it is widely taught and accepted that diamagnetic 18-electron complexes do not coordinate to a ligand to form a 20-electron complex even as a reaction intermediate[1]. One of the most prominent examples of the 18-electron rule is the structure and stability of ferrocene, which marks the beginning of modern organometallic chemistry. Ferrocene derivatives can coordinate to Lewis acidic species, such as boranes, and cationic or coordinatively unsaturated metal centers[2]. In contrast, the coordination of a Lewis basic ligand to iron atom in ferrocene has remained elusive. For example, ferrocene does not react with CO even under 150 atm[3]. In theory, this coordination would form formal 20-electron ferrocene derivatives if η^5-coordination mode of the two cyclopentadienyl groups does not change upon the coordination. However, such coordination chemistry of diamagnetic18-electron ferrocene derivatives is considered unlikely according to the 18-electron rule. Here, based on the tunable ligand design, we report the formation of 20-electron ferrocene derivatives through reversible nitrogen coordination to 18-electron analogs. Through theoretical studies, we elucidated key features that enabled this coordination chemistry and how nitrogen coordination shifts the metal−ligand bonding characters. These 20-electron ferrocene derivatives exhibit reversible $Fe^{II}/Fe^{III}/Fe^{IV}$ redox chemistry under previously unattainable, mild conditions. This work highlights the elusive coordination chemistry of diamagnetic 18-electron complexes, which underlays the foundation for future innovations in a range of synthetic chemistry.



Is it possible?

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Catalytic Deprotonative Borylation of Arenes with Iminoboranes

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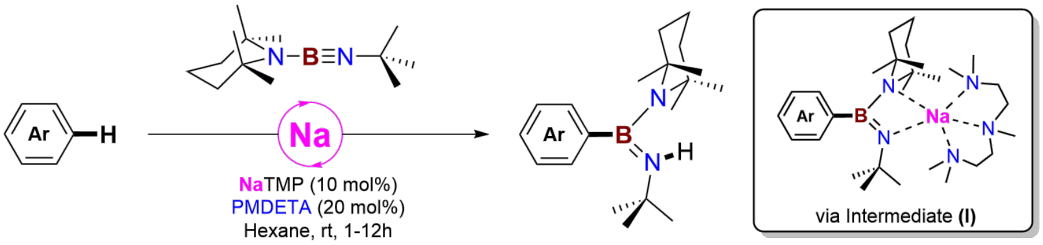
Organoboron compounds have found widespread use in the synthesis of pharmaceuticals, owing to the high functional group tolerance and mild conditions of the Suzuki-Miyaura Coupling reaction. Catalytic C-H borylation stands out as an atom-efficient strategy to prepare these compounds. However, state-of-the-art protocols require transition metals that are unsustainable, toxic or require sophisticated ligand architecture,[1,2] while transition-metal free methods generally proceed via electrophilic C-H activation.[3,4] Alternatively, deprotonative borylation can give access to the desired compounds, but requires stoichiometric amounts of organometallic reagents.[5–7]

Charting new territory in the field, we have now demonstrated the deprotonative borylation of arenes and heteroarenes using catalytic amounts of the superbasic sodium amide NaTMP and Lewis donor PMDETA in combination with the low-coordinate iminoborane as a trapping agent. This system shows improved functional group tolerance, milder reaction conditions and allows for stepwise borylation of polyfluorinated arenes. Comprehensive mechanistic understanding has been achieved through a combination of DFT calculations, reaction kinetic studies and characterisation of catalytic intermediates with single-crystal XRD and NMR spectroscopy, demonstrating the key role of iminoboranes to capture the fragile metalated arenes, but also generating a highly basic intermediate (**I**) that can further turn the catalytic cycle.



Scheme 1: Borylation of Arenes catalysed by Sodium Amides

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Bioinspired copper complexes for biomass valorization

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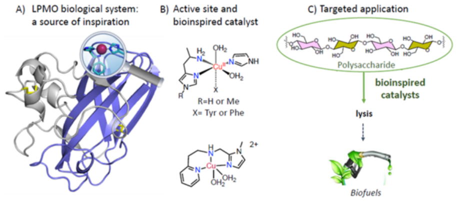
The pressing issues of global warming and the anticipated depletion of petroleum in the near to medium term are driving societies to seek sustainable alternatives to produce chemicals and fuels. One promising option is plant biomass, a major global reservoir of photosynthetically fixed carbon, which is increasingly recognized as a renewable and natural resource. [1] Utilizing non-edible plant components, such as agricultural or forestry residues (lignocellulosic biomass), for "advanced" biofuels or chemical production is particularly advantageous as it avoids competing with food or water resources.[2]A significant challenge lies in the intert nature of lignocellulose. [3] To address this, physical and/or chemical pretreatments are necessary to make the polysaccharides more accessible for further applications. Despite progress in this area, the production of biofuels or chemicals from lignocellulosic biomass remains limited due to high conversion costs. This work will specifically target polysaccharides, such as cellulose, which constitute the largest portion of plant biomass. The focus of this work is to develop low-molecular-weight, metal-based catalysts designed to oxidatively target recalcitrant polysaccharides. Its goal is to enhance their cleavage into smaller building blocks for the production of bio-based chemicals or biofuels. The development of these catalysts will be guided by bioinspiration—a creative approach that draws on natural processes to devise innovative strategies for addressing sustainable. development challenges. LPMOs (Graphic) are copper-containing enzymes that play a pivotal role in breaking down recalcitrant polysaccharides through oxidative processes.[4] They catalyze the hydroxylation of an inert C-H bond at the glycosidic linkage (either at the C1 or C4 position), which subsequently leads to bond cleavage. Remarkably, LPMOs can utilize either O_2 with an electron source or H_2O_2 as a co-substrate to drive substrate oxidation. Oxidation of polysaccharides will result in their breakdown. The active site of LPMOs features a surface-exposed copper ion coordinated by two histidine residues, including an N-terminal histidine in a unique bidentate coordination mode referred to as the "histidine brace."[5] The degree of oxidation can be controlled by adjusting the nature of the catalysts and the experimental conditions. Oxidation of polysaccharides will result in their breakdown. Consequently, the catalysts (Graphic) will be tailored for the oxidative lysis of polysaccharides to produce bio-based chemicals or advanced biofuels with air or H_2O_2 as oxidants.



PyA-Cu^{II}
[(**PyA**)Cu(NO_3)$_2$]

PyI-Cu^{II}
[(**PyI**)Cu(NO_3)$_2$]

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C^N-chelated manganese(I) carbonyl complexes as hydrogenation catalyst precursors

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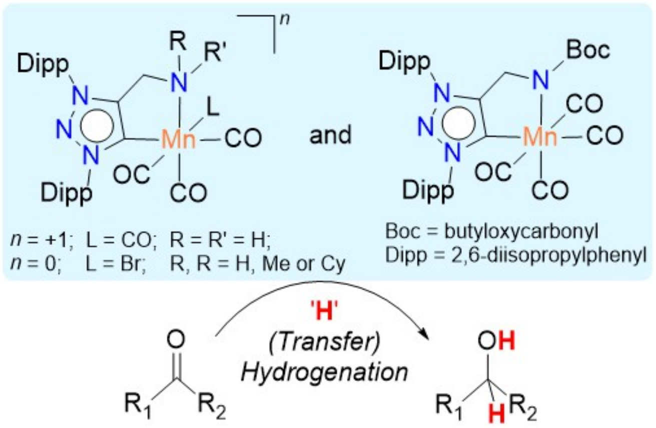
Catalytic hydrogenation of unsaturated compounds is a cornerstone of chemical synthesis. In the pursuit of finding alternatives to the traditional platinum group metal complexes that catalyze these reactions, attention has increasingly shifted to focus on the use of first-row transition metals like manganese. Well-defined molecular complexes of manganese with either pincer or chelating bidentate ligands have been shown to be particularly suited to mediate these reactions via a metal-ligand cooperative mechanism [1]. Pidko and co-workers have recently efficiently demonstrated a manganese catalyst design where the catalytic activity can be turned 'on' or 'off' by simple variation of the N-donor subsitutent in the chelated C^N-ligands (C-donor = N-heterocyclic carbene, N = amines) [2]. The use of mesoionic carbenes, such as triazolylidenes, instead of imidazolylidene-based NHC ligands for manganese complexes has been reported for application in oxidative catalysis [3], but has not yet been explored, to the best of our knowledge, in hydrogenation reactions. Here we present a series of manganese(I) carbonyl complexes featuring bidentate N-donor functionalized triazolylidene ligands (**Scheme 1**) [4]. Stoichiometric reactivity studies investigating the metal-ligand bifunctionality, as well as the application of the manganese complexes in the benchmark (transfer) hydrogenation of ketones will be explored.



Scheme 1. Series of C^N-chelated manganese(I) carbonyl complexes and their proposed (transfer) hydrogenation reaction

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Formation of a neutral silylium bora ylide by insertion of BH_3 into $Si_4\{N(SiMe_3)Mes\}_4$

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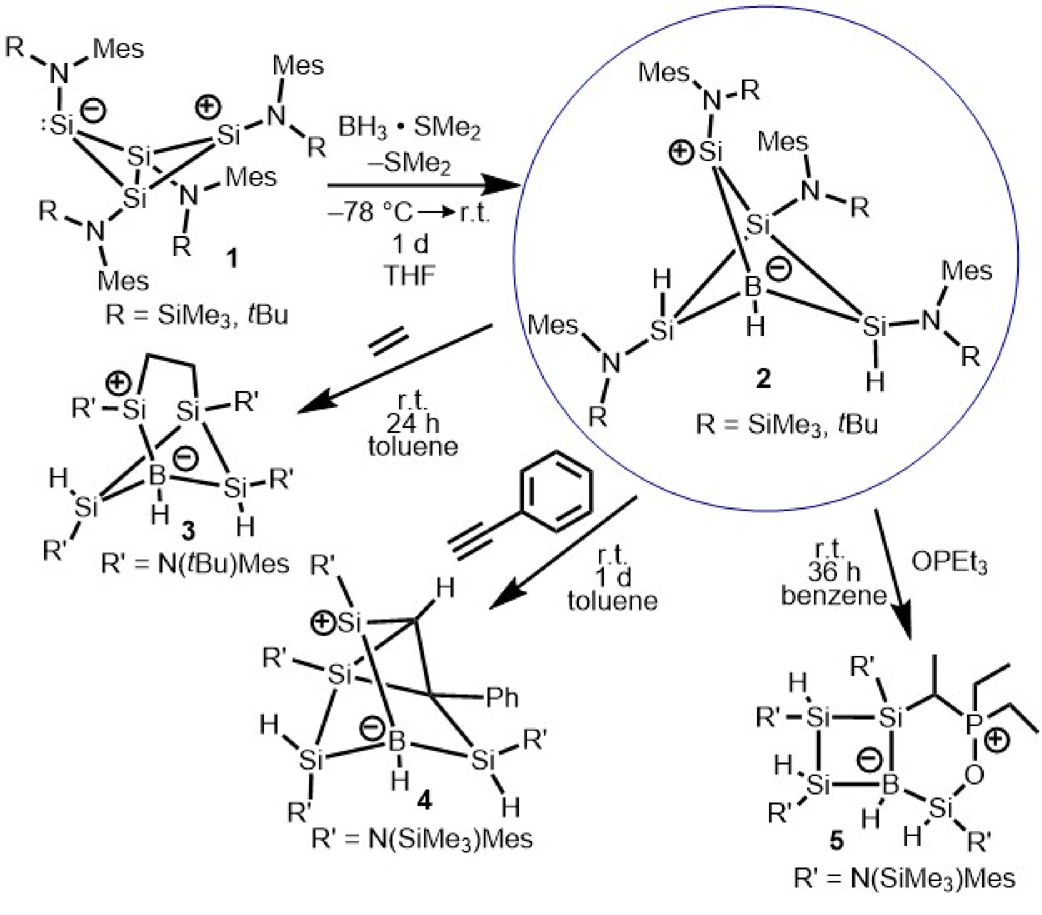
Isolable silylium ions are interesting compounds that have to be stabilized intramolecularly[1], by bulky substituents[2], or complexation to solvents[3] or anions[4].

When the bicyclic zwitterionic silicon(I) ring compound $Si_4\{N(R)Mes\}_4$ **1**[5] (R = $SiMe_3$, *t*Bu) is reacted with $BH_3{\cdot}SMe_2$, the neutral silylium borate **2** is formed by complete insertion of BH_3 into the Si–Si-bonds of **1** under formation of two Si–H bonds and a silylium ion unit. Compound **2** features a particularly low field shifted ^{29}Si-NMR signal at 246.0 ppm for the tri-coordinated silicon atom, in the region of typical silylium ions, indicating strong Lewis acidic character. Compound **2** reacts with unsaturated carbon compounds such as ethene and phenylacetylene by insertion of the π bonds into the Si–Si bonds of the scaffold. Reaction with Lewis base $OPEt_3$ affords a bicyclic ring structure **5** after C–H abstraction and insertion.



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Safe use of CO surrogates in tandem with a novel highly active phosphine ligand for the efficient alkoxycarbonylation of alkenes

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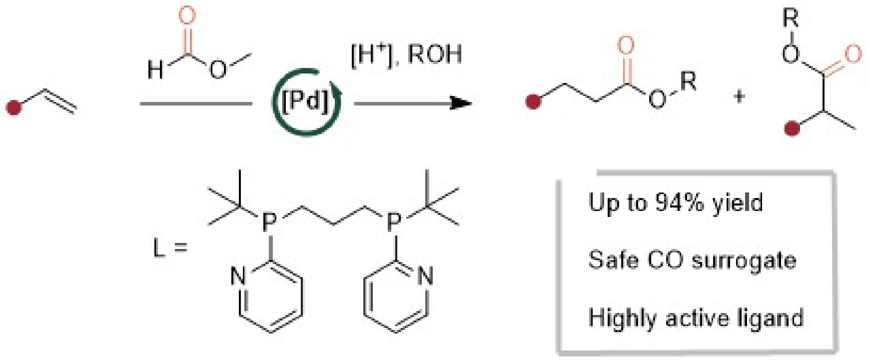
Carbonylation reactions are among the most important homogenously catalyzed processes in both industry and academia, enabling the rapid synthesis of various carboxylic acid derivatives.[1] This reaction employs highly toxic and flammable carbon monoxide (CO) gas under high pressures, making the use of specialized safety and technical equipment inevitable. A method to overcome these problems is the utilization of CO surrogates, making the reaction inherently safer and more environmentally benign.[2]

In this context a novel ligand system for the alkoxycarbonylation of alkenes employing methyl formate as a CO surrogate is reported. Traditionally ligands with aromatic backbones were employed for these reactions, whereas the exploration of ligands with aliphatic backbones, as described in this study, has been rare.[3] [4] Our findings showcase the influence of the new ligand on the reaction activity and selectivity as well as the applicability of the newly developed methodology.[5]



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Ring-Opening Polimerization of ε-Caprolactone using a Bismuth-Aminotrisphenolate catalyst

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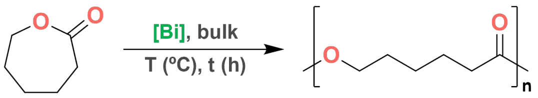
Plastic materials are fundamental for our everyday life, and they surround us everywhere. Most of them, such as polyethylene or polypropylene, are produced from fossil fuels and are non-biodegradable. As a result, in search for more sustainable solutions, bio-derived plastics have become more popular over the last few years. Poly(ε-caprolactone) has been widely studied, and its biodegradability and biocompatibility characteristics make it suitable for a range of applications.[1] This polymer can be readily synthesized from ε-caprolactone through Ring-Opening Polymerization (ROP), which can be produced from biobased sources.[2]

Bismuth is a non-toxic metal, which renders it highly attractive for the development of new catalytic systems. In the literature, a number of bismuth complexes with catalytic activity in different processes have been described.[3] In particular, in our research group we have prepared bismuth aminotrisphenolate complex which is able to catalyze the synthesis of cyclic carbonates from epoxides and carbon dioxide, taking advantage of their Lewis acid properties.[4] However bismuth catalysts have hardly been explored in catalytic ROP processes. This contribution provides an overview of the use of the bismuth aminotrisphenolate complex prepared by us as a catalyst for the ROP of ε-caprolactone, whereby impressive catalytic activities with high conversion at mild conditions is achieved.



83
Bi
Bismuth

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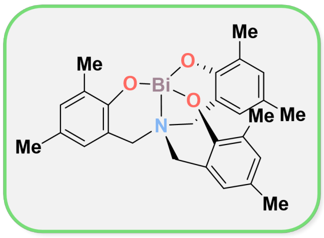

☑ **Sustainable** catalysis

☑ Use of non-toxic **bismuth** complexes

☑ **Biodegradable** and **biocompatible** polymer

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Tailoring Sodium Organometallic Reagents for Catalytic Reactions

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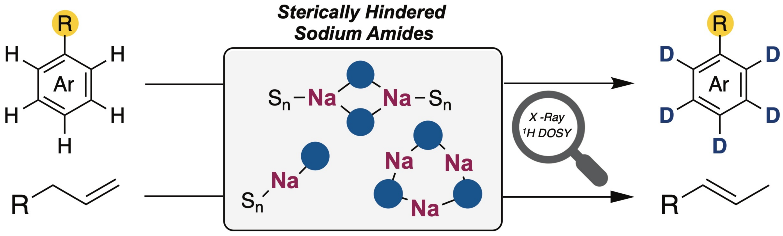
Organosodium compounds have attracted the attention of the scientific community in recent years as an alternative to widely used organolithium reagents.[1] Lithium alkyls and amides reside at the front of organometallic synthesis as key players in countless transformations, owing to their availability, substantial stability and solubility in hydrocarbon solvents.[2] However, these desirable traits are often pitfalls of heavier alkali-metal organometallics, meaning that their applications have remained underexplored.

Filling this gap in the knowledge, the preparation of organosodium compounds soluble in hydrocarbon solvents and the isolation and characterization of reactive sodium organometallic intermediates in the solid state and in solution by X-Ray crystallography and ^{1}H DOSY (Diffusion Ordered SpectroscopY) have allowed the development of new protocols for the functionalization of organic molecules. Our efforts have been focused on selective deprotonative metalation reactions of synthetically attractive arenes, providing access to the selective functionalization of these scaffolds, including the borylation [3] and the catalytic deuteration of organic substrates.[4][5] Extending the application of this methodology, we have uncovered their use for the catalytic isomerization of terminal alkenes into more synthetically useful internal olefins.[6] Moving away from transition metals, we have studied the mechanism of this reaction with stoichiometric experiments and DFT calculations, revealing the formation of the organometallic sodium intermediates via deprotonation and showing the key role of the in-situ generated amine for an effective transformation.



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Computational Characterisation of the First Neutral Al_3 ‘cyclotrialumane’

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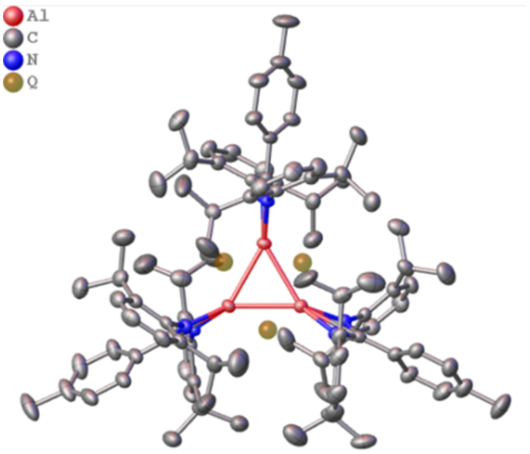
[1]King's College London

With the rising interest in moving away from precious metal mediated catalytic processes, the exploration of earth abundant s and p-block based complexes for redox-like reactivity has become an increasingly active field of research. The highly reactive nature of many low oxidation state group 13 complexes, particularly based around aluminium (Al), is now very well documented – with many examples of impressive activation reactions having been demonstrated thus far [1,2]. The reactivities of monomeric, dimeric and tetrameric Al(I) complexes have already been extensively investigated [3,4]. Despite this, there are currently no known examples of neutral complexes involving 3 aluminium atoms in the +1 oxidation state. Probing the behaviour of such a complex could be significantly important in gaining a better understanding of how to manipulate aluminium towards exhibiting useful reactivity.

Via the reduction of a series of amidine-stabilised aluminium (III) di-iodides, we have been able to isolate and explore the first known example of a neutral, cyclotrimeric Al(I) complex. The highly modular nature of the amidine (‘RN-CR’’-NR’’’) framework allows us to additionally obtain a variety of differently functionalised analogous complexes and probe their respective reactivities.

In this work, we employ DFT as a method of structural confirmation and electronic structure characterisation of this low oxidation state Al species. Using a combination of computational analysis techniques, we have been able to correlate multiple ambiguous experimental results to unique electronic properties of our system, including the presence of multiple non-nuclear electronic maxima.



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C-N Bond Oxidative Cleavage as a route to Ni(II) and Ni(I) complexes.

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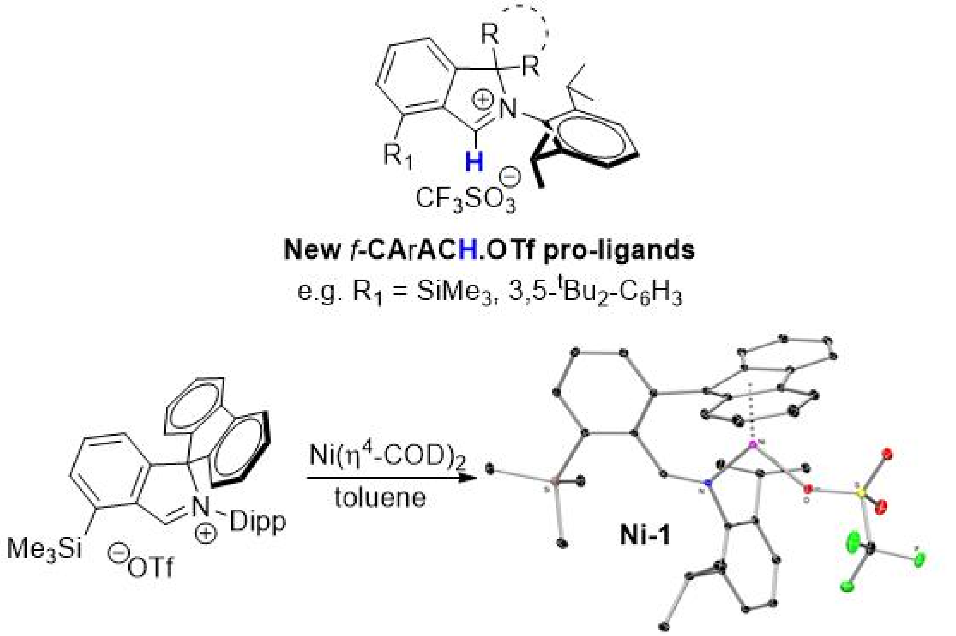
Fused **C**yclic **Ar**yl **A**mino **C**arbenes (*f*-**CArACs**[1]), have attracted interest as supporting ligands for transition metal complexes with potential applications in photonics[2] and catalysis.[3] In our research group we are investigating *f*-**CArAC** scaffolds incorporating auxiliary arene functionalities and bulky silyl moieties in an effort to modulate their stereo-electronic properties, and to that end we have successfully synthesised a series of new isoindolinium salt precursors *f-CArAC**H**.OTf*, in good to moderate yields (**Scheme 1**). Their reaction with [Ni(η^4-COD)$_2$] leads to the unprecedented fission of a C–N bond in the pro-ligand backbone giving facile access to Ni(II) organometallic complexes (*e.g.* complex **Ni-1**, **Scheme 1**) in good to excellent yields, offering insight into the paucity of *f*-**CArAC:**→Ni complexes. Furthermore, we would like to present how this new class of Ni(II) complexes are useful precursors for accessing *syn*-bimetallic Ni(I)-Ni(I) complexes *via* their mild reduction.



Scheme 1: New *f*-**CArAC** ligand precursors (*top*) and oxidative C-N bond cleavage leading to Ni(II) complexes (*bottom*)

We would like to thank the Hellenic Foundation for Research and Innovation (H.F.R.I.) and Greece 2.0 (Next Generation EU) for supporting this work (grant 15293)

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Regioselective Synthesis of Polysubstituted Borylated, Silylated Pyridines *via* Transition Metal-Catalyzed [2+2+2] Cyclotrimerization

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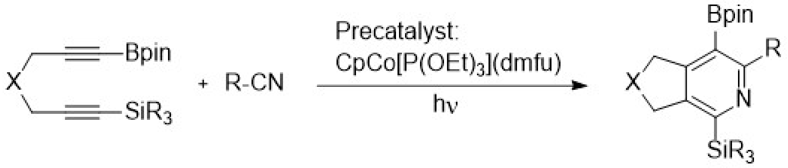
Cobalt-catalyzed [2+2+2] cycloaddition reactions of different borylated and silylated alkynes have been reported for the synthesis of different pyridines and carbocycles. [1-4] Regioselective introduction of boryl and silyl groups in pyridine rings by cyclotrimerization, however, are still not well studied. Therefore, a rather simple powerful cyclotrimerization method to generate regioselective organoboron and organosilyl substituted pyridines is desirable, considering the potential synthetic usefulness of the products.

We have developed an efficient and atom-economical methodology for regioselective synthesis of polysubstituted borylated and silylated pyridines. The reaction proceeds at room temperature under photochemical condition using a convenient cobalt precatalyst. [5] We have evaluated the regioselectivity of the pyridine formation using different diyne decorated with boryl and as well as selected silyl groups. Further synthetic transformations applying the synthesized pyridines are also demonstrated.



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Hybrid Polyoxometalate Materials: Bridging Inorganic and Organic Worlds for Multifunctional Materials

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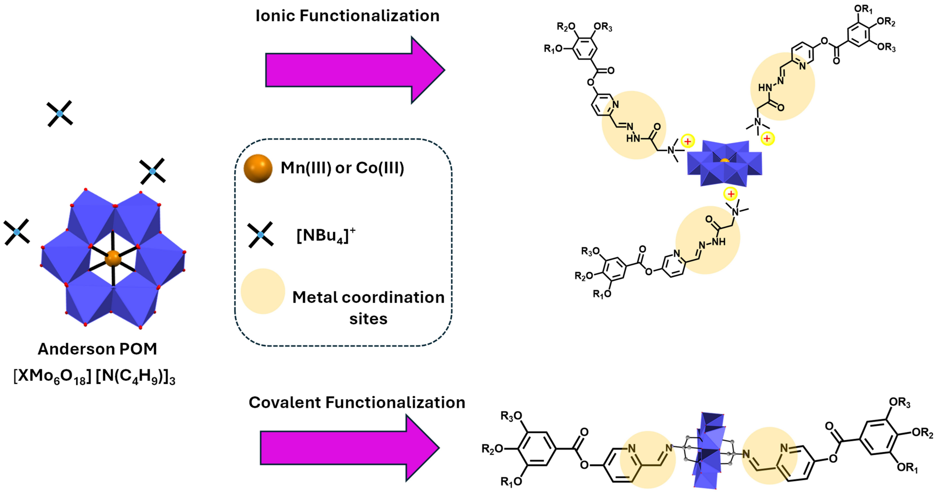
Supramolecular self-assembly has emerged as a powerful strategy for tuning the properties of molecule-based materials, particularly in the creation of hybrid inorganic–organic systems with multifunctional capabilities. Polyoxometalates (POMs) serve as ideal building blocks due to their strong electrostatic interactions, reversible redox behavior, and diverse physicochemical characteristics, making them excellent candidates for stimuli-responsive materials. However, functionalizing POMs remains challenging due to their sensitivity to reaction conditions. Functionalization approaches typically include (A) covalent organic linkage, (B) non-covalent surfactant encapsulation, and (C) multi-level functionalization, where cationic surfactants stabilize POMs and act as metal ion ligands, as explored by our group. The latter approach opens new possibilities for creating materials with highly tunable and multifunctional properties, with promising applications in catalysis, energy storage, and drug delivery. Liquid crystals (LCs) bridge crystalline solids and isotropic liquids, enabling tunable, stimuli-responsive systems. Integrating LCs with POMs introduces new opportunities for the development of functional materials. The incorporation of long aliphatic chains together with aromatic centers serves as effective inducers of these phases. Moreover, beyond their role in LC formation, these structural features also drive self-organization, enhance solubility in organic solvents, and facilitate material processing.



In this work, we present a rational design of hybrid materials using covalent and ionic bonding strategies, both capable of chelating metal centers. The inorganic platform chosen is an Anderson POM incorporating different metal centers (Co (III) and Mn (III)), while the organic platform consists of imine ligand, selected for their strong covalent bonding, conjugation, metal coordination, which help induce mesogenic properties and enhance electronic communication and charge transfer with the POMThese ligands were strategically functionalized with aliphatic chains of varying lengths and aromatic systems to promote liquid crystal phases. The design and characterization of these new functionalized POM systems not only offer promising applications in emerging technologies but also provide a rational, step-by-step platform for constructing complex, multifunctional species in a predictable manner.

Heteroaromatic phosphinoferrocenes with methylene spacers

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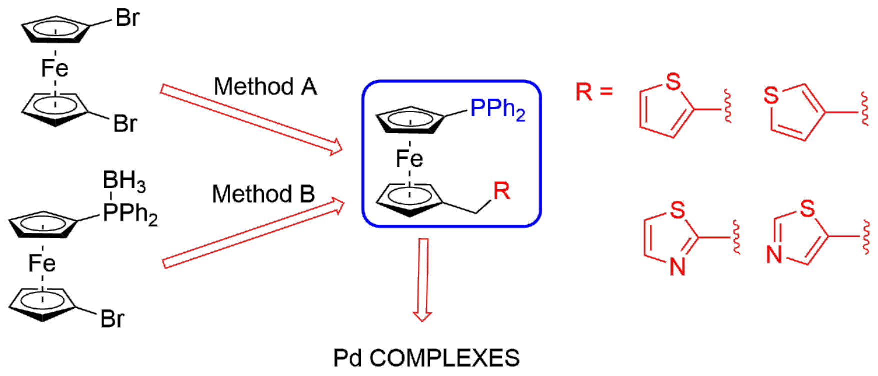
Phosphinoferrocene ligands are nowadays intensivelly studied as ligands for transition metal catalysis. Primarly, asymmetrically substituted hybrid derivatives, containing apart from the phosphine functional group also another donor atom such as nitrogen, oxygen or sulfur are the subject of many studies thanks to their possible hemilabile coordination, which makes them promising ligands for catalysis. This study focuses on expanding the mentioned class of compounds by preparation of a series of new phosphinoferrocene hybrid ligands bearing five-membered heterocyclic fragments. These fragments are separated from the ferrocene backbone by methylene spacer, which endows them with a greater flexibility.

Synthesis of these ligands depends on the attached heterocycle. In general, it requires preparation of the corresponding alcohol via lithiation and subsequent addition to a heteroaromatic aldehyde, followed by reduction of the alcohol to a methylene derivative. Compounds bearing thienyl functional group could be prepared from 1,1´-dibromoferrocene by successive lithiation/functionalization. In contrast, the synthesis of compounds bearing thiazolyl substituent required additional protection/deprotection steps. Coordination behaviour of the obtained hybrid ligands was studied in palladium complexes.



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Switchable and ring-selective hydrogenation of naphthyridine isomers

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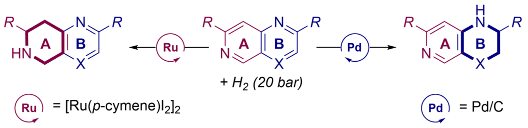
Hydrogenation of heteroarenes at a late-stage remains a challenge due to the complexity of controlling regioselectivity. Orthogonal procedures for the hydrogenation of [1,6]- and [1,7]-naphthyridines to their respective 1,2,3,4- or 5,6,7,8-tetrahydronaphthyridine counterpart are described, controlled through the use of a heterogeneous palladium catalyst or homogeneous ruthenium pre-catalyst – [Ru(p-cymene)I2]2. The procedures were applied to a wide range of [1,6]- and [1,7]-naphthyridines, tolerating a wide range of substitution patterns and functional groups without impacting selectivity. In certain cases, the addition of NaBArF4 (BArF4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) improved activity substantially. Mechanistic studies rule out reaction pathways involving a selective product inter-conversion step and indicate the two catalyst systems directly hydrogenate their respective ring. A rationale for the selectivity is provided, where for the ruthenium system selectivity is largely controlled through electronics of the rings, and the palladium system involves a subtle mixture of steric and electronic effects. Together, the two protocols allow for the selective and predictable reduction of naphthyridine rings.



A Structurally Versatile Biguanide System for Possible Metal-Metal Cooperation in ROP of Cyclic Esters

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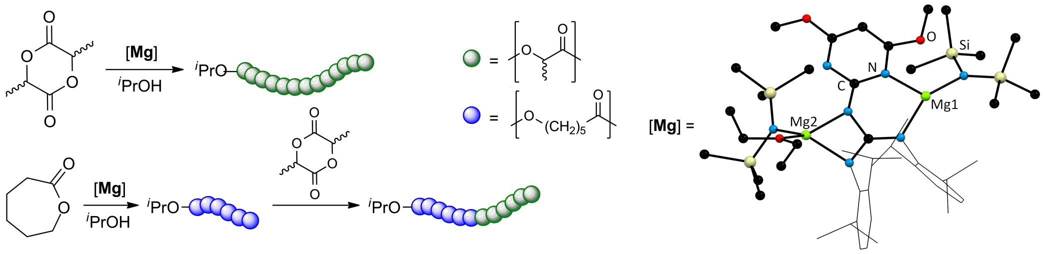
Amidinates and guanidinates are well known capable ligands used for their electronic and steric flexibility and generally configurable properties.[1] The even more electron-rich skeleton of biguanides offers flexible moiety in regards of the geometry and π-electron density delocalization and thus supports multiple structural arrangements of its complexes.[2] These could act as bi-functional molecules and are prospective candidates for multi-metallic systems with possible advantages such as cooperative effect between the metals and electronic tuning.[3]

In our group, we studied a hybrid biguanide-like guanidinate ligand able to mimic guanidinate and aza-*β*-diketiminate chelating coordination sites, which yields dianionic (hetero)bimetallic complexes. Several combinations of mostly main group (and post-transition metal) elements were explored with the ultimate aim of eventual utilization as catalytic species. An unexpected synthetic route opened the door for easy metal-substituent modification and, together with the possibility to influence a desired coordination pattern, allowed access to tailored purpose-built catalysts, tested in hydroelementation reactions and ring-opening polymerization (ROP) of cyclic esters. Some highly active and robust species were able to surpass turn-over frequencies of 60 000 h^{-1} in lactide ROP. Moreover, di- and triblock co-polymers of some combinations of lactide, *ε*-caprolactone or *β*-butyrolactone were obtained in immortal catalytic conditions. The story of development of this capable ligand platform as well as some results from ROP polymerization will be discussed.



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Copper(I)-Mediated Functionalisation of White Phosphorus

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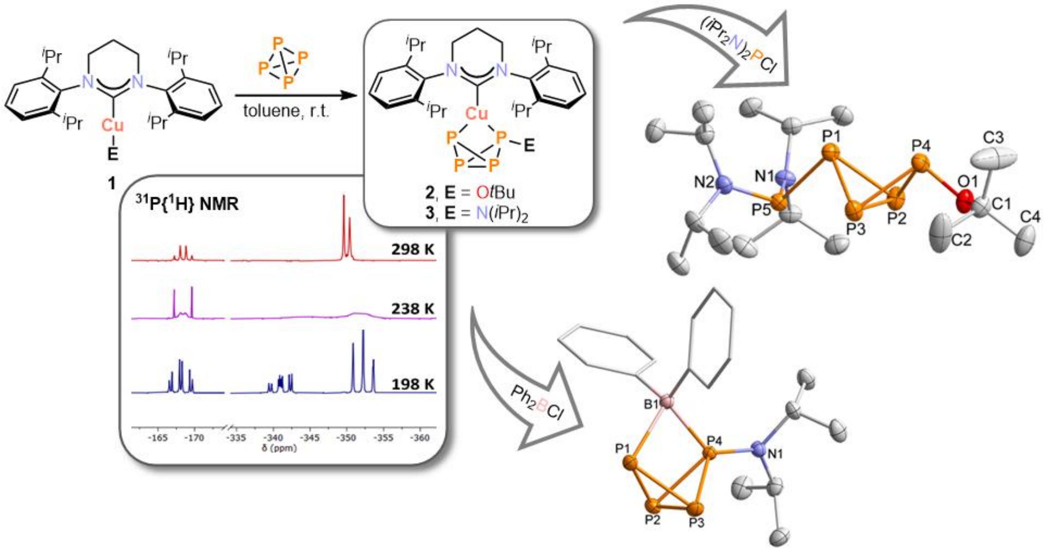
The activation of white phosphorus (P_4) by organometallic complexes has yielded a myriad of polyphosphorus motifs through aggregation and degradation of the phosphorus tetrahedron.[1] While low-valent transition metal complexes can reduce P□ to form stable polyphosphido ligands, their high stability often precludes further functionalisation to isolable organophosphorus compounds.[2]

Herein, we present the selective functionalisation of P_4 using *N*-heterocyclic carbene-supported copper(I) complexes **1**. Reactions of P_4 with (6Dipp)CuO*t*Bu and (6Dipp)CuN(*i*Pr)□ result in the cleavage of a single P–P bond, affording functionalised polyphosphido complexes **2** and **3**. These complexes exhibit dynamic solution behaviour, consistent with the rotation of the polyphosphido ligand around the Cu–P bond. Subsequent treatment with electrophiles displaces the [P□E]□ ligands and forms asymmetrically substituted, metal-free organophosphorus butterfly compounds with unique substitution patterns. This demonstrates a convenient approach to access new oligophosphorus species directly from P_4.



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Chemocatalytic Conversion of Dinitrogen to Ammonia Mediated by a Tungsten Complex

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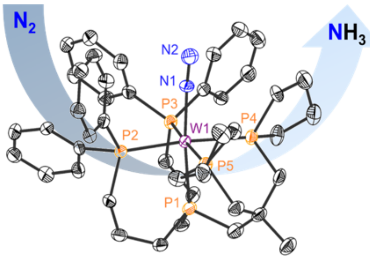
Since the 1960s, synthetic nitrogen fixation has been a highly competitive and challenging area of research focused on converting the inert nitrogen molecule (N_2) into ammonia (NH_3), a vital chemical feedstock.[1,2] Inspired by the enzyme nitrogenase, which is able to convert N_2 into NH_3 under ambient conditions, molybdenum-dinitrogen complexes have been demonstrated to be effective chemocatalysts for this conversion.[3-5] Surprisingly, all attempts with tungsten, the heavier homologue of molybdenum, have failed so far.[6-8] The reason for this difference in reactivity has not been fully explained.[6,7] Here, we present a new pentadentate tetrapodal (pentaPod, P5) phosphine ligand with phospholano (Pln) groups.[8] The derived molybdenum complex $[Mo(N_2)P5^{Pln}]$ generates 22 equivalents of NH_3 from N_2 in the presence of 180 equivalents of $SmI_2(thf)_2/H_2O$.[4,8] The analogous tungsten complex $[W(N_2)P5^{Pln}]$ produces 7 equivalents of NH_3, rendering the latter the first tungsten complex chemocatalytically converting N_2 to NH_3. The impact of the novel $P5^{Pln}$ ligand on the catalytic activity of both the tungsten and corresponding molybdenum complexes was extensively studied and compared to tungsten and molybdenum complexes that contain the established $P5^{Me}$ a pentaPod ligand, which features two dimethylphosphino groups.[8-10]



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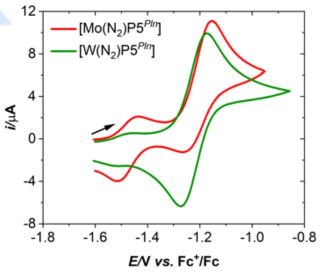

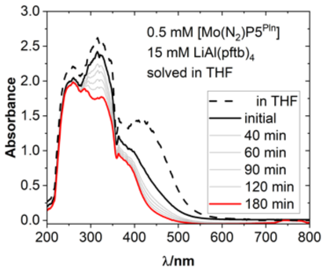

The hypothesis that tungsten complexes lack catalytic activity due to more negative redox potentials is challenged by the present $[W(N_2)P5^{Pln}]$ complex, as both the Mo and W systems investigated exhibit similar electrochemical properties. However, our results indicate that $W(N_2)$ complexes demonstrate greater acidity and are more difficult to protonate than their $Mo(N_2)$ counterparts, which, in contrast, display higher basicity.[8]

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The Pincer Platform Beyond Classical Coordination Patterns - A Redox-Active Carbodiphosphorane-Based Actor Ligand in the Coordination Sphere of Rhodium Allows for Carbon-Centered (Radical) Reactivity and Unique Cooperative Bond Activations

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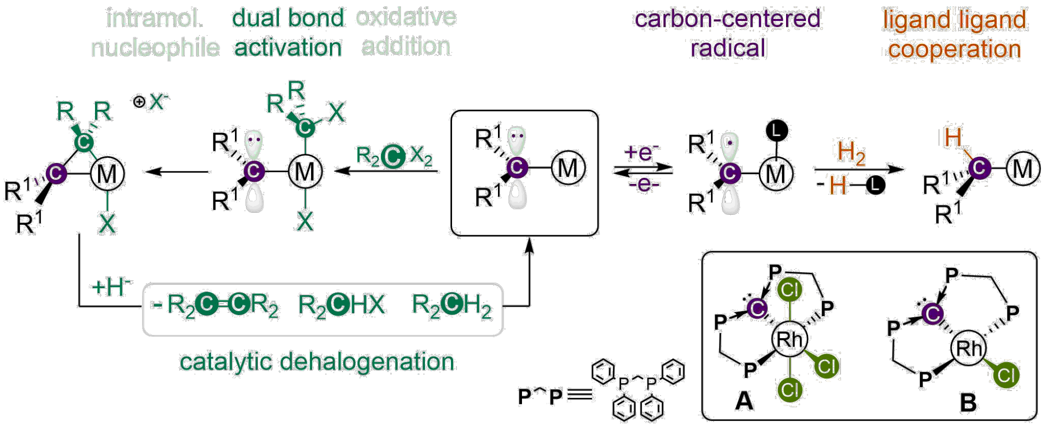
We reveal a k^3-PCP pincer-type ligand with a central carbodiphosphorane-based (CDP) moiety to be highly nucleophilic and showing redox-non-innocence in the coordination sphere of Rh rendering the CDP-pincer as a remarkable actor ligand, allowing for extraordinary types of bond activation and new pathways in catalysis:[1] Inspired by aminyl radical ligands[2] and the redox non-innocence of carbodicarbene complexes,[3] we found that complex **A** [({dppm}$_2$C)RhCl$_3$] (dppm= bis(diphenylphosphino)methane) reacts with acetyl ferrocenium salts to give the one-electron-oxidized radical compound [({dppm}$_2$C)RhCl$_3$]$^+$. Our in-depth EPR spectroscopic and quantum chemical investigations suggest a predominant organic nature of the radical with significant spin density localized on the ligating CDP−carbon nucleus. This is reflected in the preferential ligand-based reactivity, that is, hydrogen atom transfer is observed during the reaction with PhSH or ^{n}Bu$_3$SnH. Remarkably, [({dppm}$_2$C)RhCl$_3$]$^+$ also allows for the cleavage of non-polar reactants, such as H_2, prompted by the cooperation of the C-radical with an ancillary ligand (Ligand/Ligand Cooperation, right path in the Scheme) The coordinated (non-oxidized) CDP carbon atom has a strong nucleophilic character, allowing for a dual reactivity sequence: When [({dppm}$_2$C)RhCl](**B**) is reacted with a geminal halide, a classical metal-based oxidative addition of a carbon-halogen bond occurs, followed by a ligand-based intramolecular nucleophilic attack. These two consecutive S$_N$2-type oxidative additions result in the formation of a stabilized [CH$_2$] carbene fragment. The application of a hydride source (LiBH$_4$) can integrate the dual-reactivity pattern into a catalytic cycle, as the carbene fragment derived from dual activation of geminal dichlorides can be catalytically converted into olefins or hydro-dehalogenation products (left path in the Scheme). The developed method can also convert CH$_2$ClF to CH$_3$F and CH$_4$.



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Catalytic Activity and Stability of Ambiphilic Group 13 Metallacycles

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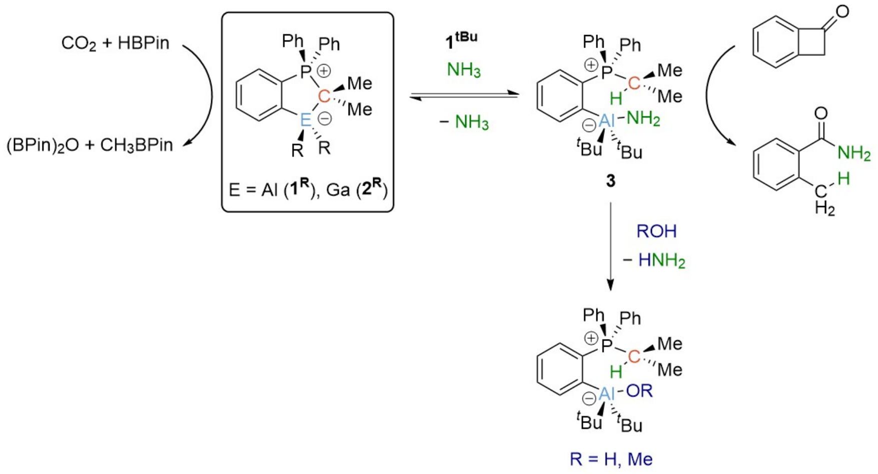
Hidden Frustrated Lewis Pairs consisting of a phosphorus ylide featuring an aluminum- (**1**$^{\mathbf{R}}$) or gallium-fragment (**2**$^{\mathbf{R}}$) in *ortho* position of a phenyl ring scaffold were synthesized via salt metathesis and applied in catalytic transformations.

Compound **1**$^{\mathbf{tBu}}$ offers a thermoneutral and reversible activation of ammonia, which was investigated experimentally accompanied by quantum chemical calculations. Therefore, **1**$^{\mathbf{tBu}}$ can be used as a main group-based catalyst for the transfer of ammonia enabling the use of ammonia as an atom-economical nitrogen source.[1] The other metallacycles showed no reaction towards ammonia or decomposed. The remarkable stability of **1**$^{\mathbf{tBu}}$ was further investigated when the formal methanol activation product was obtained from the workup of a catalytic transfer reaction. We showed that starting from the ammonia activation product **3**, the formal methanol and water activation products can be formed. Furthermore, the metallacycles catalyzed the trimerization of isocyanates.[2] Comparative studies showed that the best performance was found for **1**$^{\mathbf{tBu}}$. Additionally, the title compounds proved to be catalytically active for the reduction of CO_2 using pinacol borane as stochiometric reducing agent.[3] The comparative study showed that the gallium-based system offers a significantly increased catalytic activity for the reduction of CO_2 compared to the aluminum-based system. Inspired by these experimental findings, the development of new ambiphilic metallacycles is part of current research in our laboratories.



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BPI Ligands for Visible-Light Homolysis of E–C Bonds in Main Group Chemistry

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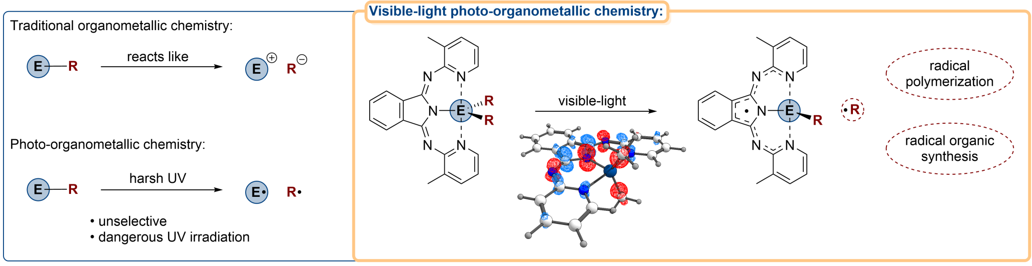
The radical reactivity of organometallic compounds is highly beneficial for applications in homogeneous catalysis, radical organic synthesis or polymer chemistry. Typically, the homolysis of E–C bonds within main group organometallics is thermally not feasible, due to the high energetics of subvalent main group radicals, thus high bond dissociation energies of the E–C bond. Even photochemically, homolytic reactivity is mostly only induced by using very harsh UV irradiation. The redox-active bis(pyridylimino) isoindolide (BPI) ligand system enables the charge-transfer induced cleavage of E–C bonds, initiated by visible light. In the case of aluminum organometallics, this was investigated by means of stationary and transient UV/Vis spectroscopy, spin trapping experiments, kinetic measurements, DFT calculations and further isolation of reduced BPI compounds to obtain fundamental insights into the molecular processes. Utilization of the formed radicals in C–C-coupling reactions was investigated, which revealed a rare example of radical-polar-crossover reactivity in main group chemistry and highlights the potential of organometallic radical sources.



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Ultrafast Bond Cleavage in Diorganyl Bis(pyridyl)imino Isoindolide Aluminum Complexes

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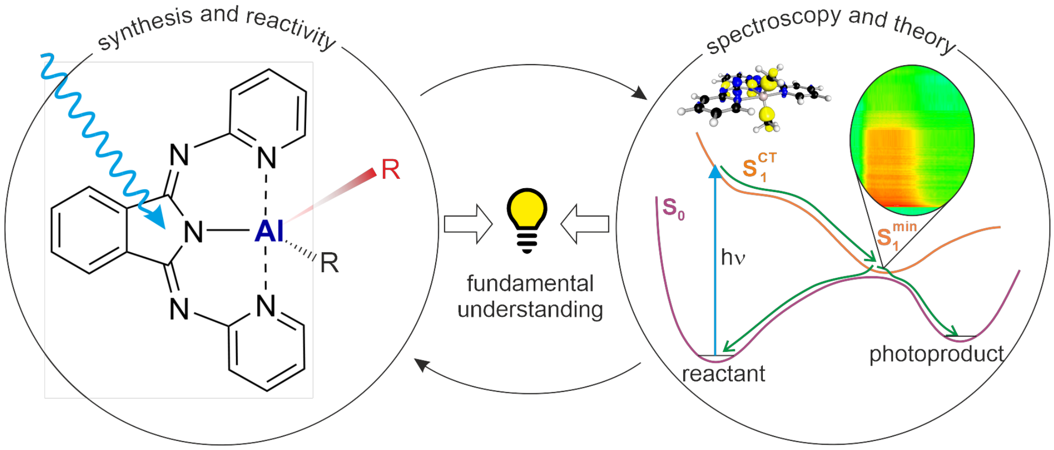
Photochemical processes are of great relevance in nature and synthetic chemistry.[1,2] An understanding of the elementary steps is of crucial importance in order to optimize photoreactions in a targeted manner or to find yet unknown reactivity. Therefore, the present work contributes to a deeper understanding of the photochemistry of main group complexes in general and diorganyl bis(pyridylimino) isoindolide (BPI) aluminum complexes in particular.[3,4] This interdisciplinary work combines the synthesis of BPI complexes with femtosecond transient absorption spectroscopy and quantum chemical calculations in order to correlate the decisive ultrafast processes with stationary properties. It is shown, that an initial charge transfer is the first relevant step after photoexcitation, which determines the fate of the molecule and thus the outcome of the reaction. Triggered by this charge transfer an elongation of one aluminum carbon bond takes place and the molecular wavepacket evolves on the S_1 potential energy surface to a region of conical intersections. Here a channel branching occurs and the molecule either relaxes back to the ground state or undergoes an ultrafast E-C bond cleavage, opening the vivid field of radical reactivity. The nature of the diorganyl substituents has a huge impact of the branching ratio and thus enables a tuning of the complexes. This understanding paves the way for the systematic development of main group photocatalysts or photoinitiators, which are currently investigated in our groups.



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Light-driven hydrodefluorination of aryl fluorides catalyzed by a heterobimetallic Ni–Ga complex

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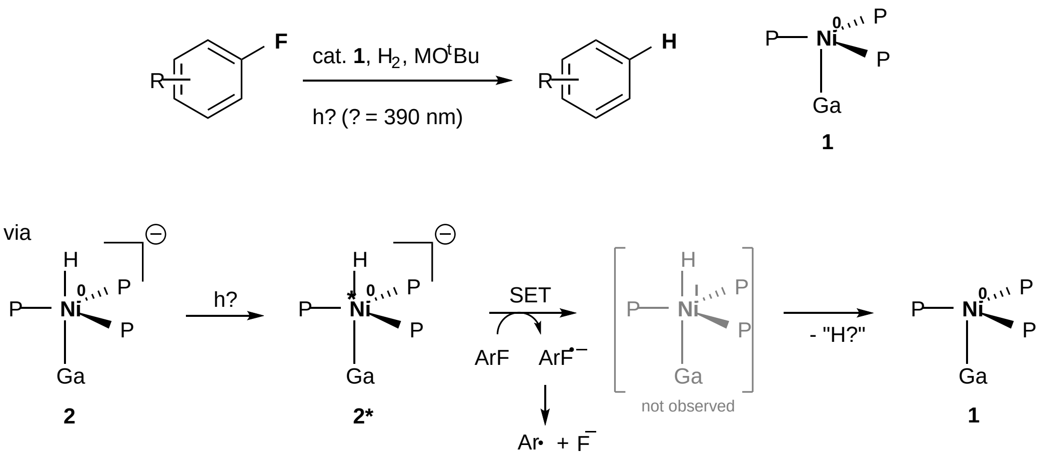
Organofluorines are widely used as agrochemicals and pharmaceuticals. However, these so called ‘forever chemicals’ are toxic to the environment and human health. The main challenge in their remediation is overcoming the strong C–F bond (BDE of up to 130 kcal mol^{-1} for CF_4).[1] Photoredox catalysis presents a potential strategy for the C–F bond activation of organofluorines. Current examples are mostly only capable of breaking weak C–F bonds and are predominantly reliant on metals that are scarce and expensive, such as rhodium and iridium.[2]-[4]

Heterobimetallic complexes offer reactivities that can be quite different compared to their monometallic analogues. Using the heterobimetallic Ni(0)–Ga(III) complex **1**, embedded in a tripodal phenylamine-based ligand framework, challenging fluoroarenes are hydrodefluorinated under irradiation of purple light (λ = 390 nm) and in the presence of H_2, as well as a stoichiometric alkoxide base.[5]

Mechanistic insights of the hydrodefluorination of fluorobenzene with catalyst **1** will be discussed. An anionic Ni(0)-hydride **2** formed by the in-situ deprotonation of an H_2-adduct plays the crucial role in the bond-breaking step. This active species is proposed to perform a photo-induced single-electron transfer (SET) resulting in the generation of an aryl radical and the eventual regeneration of the catalyst **1**.[6]

Overall, this work not only presents a rare first-row transition metal photoredox catalyst, but furthermore gives insights into its unique mechanism for the chemically difficult activation of C–F bonds.



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Reactivity studies and catalytic CO_2 reduction of Nickel(II) bis(triazolylidene)carbazolide complexes

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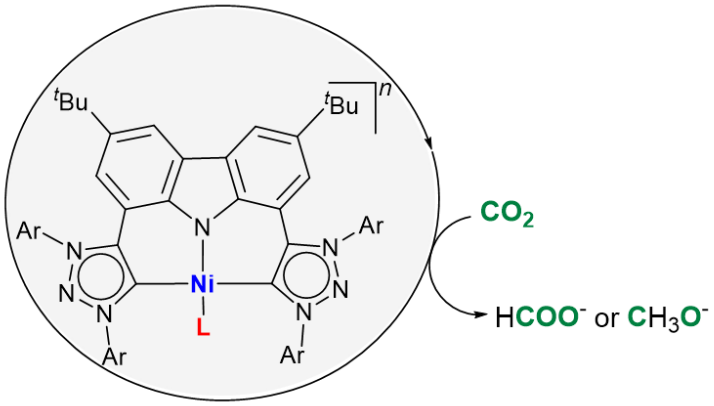
The tridentate ligand motif of a carbazole backbone with flanking donors is an excellent example of a pincer ligand that is ‘more than the sum of its parts’ [1]. Our research group has demonstrated the utility of this scaffold as a CNC-pincer ligand featuring triazolylidenes as the C-donors, both in stabilizing reactive d^8 and d^{10} transition metals [2], and for their use as molecular catalysts [3]. Related CNC-Ni(II) pincer complexes have proven to be efficient catalysts in CO_2 / epoxide coupling reactions [4] and for CO_2 hydrogenation [5].

In this work, a series of nickel(II) bis(triazolylidene) carbazolide complexes have been prepared and their coordination chemistry explored. Promising candidates for reductive CO_2 catalysis have been investigated in both CO_2 hydrogenation and CO_2 hydroboration reactions.



Ar = 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl

L = OH, Cl, N_3, OAc or $NCCH_3$

n = 0 or +1

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Two Electrons in a Lithium Cube: A Novel type of Lithium-organo-silyl Sulfide

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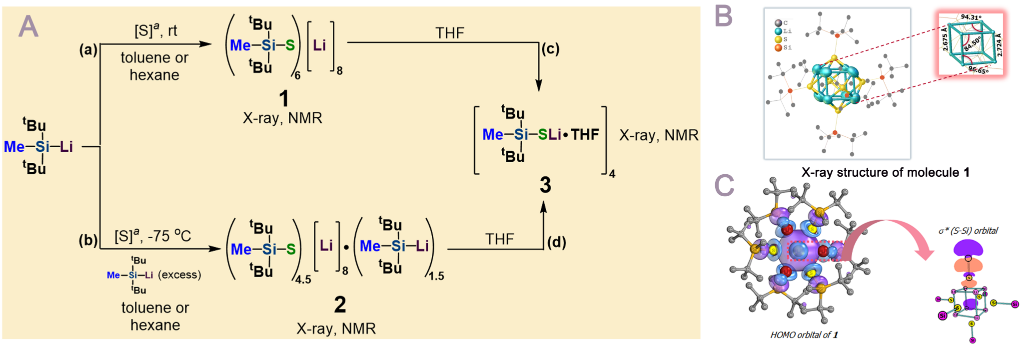
There are known molecules where electrons are stabilized on surfaces or on small molecules.[1,2] Electrons **inside** the molecular framework were hypothesized theoretically,[3] but only in 2022 a molecule with an electron **inside** a cube was experimentally generated, and it is still the only existing example.[4]

Herein, we report a novel type of cubic molecule, $({}^{t}Bu_2MeSiS)_6Li_8$ (**1**), which has two extra Li-atoms and **two electrons in the center of the cubic molecule**. Molecule **1** was prepared by reaction of silyl lithium with several sulfurization reagents (CS_2, S_8, P_2S_5) in hexane/toluene solvent (Scheme 1A, step a). Furthermore, in the excess of $tBu_2MeSiLi$ we synthesized a molecule, $[tBu2MeSiS)_{4.5}(Li_8)•(tBu2MeSiLi)_{1.5}]$ (**2**), where $tBu_2MeSiLi$ is incorporated in the aggregate structure (Scheme 1A, step b). X-ray density map and NBO analysis show that **2** has comparatively higher electron density than molecule **1** at the center of the Li-cube. DFT analysis shows that the HOMO of **1** and **2** have two additional electrons in the center of the Li-cube (Scheme 1C). Molecules **1** and **2** are converted to compound $(tBu_2MeSiS)_4(Li•THF)_4$ (**3**) by addition of THF, which has a regular lithium silyl sulfide structure (Scheme 1A, steps c and d).



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Surface Deposition of Dome-Shaped Metal-Organic Complexes: A New Approach to the Generation of Single-Site Catalysts

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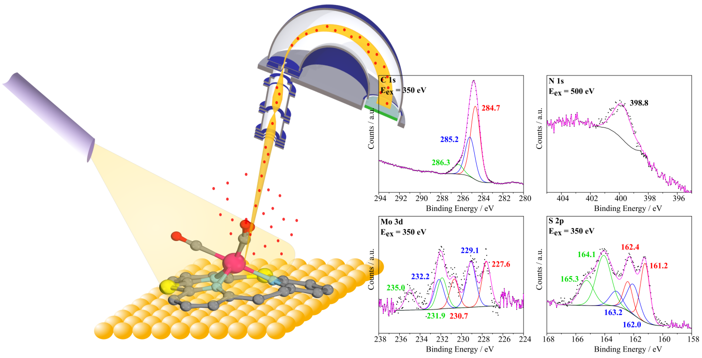
Transition metal complexes are often used in catalytic reactions for the activation of small molecules.[1,2] In order to generate interfaces that combine features of heterogeneous with those of homogeneous catalysis,[3,4] the development of well-defined single-atom active sites at surfaces has been at the focus of research recently.[5-7] Along these lines, depositing dome-shaped, organometallic complexes with a single transition metal atom on a metallic substrate offers a novel approach to fundamentally understand the electronic properties of a transition metal center in contact with an underlying surface and, in particular, study their influence on the binding, exchange or activation of small molecules at the metal center.[8-10]

With these goals in mind we have synthesized a new dithia-[2.1.1]-(2,6)-pyridinophane ligand and its corresponding molybdenum(0) tricarbonyl complex and characterized both in the bulk and in solution, respectively. Monolayers of the complex were deposited on Au(111) and their ability to activate small molecules was assessed by employing infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS). In addition, the reactivity of the complex towards dioxygen was evaluated and compared to analogous complexes supported by aza- and thiacalixpyridine ligands.[11]



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Rollover cyclometalated complexes as novel metallodrugs

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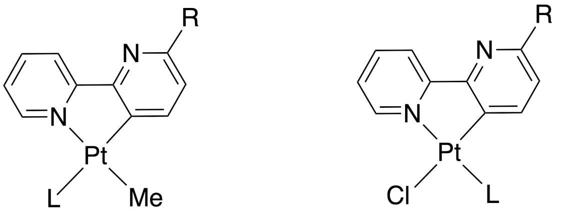
Antimicrobial Resistance (AMR) has become one of the most urgent public health problems worldwide, and Multidrug Resistance (MDR) is another point of concern. In an effort to find new classes of antibiotics, recent studies have revealed that several coordination and organometallic compounds of noble metals show promising biological effects both in vitro and in vivo, deserving attention as a new class of possible antimicrobial agents.[1]

Cyclometalated complexes constitute an important family of organometallic derivatives, featuring an enhanced stability due to chelation effect. Among the various fields of applications, these complexes have found increasing potentialities in biomedicine, in particular as antitumor and antimicrobial metallodrugs.[2] Beyond classical cyclometalated complexes, variations on the theme have produced novel series of subclasses, such as that of the so-called "rollover complexes", derived from heterocyclic bidentate donors after an internal rotation and activation of a remote C-H bond.[3]

Herein we report a series of Pt(II) and Pd(II) rollover cyclometalated complexes with substituted 2,2'-bipyridines, which have been synthesized and characterized by means of 1D and 2D NMR spectroscopy, Cyclic voltammetry, and X-ray diffraction.



Examples of Pt(II) rollover complexes with substituted 2,2'-bipyridines
(R = Me, Ph, Cl, Br, etc, L = neutral ligand)

The complexes have been tested against Gram-positive (*S. aureus, S. pyogenes*), Gram-negative bacteria (*P. aeruginosa*, *E. coli and K. pneumoniae*) and Yeast (*C. albicans),* cultured in a liquid medium and in planktonic status. The study has been extended to bacteria cultivated in vitro as biofilm. The promising preliminary results will be reported.

The work has been carried out under the framework of the project ""Noble metal complexes with heterocyclic nitrogen ligands: application as antimicrobials" Financed by the European Union - NextGenerationEU - mission 4, component 2, investment 1.1. Project code MUR P2022PZ8JE.

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