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Posters
Session A

Pd(II)-catalyzed ethylene/methyl acrylate copolymerization: effect of the substituent on *para* position.

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Pd(II) complexes of general formula [Pd(Me)(MeCN)(N-N][PF_6] (N-N = alpha-diimines) have been extensively studied as homogeneous catalysts for the copolymerization of ethylene with polar vinyl monomers, such as acrylic esters, to produce functionalized polyolefins (**FPO**),[1,2] very interesting macromolecules that could represent an environmental-friendly improvement with respect to simple polyolefins.[3] We found that the presence of a pendant arm substituted with pyrene in *para* position of the alpha-diimine resulted in excellent catalytic performances.[4]

Thus, we have now investigated the role of the functional group in this key position by moving from the simple methyl, to bromide and hydroxy (Figure).

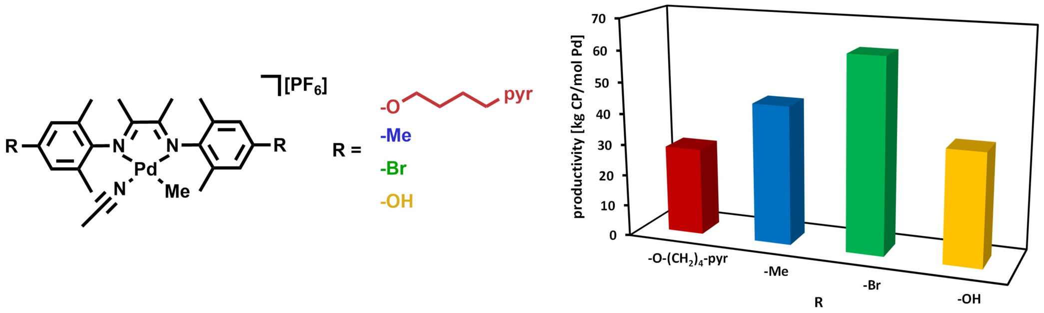

Figure: The studied Pd(II) complexes and their effect on catalyst productivity.

The copolymerization experiments were carried out in both dichloromethane (DCM) and 2,2,2-trifluoroethanol (TFE). A remarkable effect of the substituent on catalyst performances was found. As an example: the catalyst with the bromo-substituted ligand showed the highest productivity (61.89 kg of copolymer/mol of Pd), whereas that one with the hydroxy-substituted alpha-diimine led to the macromolecules with the highest methyl acrylate incorporation (3.9 mol %).

Acknowledgement:

MUR (PhD PON Program) is acknowledged for the fellowship (K.A.H.).

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Sequential One-Pot *N*-Alkylation and Aminocarbonylation of Primary Amines Catalyzed by Heterobimetallic Ir/Pd Complexes

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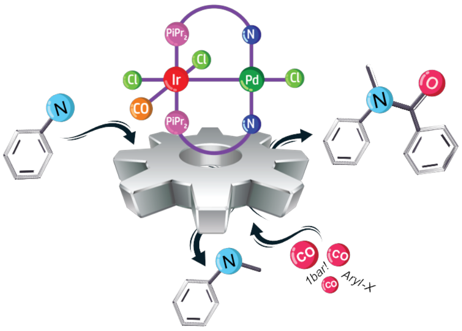
Bimetallic complexes can be superior in terms of their properties and activity compared to their monometallic analogues. Although processes for a better activity of heterobimetallic complexes as compared to their monometallic analogues are well established, one-pot activity for sequential reaction pathways of such complexes is limited. Sequential one-pot catalysis serves as incorporating multiple catalytic steps in a predetermined sequence. The catalyst facilitates specific transformation, and the intermediates generated in one step serve as substrates for the subsequent step without the need for isolation or purification between reactions.[1]

The development of a catalytic one-pot process including N-alkylation sequentially coupled with aminocarbonylation is presented on utilizing bimetallic systems of Iridium and Palladium. The catalyst shows superior activity compared to a mixture of monometallic counterparts. The sequential one-pot tertiary amide synthesis involves an N-alkylation of anilines, utilizing bimetallic precursors such as [IrPdCl3(CO)(PiPr2ImdMe)2] (ImdMe = 1-methyl-1H-imidazole) and KOtBu as a base. Methanol served both as a reagent and solvent in this process. The study successfully explored 13 different secondary amines, achieving yields ranging from 90% to 100% via a borrowing hydrogen mechanism.[2] Subsequently, the produced secondary amines reacted with CO (1 bar) and aryl iodide without further catalyst loading, leading to amide bond formation. This approach conveniently offers a streamlined strategy for tertiary amide synthesis.



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Ruthenium(II) Polypyridyl Complexes Supported on Vinylic Addition Polynorbornenes as Recyclable Photocatalysts

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Visible light-driven catalysis is becoming increasingly important due to its environmental benefits, capacity to enable selective reactions, and viability as a sustainable alternative to conventional thermally-driven catalytic approaches. This work consists of the synthesis of metal polypyridyl-based photocatalysts, specifically $[Ru(phen)_3]^{2+}$ complexes anchored to a solid support to develop sustainable systems that can be reused. Vinylic addition polynorbornenes (VA-PNB) serve as excellent supports for this type of catalysts because of their entirely aliphatic backbone, enhancing their thermal and chemical robustness and transparency. They are also insoluble in commonly used solvents. This facilitates the convenient recovery of the catalyst, usually through simple filtration processes.[1] Moreover, the reusable nature of these catalysts simplifies the reaction processing while also reducing heavy metal contamination in organic products. In this work, a Ru (II) complex of the type $[Ru(phen)_2(phenOProp)](PF_6)_2$ (phen = 1,10-phenanthroline; phenOProp= 4-(propagyloxy)1,10-phenanthroline) was anchored on a functionalized vinylic addition polynorbornene (VA-PNB) via a CuCCA click reaction. (Figure 1). To evaluate the supported catalyst's reactivity, three different photocatalytic reactions were studied, each following different photocatalytic mechanisms, based on electron and energy transfer pathways. [2-3] The recyclability of the catalyst was examined, showing that it maintains its effectiveness even after repeated recycling processes.

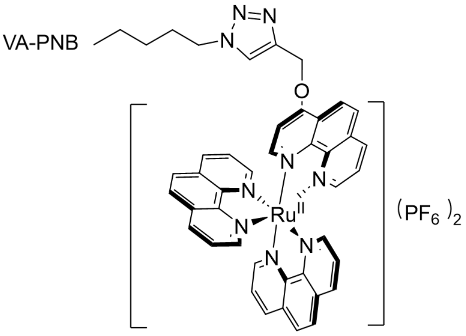

Figure 1: Ruthenium(II) Polypyridyl Complexes Supported on Vinylic Addition Polynorbornenes (VA-PNB).

Acknowledgements: The financial support of the Spanish MICINN (PID2022-142100NB-I00) and the EU/MICINN/JCyL (C17.I01.P01.S21, H2MetAmo) and the Junta de Castilla y León (VA016G24) are gratefully acknowledged.

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“Abnormal” Carbene Coinage Metal Amide in the Domain of Photoemitters

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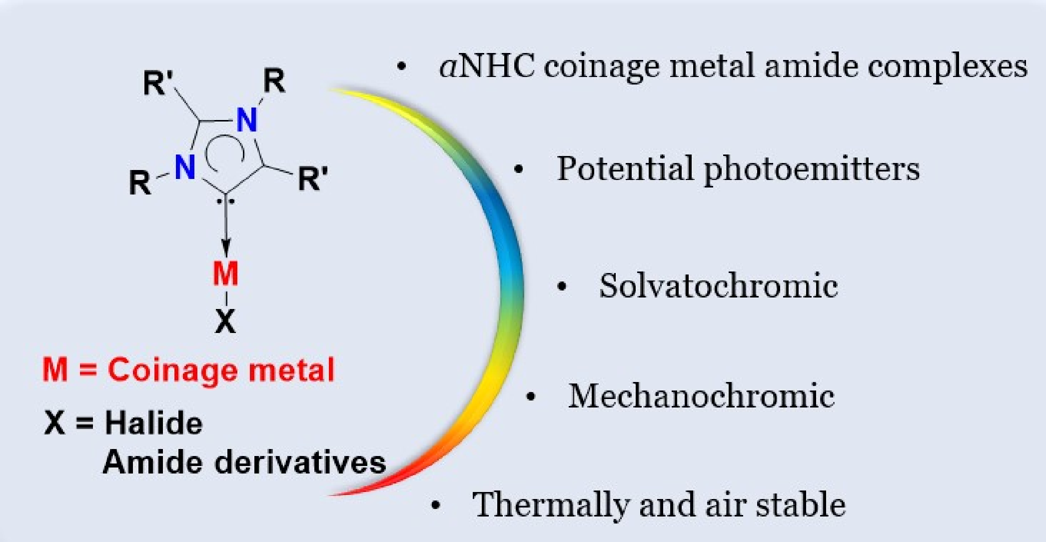
N-Heterocyclic carbenes (NHCs) isolation by Arduengo *et al.* is considered a turning point in carbene chemistry. This backbone has been explored extensively in the fields of catalysis, nano-chemistry, and OLED fabrication.[1] In NHCs, C2 carbon is utilized for the coordination to the metal centre. However, later it was realized that the C4/5-centers of the imidazolium ring are also susceptible to metalation *via* C-H bond activation.[2] After years of attempts by other research groups, Bertrand and coworkers were the ones who isolated the first metal-free aNHC (abnormal N-Heterocylcic carbene).[2a] Positioned at C5, the carbene centre renders aNHCs less thermodynamically stable yet stronger donors than normal NHCs. This work highlights the preparation of aNHC (abnormal N-heterocyclic carbene), posing the C5-centre as a donor site. Further to explore the coordination properties and photophysical aspects we prepared aNHC-coinage metal (Cu, Ag, and Au)-amide framework. Single-crystal X-ray diffraction studies, NMR spectroscopy, and mass spectroscopy have validated the solid-state structures of these complexes. In photophysical properties, variations in crystal packing significantly impact bulk-phase behaviour. In particular, complexes crystallised in the non-centrosymmetric $P2_12_12_1$ space group with substantial void volume, exhibit remarkable mechanochromic luminescence. In contrast, centrosymmetric packing and reduced void volume, remain unresponsive and less responsive to mechanical stimuli. Our findings provide key insights for designing the next generation of stable abnormal carbene-metal-amide photoemitters.



- *a*NHC coinage metal amide complexes
- Potential photoemitters
- Solvatochromic
- Mechanochromic
- Thermally and air stable

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Photooxygenation of p-xylene catalyzed by Fe(III) pyclen complexes: an insight into the magnetic and spectroscopical properties of the catalysts.

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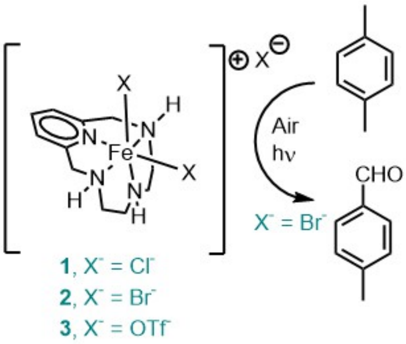
Abstract: Iron complexes have long been studied in oxidative transformations as biomimetic models of enzyme active sites. In this context, while many examples of iron-mediated oxidation of organic compounds under thermal activation have been reported, the photochemical activation of iron complexes is a less explored field[1]. We report herein the synthesis and detailed characterization of a series of [Fe(III)(X_2)pyclen]X complexes (X = Cl, Br, OTf; pyclen = 3,6,9-triaza-1(2,6)-pyridinacyclodecaphane, complexes **1**–**3**, **Figure 1**), relevant to the selective photocatalytic oxidation. Structural analysis, Mössbauer spectroscopy, magnetization studies, and UV-vis absorption spectroscopy combined with DFT calculations were employed to investigate their properties. Notably, the complexes display extended absorption into the visible range, attributed to ligand-to-metal charge transfer transitions involving the pyclen and halide/triflate ligands. Evidence suggests that light absorption can promote homolytic cleavage of the Fe–X bond, particularly for X = Cl and Br. Inspired by these findings, the photochemical behavior of the complexes under visible light irradiation (up to 415 nm) was explored for the aerobic oxidation of *p*-xylene. The nature of the halide ligand was found to influence the reactivity: the bromide complex (**2**) promoted the selective formation of *p*-tolualdehyde via a hydrogen atom transfer (HAT) mechanism, while the chloride (**1**) and triflate (**3**) analogs showed negligible activity. These results not only demonstrate the catalytic potential of photochemically activated iron complexes but also provide a foundation for future studies aimed at developing sustainable, light-driven oxidation processes.



1, X^- = Cl^-
2, X^- = Br^-
3, X^- = OTf^-

- ☐ Additive free
- ☐ White Light
- ☐ Under air
- ☐ Room temperature
- ☐ High selectivity

We thank the MUR-Italy (PRIN 2022, PROMETEO project- 2022KPK8WM, financed by the European Union - Next Generation EU, Mission 4 Component C2 CUP G53D23003390006) for financial support.

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Pd-Catalyzed Chemoselective C(sp^2)–H Arylation of Enolizable Aryl Alkyl Ketones

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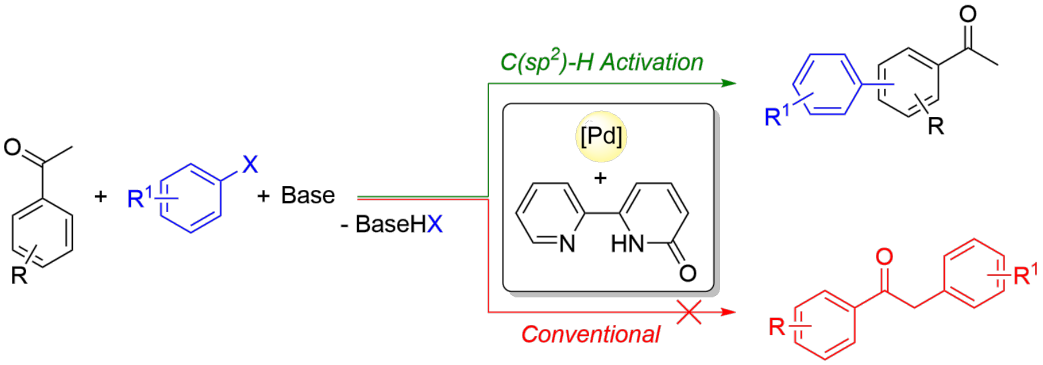
Palladium-catalyzed cross-coupling reactions of hydrocarbons via C–H activation offer a more sustainable alternative to conventional coupling methodologies. The direct use of hydrocarbons eliminates the need for prefunctionalized reagents employed in conventional coupling therefore improving the sustainability and step-efficiency of chemical processes.[1] Key to C–H functionalization is the use of cooperating ligands that facilitate the C–H bond cleavage.[2] Our group has previously developed catalytic systems based on a C-H activation step using the ligand [2,2’-bipyridin]-6(1*H*)-one (bipy-6-OH), which has demonstrated high efficiency in the direct arylation of arenes. The easier C–H activation by this ligand also allows to perform chemoselective transformations of unprotected anilines.[2c]

In this work we describe the Pd-catalyzed chemoselective direct C-H arylation of enolizable aryl alkyl ketones. The reaction leads to the Csp^2-Csp^2 coupling product (aryl arylation) while suppressing the formation of de Csp^2-Csp^3 product (alkyl arylation), which is typically observed in traditional cross-coupling processes. The scope of this reaction has been explored using various aryl alkyl ketone derivatives with different electron-withdrawing and electron-donating groups. The selection of the reaction conditions and the use of the cooperating bipy-6-OH is crucial for the success of the process. The mechanism of the reaction has been probed by experimental and computational methods.



Acknowledgments

We thank the Spanish MICINN (PID2022-142100NB-I00), the EU/MICINN/JCyL (C17.I01.P01.S21, H2MetAmo) and the Junta de Castilla y León (VA016G24) for financial support.

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Redox-Driven Photoselective Self-Organization

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Self-organization via non-covalent intermolecular interactions, driven by self-recognition, is crucial for achieving complex architectures with advanced functionalities, characteristic of living systems [1-3]. However, the inherent weakness of non-covalent interactions and the delicate balance between thermodynamic and kinetic factors have constrained progress in this field [4,5]. Indeed, a paradigm shift has been proposed, advocating for a noncovalent synthetic chemistry approach akin to organic chemistry [6]. This would enable stepwise construction of complex structures, enhancing reproducibility and control. Herein we present the investigation of this concept by coupling the self-organization of Pt(II) complexes with a redox reaction. Upon oxidation to Pt(IV), the Pt(II) complex forms a non-emissive "protected" monomer that can be reduced back to Pt(II) to initiate self-organization. This reduction produces luminescent gels with distinct kinetic and thermodynamic pathways that are inaccessible directly from Pt(II). Additionally, we discover that UV irradiation of Pt(IV) promotes photoreduction, leading to the formation of metastable supramolecular fibers. These fibers, characterized by Pt···Pt metallophilic interactions, exhibit enhanced photophysical properties, including visible light absorption up to 550 nm. This capability enables unprecedented photoselective growth, as the low-energy irradiation absorbed by the fibers allows them to convert the surrounding Pt(IV) to Pt(II), favoring growth at the expense of the formation of new nuclei, observable by real-time fluorescence microscopy.

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Rational Design of Guanidine-Based Ruthenium Metallodrugs as Versatile Scaffolds for Antitumor Therapy

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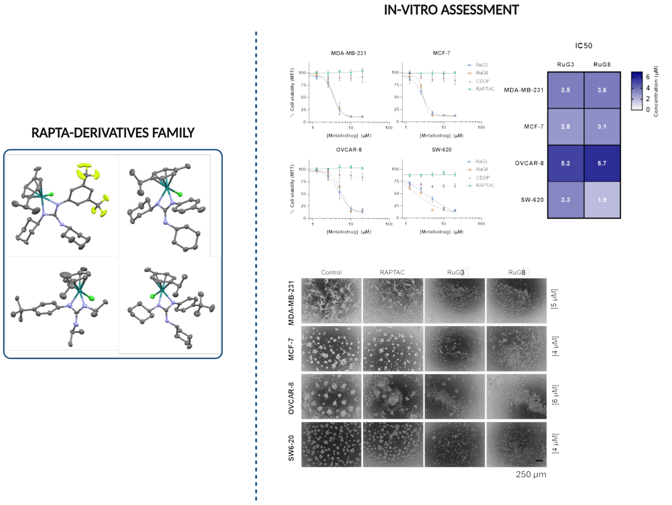
The straightforward catalytic synthesis of guanidine ligands has been assessed as a strategy for rapidly developing ruthenium metallodrugs as antitumoral therapeutic agents.[1] A series of structurally guanidine ligands obtained by guanylation reaction were used as scaffolds for generating RAPTA-C derivatives.[2] Therefore, a novel family of guanidine-ruthenium derivatives was synthesized, fully characterized, and evaluated as potential alternatives to platinum-based chemotherapy for cancer treatment. The antitumor activity of these compounds was assessed in vitro across various breast cancer cell lines, with RAPTA-C and cisplatin as metallodrug controls. In this study, we identified a ruthenium metallodrug supported by ancillary guanidine ligands as the most promising candidate within the series. Notably, its significant cytotoxicity in triple-negative breast cancer (TNBC) cell lines suggests a mechanism of action that is independent of receptor status. In vitro assays, including cell cycle analysis and apoptosis studies, confirmed this mechanism. As a proof of concept, fluorescence lifetime imaging microscopy (FLIM) was used to visualize the intracellular distribution of a luminescent derivative of the series in MCF7 human breast cancer cells. The results revealed that such compounds are homogeneously distributed in the cytoplasm, while the guanidine ligand enhances stability. These findings provide valuable insights into the potential of guanidines as ancillary ligands for the generation of promising antitumoral ruthenium metallodrug candidates.



	RuG3	RuG8
MDA-MB-231	3.5	3.6
MCF-7	2.8	3.1
OVCAR-8	5.2	5.7
SW-620	3.3	1.9

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Matteson homologation reaction catalyzed by Chiral Lewis Acids

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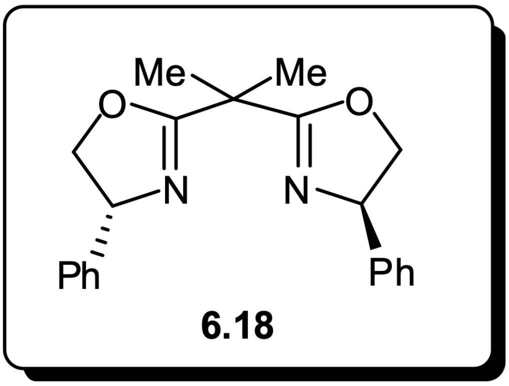
Based on improving the enantiomeric excess percentage by adding a chiral Lewis acid catalyst, so far, only Prabhakar K. Jadhav and Hon-Wah Man1 have carried out a Matteson-type homologation with an achiral boronic ester, namely 2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.17, Scheme 1), and an achiral reagent, but in presence of a chiral ligand bis-oxazoline derivative and a metal triflate (including Yb(OTf)$_3$, Zn(OTf)$_2$, Cu(OTf)$_2$, and Lu(OTf)$_3$ as Lewis acid.[1] They obtained (S)-pinanediol 1-chloropentylboronate (6.20) in 88% diastereomeric excess as their best result by use of the chiral ligand [(-)-2,2'-isopropylidene-bis[(4S)-4-phenyl-2-oxazoline] (Figure 1) (5 equivalents) with Yb(OTf)$_3$ (0.3 equivalents).

1 Figure. 1 Structure of ligand 1 Jadhav1 had found that lithium chloride produced in situ was competing for the chiral ligand, and therefore led to some uncatalysed reaction that explained the need for the use of excess ligand in such reactions (Figure 1).



6.18

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Unravelling the mechanism of the alkoxycarbonylation of butadiene: what is the role of the base?

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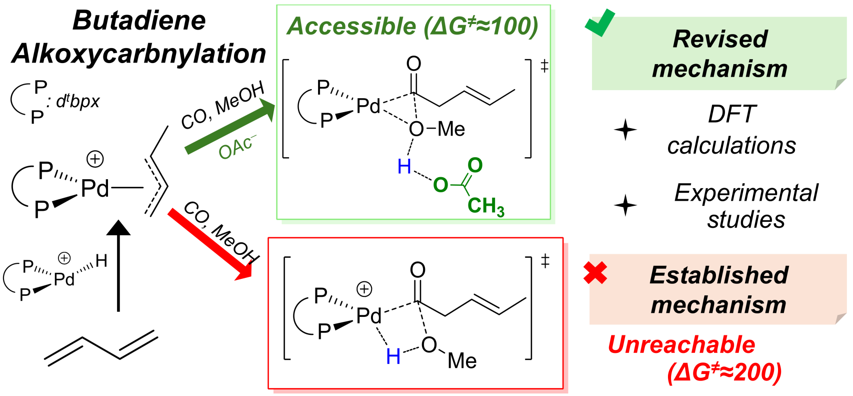
The mono alkoxycarbonylation of butadiene with CO and an alcohol, to produce C_5 platform carbonyl compounds, is highly valued in synthetic chemistry for its environmentally friendly and atom-efficient conversion. [1] The resulting methyl 3-pentenoates (3MP) are crucial intermediates for producing large-scale monomers such as adipic acid and ε-caprolactam. [2]

Significant progress has been made in designing efficient palladium catalytic systems by many research groups over the past two decades. [3] However, despite numerous reported catalytic systems for this reaction, none have been adopted for industrial processes due to still low activity, selectivity, or inefficient recyclability. [3] Recently, Beller's team reported a catalytic system based on $Pd(TFA)_2$ and the dtbpx diphosphine ligand, enabling the double alkoxycarbonylation of butadiene with remarkable yield and selectivity towards the linear diester. [4]

While the mechanism for this reaction is well-documented with simpler olefins like ethene [3], a noticeable gap exists in our understanding when it comes to butadiene. In this work, we aim to deepen the understanding of the butadiene mono-alkoxycarbonylation reaction pathway. Density Functional Theory (DFT) calculations reveal that the transition state of the first methanolysis step faces a significant energy barrier (ca. 200 kJ·mol^{-1}). This high barrier arises due to the formation of a highly stable Pd(η^3-allyl) intermediate, as confirmed by both DFT calculations and Nuclear Magnetic Resonance (NMR), raising questions about the validity of this well-established mechanism.

Upon coupling DFT calculations and experimental analysis, we proposed a revised mechanism founded on a "base assisted" pathway where the mono-alkoxycarbonylation of dienes exhibits a significantly decreased free energy of activation (ca. 100 kJ·mol^{-1}). By considering various acid/base pairs, we further refined these findings and demonstrated that an optimum balance between the acid and the base must be found, regarding strengths and concentrations, to maximize the catalytic activity.



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Structure and Bonding of Solvent-Free Neopentyl Sodium and its Applications for the Metalation of non-Activated Substrates

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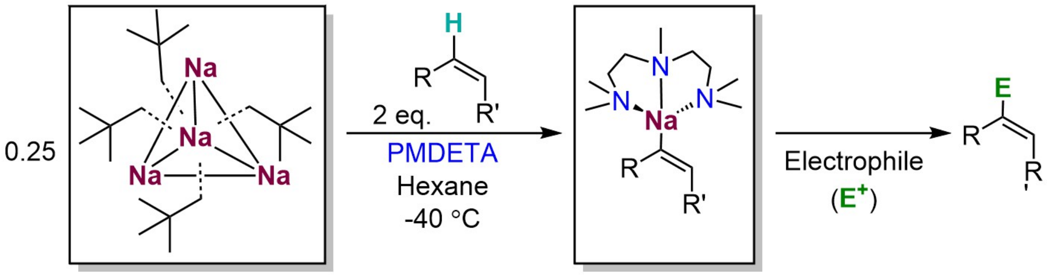
From as far back as the 1940s, alkyl sodium reagents have been examined for their powerful basicity, with the ability to deprotonate unactivated aromatic and vinylic C-H bonds. Pioneering work by the likes of Morton and Finnegan demonstrated how pentylsodium could be synthesised in situ from pentyl chloride and sodium metal to react with alkyl substituted benzene derivatives and various olefins to afford organosodium intermediates which could subsequently be trapped with simple electrophilic quenches.[1] These studies however often required very long reaction times due to the very poor solubility of the sodiated species and the nature of the organosodium intermediates found in these complex mixtures remained unknown. With an increase in understanding of organolithium reagents as powerful bases these organosodiums were left behind as mere curiosities.

Or group has recently been highlighting the potential of alkyl sodium reagents. We have shown how the alkyl sodium reagent $NaCH_2SiMe_3$ can have its solubility and thus reactivity tuned with the addition of Lewis donors such as PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine), forming a hydrocarbon soluble alkyl sodium reagent used in benzylic metalations.[2][3] In this communication, we report on the synthesis and characterisation in the solid and solution states of a highly basic alkyl sodium complex, neopentyl sodium, combined with in-depth bonding analysis. The enhanced solubility of this reagent adds to its ability to metalate stoichiometric quantities of nonactivated substrates such as benzene or simple cyclic olefins with the addition of the Lewis donor PMDETA, an electrophilic quench was subsequently carried out to demonstrate the high efficiency of the sodiations carried out under these conditions. The sodiated intermediates could be isolated and characterised using a combination of X-ray crystallography and ^1H NMR DOSY (Diffusion Ordered SpectroscopY), revealing rare examples of aryl- and vinyl sodium complexes, further expanding our understanding on the constitution of these reaction intermediates, advancing our understanding of how these systems operate in solution.



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

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Exploring New Frontiers in Intracellular Redox Chemistry Mediated by Half-Sandwich Cobalt(III) Complexes

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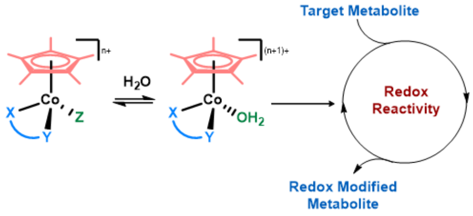
Intracellular redox chemistry mediated by half-sandwich complexes of Ru(II), Os(II), Rh(III), and Ir(III) has emerged as a powerful strategy to monitor and modulate biological processes at the molecular level, with impactful applications in medicine and diagnostics.[1] The results obtained so far, provide a strong foundation for expanding the scope of organometallic-mediated intracellular redox chemistry to other metal complexes and substrates. Cobalt is a biologically essential first-row transition metal found in various cofactors and redox enzymes.[3] Compared to rhodium and iridium analogues, half-sandwich organometallic Co(III) complexes display distinct properties: different thermodynamic and kinetic stabilities, greater electronegativity, a harder Lewis acid character, and a richer redox chemistry, with accessible oxidation states ranging from 0 to +4 via one- or two-electron processes.□ These properties make cobalt-based systems not only a more economical and biocompatible alternative to noble metal complexes but in some cases a unique platform for unlocking redox pathways inaccessible to their heavier counterparts.□



Herein, we report the development of a library of half-sandwich Co(III) complexes with the general formula [CoCp*(X-Y)Z]. These complexes were synthesized and fully characterized, incorporating diverse bidentate ligands (X-Y = N-N'; N-O; or N-C) and monodentate anions (Z = Cl□ or I□). The variation in chelating and anionic ligands is designed to modulate the stereo-electronic properties and fine-tune the reactivity–stability balance in aqueous biological environments. The hydrolysis and stability of the complexes were systematically investigated, along with the pH speciation to support their application in biological systems. Cytotoxicity assays were conducted on various human cell lines to evaluate their potential bioactivity. Additionally, preliminary studies on their redox mediated reactivity in aqueous media were performed, laying the groundwork for translating Co-based redox catalysis into cellular systems.

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Complexes and reactions of ferrocene phosphinostibine ligand

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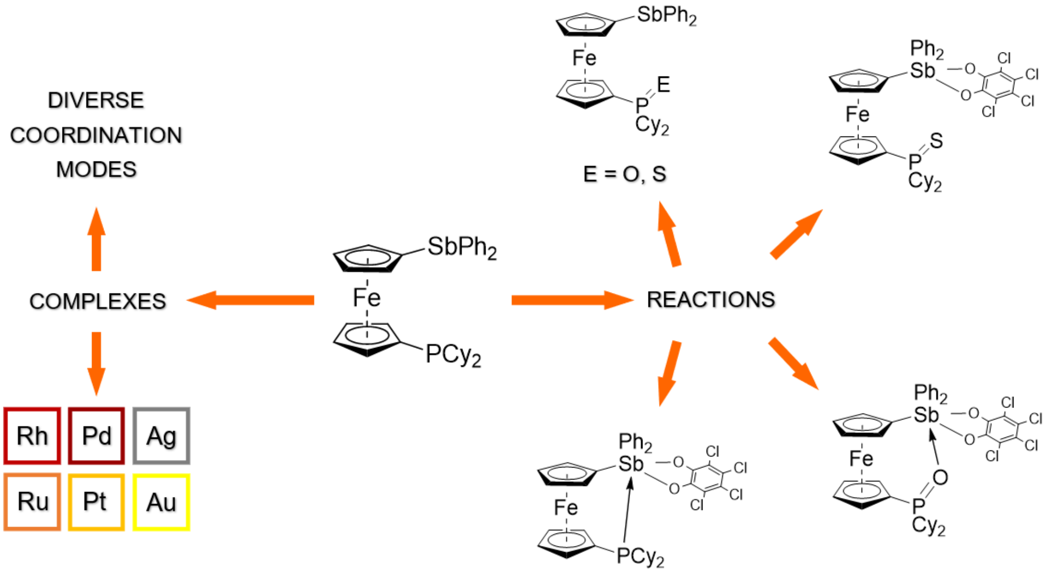
While numerous ferrocene compounds with phosphine donor moieties have been reported, the chemistry of ferrocene ligands containing heavier group 15 elements remains nearly unexplored. This contribution focuses on the ligating properties and reactivity of hybrid phosphinostibine ligand, $Cy_2PfcSbPh_2$ (**L**, fc = ferrocene-1,1′-diyl, Cy = cyclohexyl). The ligand was prepared by metalation of the corresponding 1-bromo-1′-phosphinoferrocene with *n*-BuLi and subsequent reaction with chloro(diphenyl)stibine [1]. The ability of **L** to act as a ligand was probed via its reactions with various transition metal precursors (Ru(II), Rh(III), Pd(II), Pt(II), Au(I)), to which **L** binds in diverse modes. Further research was focused on the reactivity of **L**, specifically on the preparation of chalcogenides $Cy_2P(E)fcSbPh_2$ (E = O, S) and the corresponding stiborane derivatives $Cy_2P(E)fcSbPh_2(O_2C_6Cl_4)$ (E = void, O, S), in which the stiborane center bears tetrachloropyrocatechol substituent, which makes it Lewis acidic and potentially prone to behave as an acceptor of electron pair from the $Cy_2P(E)$ moiety. The presence of this interaction was confirmed by single-crystal X-ray diffraction analysis and $^{31}P\{^1H\}$ NMR spectroscopy only if E = void or O. The nature of this interaction was clarified using computational methods. All substances were characterised by using standard analytical techniques. When possible, the crystal structure was determined.



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Planar Hydride Nanoclusters of Manganese and Iron: Synthesis, Catalysis and Insights into Growth Mechanisms

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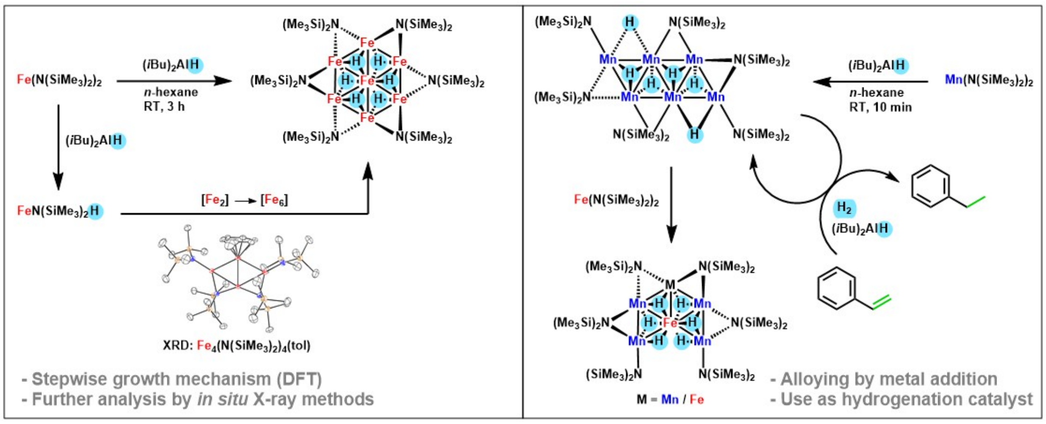
Nanoclusters (NCs) consist of a finite number of metal atoms, connected by direct metal-metal bonds, with sizes falling between those of monometallic coordination complexes and nanoparticles. While a number of three-dimensional NCs of coinage metals like copper with stabilizing ligands such as carbon monoxide has been reported, the controlled assembly of discrete planar NCs as snapshots at the nanoscale of cluster growth is more challenging. Recently, our research group has presented Fe_7 and Mn_6 hydride NCs with such unprecedented topologies, being synthesized by the reaction of the respective metal bis(trimethylsilyl)amide and $(i\mathrm{Bu})_2AlH$.



DFT calculations indicate a stepwise, thermodynamically favored growth of the Fe_7 NC, which is supported by the isolation of an Fe_4 intermediate species when using toluene as the solvent. Moreover, we are currently studying the NC formation by *in situ* pair distribution function (PDF) at Deutsches Elektronen-Synchrotron (DESY). This X-ray method could allow to detect other intermediates by their unique Fe–Fe distances. The NCs are characterized by their paramagnetism, low oxidation states of the metal atoms and a strong electronic metal to metal communication. The presence of μ^2 / μ^3-coordinated hydrido ligands fostered our interest in investigating the suitability as catalysts. Indeed, the Fe_4 and Mn_6 NCs exhibit catalytic activity in the hydrogenation of olefins and alkynes. Building up on these results, we currently focus on a broader exploration of this substance class. Exemplarily, we found that heterobimetallic Fe,Mn nanoclusters are formed by the substitution of the Mn_6 NCs with $Fe(N(SiMe_3)_2)_2$. Furthermore, the potential use of other 3d metals (Cr, Co, Ni), bulkier amide ligands or a secondary ligand type (phosphines, thiols) offers plenty of opportunities to synthesize NCs with applications in catalysis or materials.

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Transuranic Organometallics and their Small Molecule Activation Chemistry

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The synthesis of transuranic organometallic complexes (those containing an element beyond uranium) has seen a dramatic increase in recent years, even though they still represent much less than one percent of the crystal structures in the CCDC. However, their reactivity with small molecules has yet to be reported, in sharp contrast to observations of uranium complexes' redox reactivity with molecule such as N2, CO and CO2.

We will report new organometallic molecules ranging from Th to Bk, and show some of their complementary small molecule reactions.

Stabilization of Reactive Rare Earth Alkyl Complexes through Mechanistic Studies

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Rare earth tris(alkyl) complexes such as $M(CH_2SiMe_3)_3(sol)_n$ are widely used as precursors for many compounds and as homogeneous catalysts for alkene polymerization and alkane functionalization. However, the thermal instability of those most conveniently made from the commercially available lithium salt of the neosilyl anion, $LiCH_2SiMe_3$, Li(r), restricts their utility. We present a new range of synthetically useful, more kinetically stable rare earth neosilyl solvates, derived from a full kinetic study of the various possible decomposition mechanisms of 7 known and 12 new solvated rare earth neosilyl complexes $M(CH_2SiMe_3)_3(sol)_n$ M = Sc(III), Y(III), Lu(III), Sm(III), and sol = THF; TMEDA; DMPE, diglyme ($CH_3(OCH_2CH_2)_2O$, G_2), triglyme ($CH_3(OCH_2CH_2)_3O$, G_3). Surprisingly, simply using higher-denticity donors to sterically disfavor neosilyl *gamma*-H elimination is not effective. While $Sc(r)_3(CH_3(OCH_2CH_2)_2O)$ has a half-life, $t_{1/2}$, of 258.1 h, six times longer than for $Sc(r)_3(C_4H_8O)_2$ ($t_{1/2} = 43$ h), $Lu(r)_3(CH_3(OCH_2CH_2)_2O)$ and $Y(r)_3(CH_3(OCH_2CH_2)_2O)$ do not show the expected, analogous increased $t_{1/2}$. This is because new decomposition pathways appear for poorly fitting donors. Finally, kinetic studies demonstrate the impact of small, and increasing amounts of LiCl on the kinetics, and changing the mechanism of the reactivity of the alkyls $Y(r)_3(THF)_2$ and $Lu(r)_3(THF)_2$; molecules used in hydrocarbon chemistry and catalysis for fifty years. A new route to pure $Y(r)_3(THF)_2$, which avoids the traditional use of Li(r), is presented.

Stabilization of reactive rare earth alkyl complexes through mechanistic studies. E. Tanuhadi, A. S. Bair, M. Johnson, P. Fontaine, J. Klosin, S. Pal, P. L. Arnold, Chem. Sci. 2025, 16, 280-287. doi:10.1039/D4SC05983B.

A Mechanistic Investigation of $Co_2(CO)_8$ Catalysed Photoaminocarbonylation

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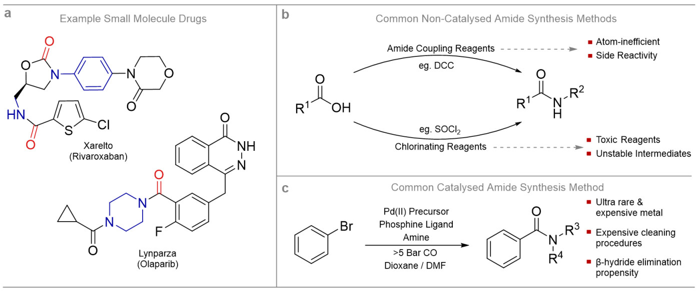
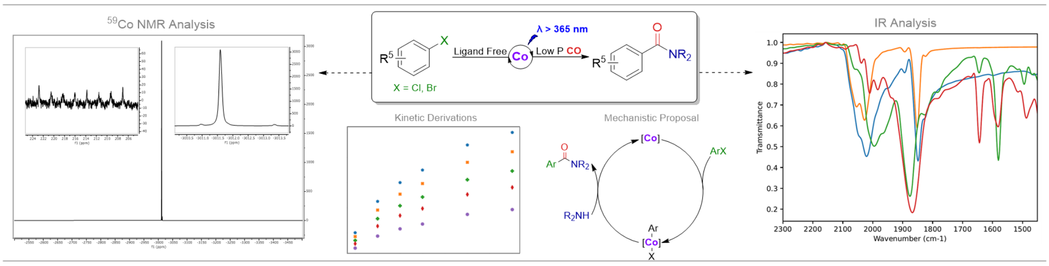
The catalytic production of amides is a highly sought after transformation in modern chemical synthesis. In 2023, amide functional groups were present in 71 of the top 100 small molecule drugs, with similar high occurrence seen in agrochemical and flavours & fragrances (F&F) industries.[1] Although the synthesis of amides can be achieved from a range of precursors, catalytic routes are attractive as they offer the potential for high atom efficiencies and broad reaction scope. Challenges remain on translating such catalytic routes to large scale production. For example, Pd-catalysed aminocarbonylation of aryl and alkyl halides offers a desirable solution, but due to metal scarcity, negligible cost benefits and side-reactions, the technology has seen limited uptake industrially.[2]



Photocatalysis shows promise in addressing these limitations. Following seminal discoveries for photocatalysed aminocarbonylation using Pd, further research in the area has focused on the development of efficient catalyst based on first-row transition metals including Co, Cu and Ni.[3] Despite contemporary interest in these systems, little is known about their mechanisms of operation. To address this knowledge gap, we have successfully conducted a kinetic investigation into the $[Co_2(CO)_8]$ catalysed photoaminocarbonylation of aryl halides.[4] Stoichiometric reactions have been used to elucidate potential on-cycle catalytic intermediates, with less-conventional analytical techniques such as EPR and ^{59}Co NMR being used to support findings. A substrate scope has been used to exemplify the benefits of understanding our system, with marked improvements to functional group tolerance, catalyst loading, and reaction time all being afforded versus prior state-of-the-art reaction conditions.



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The conformational properties and effects of ferrocene peptides on viability, cell cycle and apoptosis in HeLa cells

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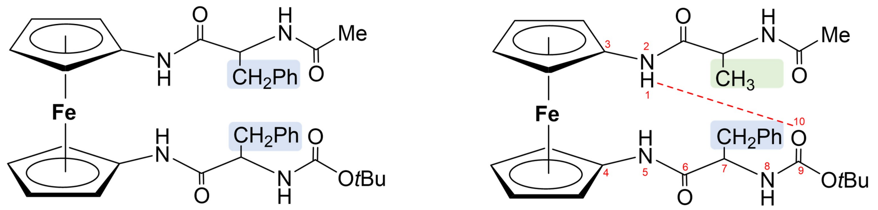
The symmetrically disubstituted peptides Ac–L/D-AA^1–NH–Fn–NH–L/D-AA^2–Boc (Fn = ferrocenyl, AA^1 = AA^2 = Val, Leu and Phe, respectively) [1], derived from ferrocene-1,1'-diamine as a turn-inducing scaffold [2], were tested for their conformational properties and antiproliferative activity against several cancer cell lines. It was found that Phe-containing peptides **i** and **ii** do not adopt a turn structure and show no inhibitory effect in Hela cells (IC_{50} > 350 µM) [1]. Considering the influence of structure on conformation and biological activity, we replaced one Phe moiety of peptides **i** and **ii** with Ala to improve the conformational stability and antiproliferative activity of the new peptides **1** and **2** (Figure 1).



i, L-Phe, L-Phe (IC$_{50}$ > 350 µM)
ii, D-Phe, D-Phe (IC$_{50}$ > 350 µM)

1, L-Ala, L-Phe (IC$_{50}$ = 22.70 µM)
2, D-Ala, D-Phe (IC$_{50}$ = 17.03 µM)

Figure 1. The conformational patterning and antiproliferative activity of ferrocene peptides.

The replacement of the benzyl side chain of one Phe unit with methyl group of Ala allowed (i) the adoption of the stable conformation of ß-turn and (ii) contributed to a significant improvement in the antiproliferative activity against the HeLa cell line with IC_{50} values even lower than those of cisplatin (46.14 µM) (Figure 1). The viable and apoptotic cells and the effects of **1** and **2** on the cell cycle were analysed by flow cytometry. The results showed that there was no statistically significant difference between treated and untreated cells. In the case of peptide **2**, a concentration of 1 µM significantly reduced the proportion of cells in the G0/G1 phase compared to untreated cells.

ACKNOWLEDGEMENTS: This work was supported by the Croatian Science Foundation under the project IP-2020-02-9162.

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^{n}Butylcalcium: synthesis and reactivity

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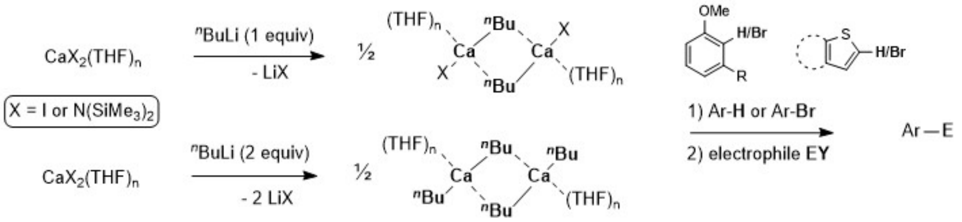
Mono- and dialkylcalcium species are highly sensitive and are therefore difficult to handle and characterise. For the handful of known alkylcalcium compounds, the presence of specific functional groups or bulky stabilising is generally required.[1,2] To access organo- and diorganocalcium species, three synthetic strategies can be envisaged. The first involves salt metathesis, *e.g.* to generate sterically sheltered alkylcalcium species such as $Ca[CH(SiMe_3)_2]_2(THF)_2$. Oxidative addition onto activated calcium(0) is known, but it is difficult to implement. Last, organocalcium complexes can be obtained *via* deprotonation of relatively acidic substrates by a sufficiently strong calcium base.[3]

This presentation will focus on the preparation of alkylcalcium species through combinations of ^{n}BuLi and a calcium sources such as CaI_2 (salt metathesis) or $Ca[N(SiMe_3)_2]_2$ (transmetallation). Although the combination of $Ca[N(SiMe_3)_2]_2$ and ^{n}BuLi has been exploited in butadiene polymerisation,[4] its reactivity in organic chemistry, and in particular in deprotometallation[5] and halogen-metal exchange reactions of aromatic compounds, remains essentially unexplored.

Our work[6] focuses on the formation of ^{n}butylcalcium species, generated from ^{n}BuLi and a calcium source at very low temperature. These compounds were characterised by high-resolution solution NMR spectroscopy (**Scheme 1**); in addition, the formation of other products, *e.g.* $[Ca\{N(SiMe_3)(SiMe_2\text{-}\mu\text{-}CH_2)\}\{N(SiMe_3)_2\}.(THF)_3]_2$ was also evidenced by NMR and X-ray diffraction. The [Ca]-alkyl species were then used in functionalisation reactions, *e.g.* nucleophilic addition, and deprotometallation- or bromine/metal exchange-electrophilic trapping sequence. The outcome of these investigations will be presented herein.



Scheme 1. Formation of ^{n}butylcalcium species and *in situ* functionalisation reactions.

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Formation of a Novel High-Spin, Low-Valent Alkene Stabilised Fe(0) Silyl Complex

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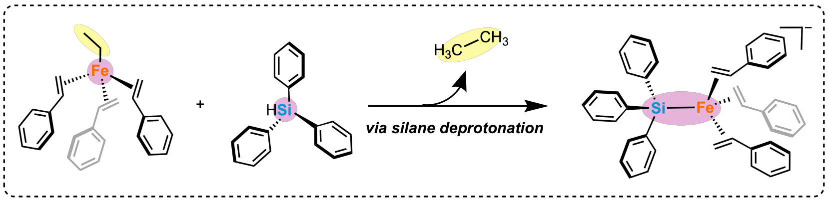
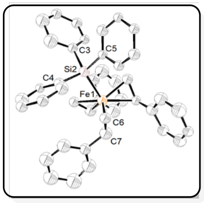
Earth-abundant transition metal complexes containing a silyl bond have been a source of significant research interest in recent years, especially in TM-catalyzed reactions resulting in the formation of new Si-C bonds. Moreover, there remains few examples of Fe-Si bonds within literature, oftentimes using CO or *Cp moieties as stabilizers but reducing any chance of reactivity through strong pi bonds. Modern alternatives have included the use of chelating PSiP or PPPSi ligands, and while they provide limited reactivity such as hydrosilylation and hydroboration, there remains a barrier for increased reactivity in the ligand scaffold.[1,2] One possibility to overcome the current ligand sets is to employ weak π-bonding ligands, such as alkenes. The Neidig group has recently published a study with a synthetic design to form low-valent alkene stabilized iron(0) alkyls, acting as the reactive catalytic species in C-H activation.[3,4] Herein, we exhibit a pathway to substitute out alkyl groups for heteroatom species such as silanes through a protonation/deprotonation reaction to produce the first high-spin, low valent Fe(0)(styrene)$_3$SiPh$_3$.





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Cooperative Light-Driven Hydrodefluorination by a Ce(III)–Rh(−I) Heterobimetallic Complex

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[1]Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Str. 1, Bonn 53121

In recent years, the use of Lewis acidic metals as Z-type ligands to modulate the electronic properties of transition metal (TM) complexes has gained significant interest.[1] The Lu group showed the utility of Group 13 metals in stabilizing and enhancing the reactivity of electron-rich transition metals through the hydrodefluorination (HDF) of fluoroarenes with Rh–Group 13 bimetallic complexes.[2] However, examples for incorporation of lanthanides and especially cerium into bimetallic complexes remain scarce. Cerium presents an interesting target for such systems due to its accessible Ce(III)/(IV) redox couple and photo-induced *4f→5d* excitation.[3] In this work, we explore the possibility that Ce is the redox-active center that shuttles electrons to the active site on Rh.

An anionic Ce(III)–Rh(−I) and a neutral Ce(IV)–Rh(−I) bimetallic complex were synthesized and characterized. These complexes exhibit short Ce–Rh bonds (2.4822(4) and 2.2396(4) Å, respectively). The physical and spectroscopic data are consistent with the oxidation state assignments.The Ce(III)–Rh(−I) species is capable of the HDF of fluoroarenes under irradiation with purple light (λ = 390 nm), while being oxidized into the Ce(IV)–Rh(−I) species. Furthermore, the active species can be regenerated after HDF via a stoichiometric one-electron reduction of the Ce(IV)–Rh(−I) species. This represents a complete catalytic cycle for the light-driven HDF of fluoroarenes and provides a platform to investigate the unique role of Ce in heterobimetallic photoredox chemistry.

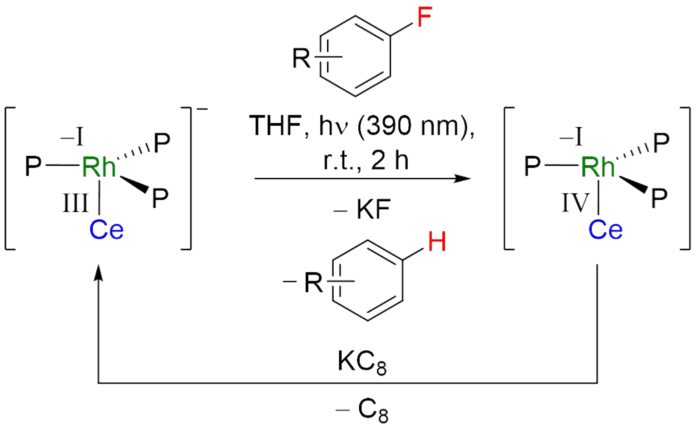

Figure 1: Scheme of the HDF of Fluoroarenes using a Ce(III)–Rh(−I) species under irradiation with purple light (390 nm), and subsequent regeneration of the active species. The bimetallic species have been truncated to the first coordination sphere of Rh.

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Cooperative Alkene Isomerization Catalysed by a Molecular Nickel-Aluminate Complex

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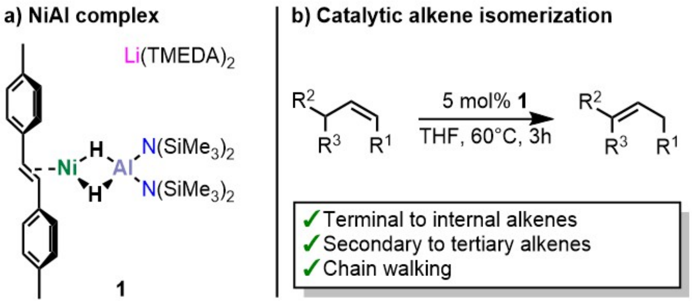
Cooperative catalysis, in which two metals collaborate to facilitate a chemical reaction, has emerged as a promising strategy for replacing noble metal catalysts by those based on earth abundant metals. However, only relatively few examples of heterobimetallic cooperativity in catalysis are known and understood, which currently hampers the rational use of this strategy in catalysis. In our work we synthesized a nickel-aluminate complex (**1**) featuring two bridging hydride ligands, which does not require the use of a specialized ligand for supporting the bimetallic assembly (Figure 1a). NiAl hydride complexes are very rare with only a handful of reported examples.[1] Interestingly, a NiAl hydride complex supported by multidentate PN_2O_2-ligand was reported to catalyse the hydroboration of N-heterocycles through a cooperative mode of action.[2] We found that our complex **1** is an active catalyst for the isomerization of alkenes (Figure 1b), a reaction typically caried out with noble metal hydrides.[3] Comparing the reactivity of **1** with the separate nickel stilbene and LiAl hydride species used in its synthesis shows that **1** far outperforms these in the catalytic isomerization reaction, indicating the cooperative nature of this reaction. By studying the stoichiometric and catalytic reactivity of **1** with alkenes and other unsaturated molecules we provide fundamental insights into this cooperative reaction to shed light on how nickel and aluminium can cooperate in catalytic reactions.



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N-Heterocyclic Carbene-Phosphinidene Manganese Complexes: A new Class of low-valent Manganese Compounds

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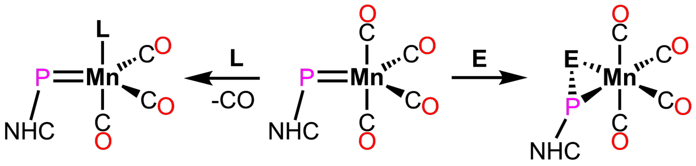
Low-valent phosphorus species, such as N-heterocyclic carbene-phosphinidene adducts (NHC)PR,[1] have garnered attention as strongly and inversely polarized phosphaalkenes,[2] a property that can be attributed to the ability of the imidazole ring to effectively stabilize a positive charge.[3] Expanding on this concept, transition metal complexes of the type [(NHC)PML$_n$] feature phosphorus(I) ligands, which can develop strong and covalent metal-phosphorus π-interactions.[4–7]

Herein, we present the synthesis of the NHC-phosphinidene manganese complex [(NHC)PMn(CO)$_4$] (NHC = IDipp = 1,3-(diisopropylphenyl)imidazolin-2-ylidene) from the reaction of the NHC-phosphinidene adduct (NHC)PSiMe$_3$ and [Mn(CO)$_5$Br].[8] [(NHC)PMn(CO)$_4$] undergoes CO substitution reactions yielding the complexes [(NHC)PMn(L)(CO)$_3$] (L = PMe$_3$, PPh$_3$, 1,3,4,5-tetramethylimidazolin-2-ylidene (IMe), 2,6-dimethylphenylisocyanide (XyNC)) via an associative mechanism akin to the nitrosyl complex [Mn(NO)(CO)$_4$], with the (NHC)P ligand switching between three-electron and one-electron donor modes. Phosphinidene transfer and chalcogenation reactions along the Mn–P double bond afford metalladiphosphiranes and metallaphosphachalcogeniranes with unusual three-membered MnPE (E = PH, PPh, Se, Te) rings.



L = PMe$_3$, PPh$_3$, IMe, XyNC; **E** = PH, PPh, Se, Te

Scheme 1: Reactivity of the NHC-phosphinidene Mn complex [(NHC)PMn(CO)$_4$].

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Catalytic Activity of Mono-and Bimetallic Rhodium(I) and Iridium(I) Complexes Bearing Carbon-Ether-Carbon (COC) Ligand for the Intramolecular Cyclization of 4-Pentynoic Acid

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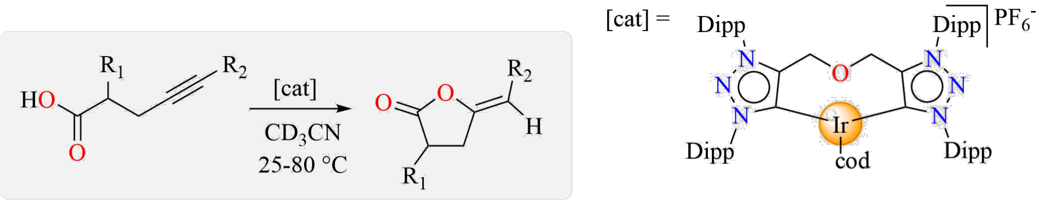
Lactones are well known intermediates in a plethora of reactions as synthetic intermediates[1] and therefore atom-economic preparations of lactones are of high relevance. Intra-molecular lactonization of alkynes has been satisfactorily performed by heavy transition metals.[2a,b] Still the availability of more efficient and ready available catalysts for this transformation is of great interest. Recently we reported the synthesis of a series of mono- and bimetallic Ir(I) and Rh(I) complexes coordinated to chelating or bridging bis-triazolylidene ligands.[3] Their catalytic performance was first evaluated towards the hydrothiolation of terminal alkynes resulting in very efficient and selective formation of the a-vinyl sulfide product.[4] Seeking to expand their applicability in a different alkyne transformation we have focused now on the intramolecular cyclization of acetylenic carboxylic acids to alkylidene lactones.[5] Among them, the chelated mononuclear cationic complex [Ir(cod)(COC)]PF_6 (cod = 1,5-cyclooctadiene; COC = biscarbene ether) displayed the highest reaction rate for 4-pentynoic acid to form g-methyl-ene-g-butyrolactone (5-methylenedihydrofuran-2(3*H*)-one) (Scheme 1). In this contribution, selected studies including catalyst screening, reaction scope evaluation using substituted 4-pentynoic acid derivatives and mechanistic studies via DFT calculations will be presented.



R_1 = H, EtOOC, MeOOC, HOOC.
R_2 = H, Bz, propargyl

Dipp = 2,6-diisopropylphenyl;
cod = 1,5-cyclooctadiene

Scheme 1 Intramolecular lactonization of alkynoic acid derivatives catalyzed by an iridium chelated complex featuring mesoionic carbenes.

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Metallomimetic C–F Activation Catalysis by Simple Phosphines

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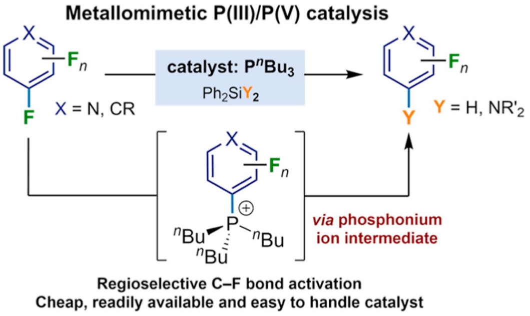
Fluorine-containing organic molecules are found in a wide range of applications.[1] As such, there is a synthetic requirement to develop efficient and selective methods for the formation of these types of compounds. Furthermore, in recent years there has been considerable interest in the activation and functionalisation of small molecules and strong bonds by main-group-element compounds, mimicking transformations typically promoted by transition metals.[2]

This work demonstrates that simple, inexpensive and readily available trialkylphosphines are able to hydrodefluorinate and aminodefluorinate polyfluoroaromatics without the need to enforce unusual geometries at phosphorus or use external oxidising/reducing agents.[3] Experimental and computational mechanistic studies indicate that catalytic hydrodefluorination reactions are supported by metallomimetic behaviour: phosphines undergo oxidative addition of the fluoroaromatic substrate *via* a Meisenheimer-like transition state, followed by a pseudotransmetallation step with a silane and a final reductive elimination of the product to reform the phosphine catalyst.



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Boron-substituted Xanthene dyes for bioimaging applications

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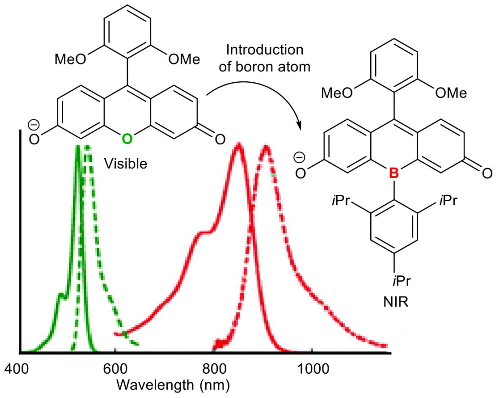
Xanthene dyes such as fluoresceins and rhodamines have been intensively studied since their first synthesis in 1871 and 1887[1]. An interesting way of extending their absorption and emission wavelengths is to substitute the central oxygen by a group 14, 15 or 16 element such as Si, P, C or Se[2]. Boron-substituted xanthenes have been synthetised but are yet to be furtherly investigated. Tricoordinated boron-substituted fluoresceins displayed the largest wavelengths shifts amongst heteroatoms, allowing emission in the near-infrared region, despite low fluorescence quantum yields[3]. The vacant p orbital of the tricoordinated boron atom allows p-π^* interactions, stabilising the LUMO, which results in an increase of the wavelength.

Improving the synthesis, increasing the quantum yields and extending the process to rhodamines and rhodols opens a path towards several applications such as bioimaging, TADF, pH sensors… As these molecules are Lewis acids, their properties in tetracoordinated form are heavily modified, depending on the Lewis base used, making them versatile fluorophores for sensing applications.

In this poster, we will present the advances in the synthesis of new boron-substituted xanthene dyes.



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Tailored Iron Pyclen Complexes as Photocatalyst for the Selective Oxidation of Benzyl Alcohols

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Macrocyclic ligands, particularly pyclen derivatives, are of significant interest in coordination chemistry due to their ability to form stable complexes with transition metals **[1,2]**. This study presents the synthesis and comprehensive characterization of pyclen-based ligand, with the general formula **PcL**, complexed with **iron** $^{II/III}$ ions alongside various counterions, including bromide (**Br**), chloride (**Cl**), and triflate (**OTf**). The **PcL** ligand was characterized via **^{1}H NMR** spectroscopy, while detailed structural and electronic properties of the complexes were elucidated through single-crystal **X-ray** diffraction, mass spectrometry, and elemental analysis. Crystals suitable for **X-ray** analysis were obtained for **$Fe^{III}PcLCl_3$**, which crystallizes in the ***monoclinic*** system with a C_m space group. Magnetic moment calculations in the solid state, confirmed by **ZFC** and **FC** measurements, Mössbauer spectroscopy and in solution **([D6]DMSO)** using the **Evans NMR** method, revealed that the iron centers are in a high-spin state. The catalytic activity was explored in the photochemical oxidation of benzyl alcohol utilizing **O_2** as the oxidant. Reaction parameters, such as time, catalyst concentration, solvent and catalytic loading, were systematically optimized. Among the systems studied, **$Fe^{III}PcLBr_3$**, exhibited exceptional activity and selectivity, achieving an **86%** yield of benzaldehyde within **24 hours** in ambient pressure of oxygen. These findings underscore the pivotal role of **O_2** as a sustainable and eco-friendly oxidant, while further demonstrating the versatility of pyclen-based iron complexes competent catalysts green processes.

Keywords: Pyclen, Iron, X-ray diffraction, Mössbauer spectroscopy, Photochemical oxidation, Benzyl alcohol

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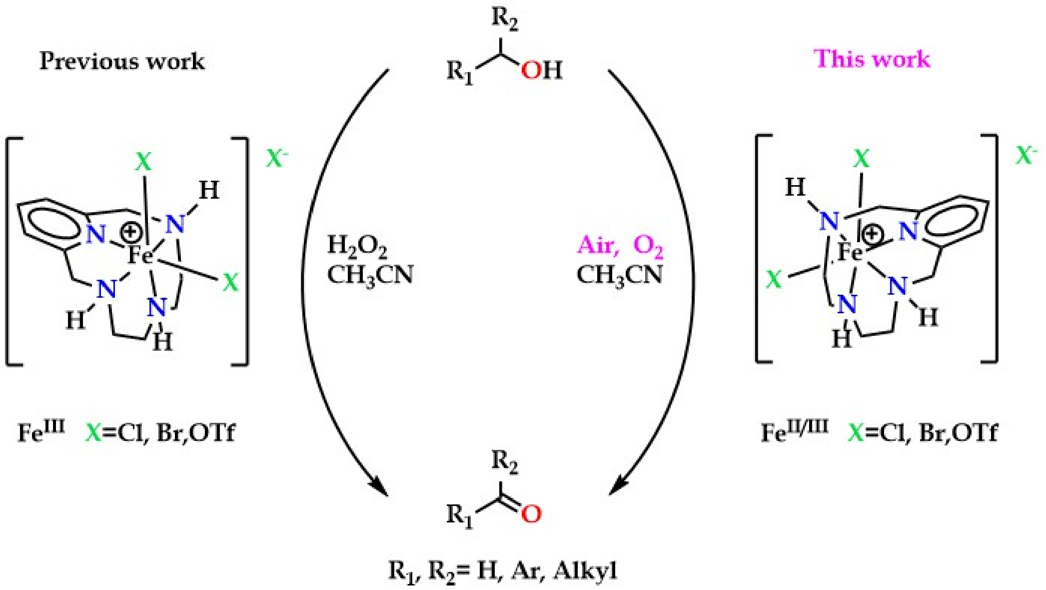

PROTAC Delivery biomass polymer-based nanosystem for the treatment of breast cancer

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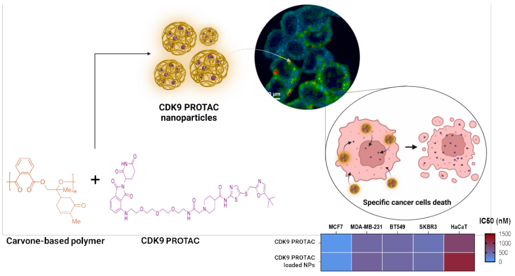
Targeted therapy based on nanotechnology is a strategy to increase efficacy and reduce toxicity of current or potential cancer treatments. Among many materials used in nanomedicine with promising properties, new polymeric materials from inexpensive, biodegradable, and renewable feedstocks need to be explored. In this sense, a carvone-derived polyester was obtained via ring-opening copolymerization of cyclic anhydrides and epoxides (ROCOP) to generate PROTAC delivery systems. Herein, we describe the organocatalytic synthesis of bio-derived polyesters via ROCOP of cyclic anhydrides and epoxides [1], and their use as nanocarrier for controlled drug delivery. As a proof of concept and to enhance the antitumoral activity of the THAL-SNS-032 PROTAC for breast cancer treatment by reducing the on-target off-tumor toxicity profile of the degrader, THAL-SNS-032 loaded carvone-derived polymeric nanoparticles were obtained by nanoprecipitation and double emulsion methods. The nanodevices were fully characterized by reporting hydrodynamic radius, polydispersity, biosafety, encapsulation efficiency, loading efficiency, enzymatic degradation, stability over time and drug release profile of the formulation. Nanoparticles obtained by nanoprecipitation showed best properties as nanomedicines. The toxicity of the loaded NPs in non-transformed epithelial cells was also evaluated in vitro. THAL-SNS-032-loaded NPs showed toxicity in non-tumoral cells but with IC50 value lower than free THAL-SNS-032, supporting the strategy based on nanotechnology as capable of reducing the on-target off-tumor toxicity profile of the degrader (Figure 1). In addition, the detailed cytotoxicity in vitro tumour efficacy studies show that the loaded NPs showed a similar IC50 to the free degrader in all cell models used (Figure 1). In vitro studies including cycle analysis and apoptosis showed the same mechanism of action as the free degrader. Finally, uptake studies showed improvement in cellular internalization to support the cytotoxic enhancement



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Lifting The Lid on Iron-Catalysed Reductive Alkyl-Alkyl Cross-Couplings

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Transition metal catalysed alkyl-alkyl bond formation, *via* cross-coupling, plays an important role in the organic synthesis toolkit. Despite considerable progress in recent years, iron's utility in this area has remained stunted due to a reliance on organometallic substrates, such as Grignard reagents, which bring with them functional group incompatibilities.[1] The emerging field of iron-catalysed reductive cross-couplings aims to circumvent this issue *via* the use of "mild" reducing agents to generate reactive iron intermediates.[2,3] Examples of iron-catalysed reductive cross-couplings remain limited with no mechanistic insights into iron speciation contributing to their slow development. Molecular level insights into such reactions will permit design principles to be established for efficient alkyl-alkyl bond formation, in turn, advancing method development.

Towards this goal, we are carrying out the first detailed mechanistic investigation into an iron-catalysed reductive cross-coupling between alkyl halides and olefins reported in 2023 by G. C. Fu and co-workers (Figure).[2] Using Mössbauer spectroscopy and single-crystal X-ray crystallography, we have been able to identify iron speciation during catalysis, allowing for a working model of the catalytic cycle to be established.

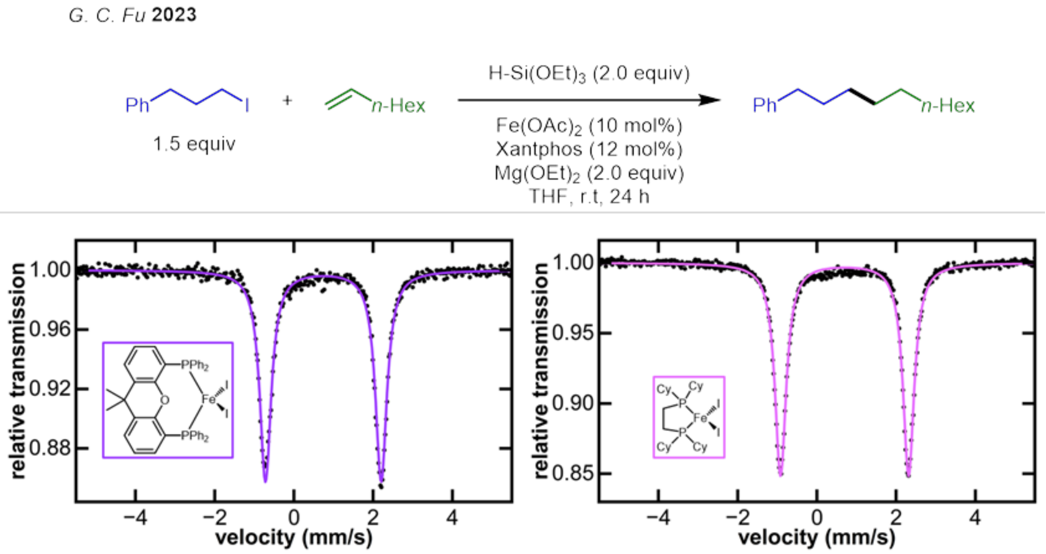

Figure 1. Iron-catalysed reductive cross-coupling between olefins and alkyl halides and 80 K ^{57}Fe Mössbauer spectroscopy as a tool for investigating iron speciation.[2]

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Synthesis of Triazolylidene-Metal Complexes *via* an Unprecedented Free NHC Oxidative Addition Mechanism

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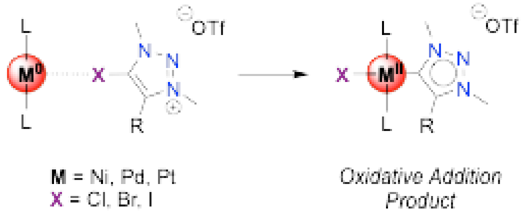
N-heterocyclic carbene (NHC)-supported metal complexes have been extensively studied in the last decades and now represent the state-of-the-art catalysts for several key synthetic applications.[1–3] Among those, 1,2,3-triazol-5-ylidene complexes demonstrated superior performances in some catalytic reactions with respect to the Arduengo-type carbene complexes, thus attracting growing interest in the field.[4,5] Therefore, accessibility to these carbene metal complexes is pivotal. Here, we will present the synthesis of metal-triazolylidene complexes via oxidative addition of 5-halotriazolium salts to Pt(0), Pd(0) and Ni(0) precursors. The immediate and exclusive formation of products in trans configuration, along with the detection of unexpected side products, contradicts the conventional concerted oxidative addition pathway. Supported by trapping experiments of the intermediates and DFT investigation, we will discuss a new mechanism of oxidative addition and its scope to a wider range of polarized C–X bonds.



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A Revised Understanding of the Speciation of Gold(III) Dithiocarbamate Complexes and Their Use as Molecular Precursors to Thin Films of Gold

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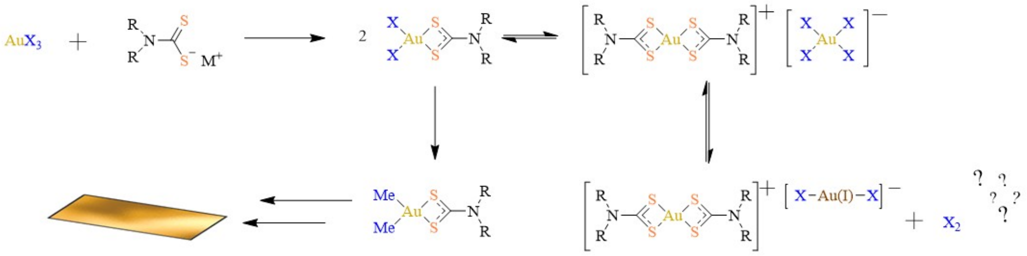
Gold(III) dihalo dithiocarbamate (DTC) complexes have been investigated in recent years for applications in anti-cancer drugs,[1],[2] homogeneous catalysis[3] and as precursors for Atomic Layer Deposition (ALD) reagents to form thin gold films.[4] Such complexes have been lauded for their apparent ease of synthesis from suitable "AuX_3" metal precursors and dithiocarbamate salts. However, a closer inspection of the literature has revealed a greater complexity with regards to their synthesis and behaviour in the solution phase. Our more extensive studies into these gold(III) dithiocarbamates have revealed an equilibrium relationship between the anticipated $AuX_2(R_2DTC)$ (X = Cl, Br, R = Me, Et, ^{i}Pr, ^{i}Bu, pyrrolidinyl, piperidinyl, *p*-tolyl) neutral and the bis-cationic $[Au(R_2DTC)_2]^+$ forms, when employing a 1:1 ratio of "AuX_3" and the dithiocarbamate salt.[5] Furthermore, there tends to be a preference for the $[Au(R_2DTC)_2]^+$ to form as the majority species, and our XRD studies of these bis-cationic gold(III) complexes have exhibited a range of different counter-anionic species, including $[AuX_4]^-$, $[AuX_2]^-$ and X^-. Many of the typical characterisation techniques used to analyse these complexes can sufficiently disguise the presence of the undesired bis-cationic gold(III) impurity, hence resulting in unreliable conclusions for the efficacy of the neutral form in different applications - most importantly in anti-cancer therapeutics given that shifting of the equilibrium position *in vivo* could drastically affect both the efficacy of the drug and its toxicity.[6]



Despite the persistent equilibration of these gold(III) complex forms, appropriate synthetic conditions can significantly shift the equilibrium position and increase the yield of the desired neutral species, which can be subsequently isolated in high yield utilising fractional crystallisation. Methylation of the halide ligands using a suitable Grignard reagent has provided substantially higher yields (80-99%) for the conversion of the purified $AuX_2(R_2DTC)$ compounds compared with a mixture of the two complex forms (50 – 60%). Thermogravimetric analysis (TGA) of our $AuMe_2(R_2DTC)$ compounds have spotlighted $AuMe_2(Me_2DTC)$ as an excellent candidate for ALD due to its volatility and high thermal stability.[7] For whichever application, a better understanding of this intriguing equilibrium behaviour can only benefit further exploration into the chemistry of gold(III) dithiocarbamate complexes.

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Nickel bidentate N-N-PYA complexes for cross electrophile couplings

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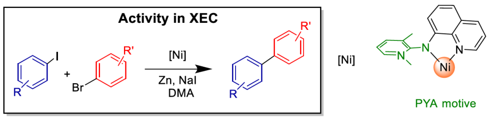
Cross electrophile coupling (XEC) is becoming an increasingly popular method to form biaryl products. The use of two electrophiles instead of the conventional use of an organometallic reagent considerably widens the pool of available coupling partners that furthermore do not suffer from stability issues.1,2 Current XEC catalysts typically are based on nickel complexes. Screening of different ligand variations revealed that (N-N') ligands such as bipyridine variations impart highest activity.3 Our group recently used (N-N') ligands with the pyridinium amidate (PYA) motive with great success for palladium α-arylation of ketones.4 PYA ligands are unique in the sense that they offer donor flexibility, which is able to impact catalysis. In addition, PYA ligands are also easy to functionalize and therefore provide an interesting target to expand the range of ligands for XEC catalyst development. We will present a series of new nickel(II) (N-N')-PYA complexes and will discuss their ability to catalyze cross electrophile coupling of aryl iodides with aryl bromide.



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Borenium-ion catalyzed homocoupling of diazo compounds

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Recently, there has been growing interest in alternative approaches to catalysis, with significant efforts directed toward the synthesis of new, more sustainable catalysts that maintain high efficiency and selectivity without relying on transition metals. Borenium ion-containing compounds have been widely studied and utilized for various catalytic purposes over the past decades. These compounds are very attractive because of their Lewis acidic properties, which make them effective in a range of transformations (including hydrogenation, hydroboration or hydrosilylation reactions)[1].

Tetraphenyl ethylenes (TPEs) are a class of compounds well-known and studied for their luminescent properties, including aggregation induced emission. These properties make them interesting for various applications, including biological probes for sensing or imaging, chemical sensing or optoelectronic systems[2].

In our previous research, we synthesized a large series of borenium compounds based on phenylpyridine scaffold and focused on studying their Lewis acidity and luminescent properties[3]. During this research, we have observed an unexpected ability of some of these compounds to catalytically transform diazo compounds into the appropriate tetraphenyl ethylene derivatives with a very high efficiency (*Fig. 1*). This newly found reactivity could bring a novel pathway for metal-free synthesis of luminescent materials, further highlighting the potential of borenium ions in modern catalysis.

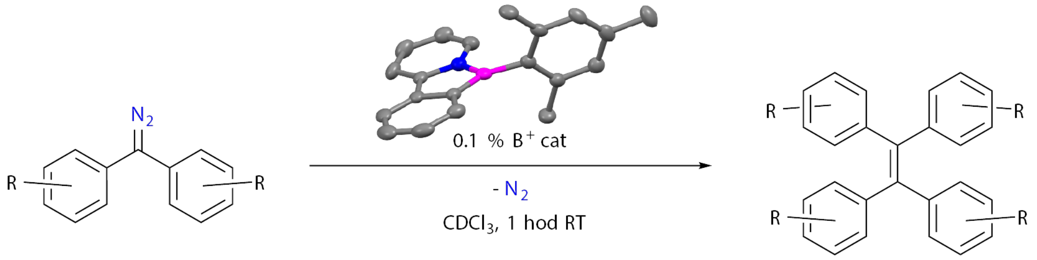

Figure 1: General scheme of the studied diazo homocoupling reaction. Phenylpyridine based borenium catalyst shown above the arrow has a tetrakis(pentafluorophenyl)borate counterion, which is omitted for clarity.

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A Dinuclear Vanadium(III) Complex with Four Bridging Methyl Groups and Its Thermal Decomposition in Hydrocarbon Solvents

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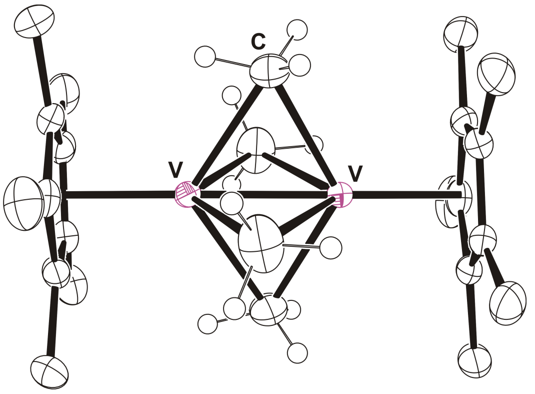
The application of earth abundant metals in synthesis and catalysis is one of the most important tendencies in modern chemistry. In comparison to other early transition metals, the chemistry of mid-valent monocyclopentadienylvanadium derivatives remains underdeveloped due to their high air-sensitivity, paramagnetic nature, and the lack of general synthetic routes for these combinations. Recently, we reported a multigram, simple and non-toxic entry to $[\{VCp^*(\mu\text{-}Cl)_2\}_3]$ ($Cp^* = \eta^5\text{-}C_5Me_5$), an excellent precursor for vanadium complexes in mid- and low-oxidation states.[1]

Herein, we show how $[\{VCp^*(\mu\text{-}Cl)_2\}_3]$ can be easily transformed to dinuclear tetramethyl or tetraamido derivatives $[\{VCp^*(\mu\text{-}X)_2\}_2]$ (X = Me (**1**), NH_2 (**2**)). Complex **1** was previously prepared through an intricated synthetic method and its characterization was incomplete.[2] In this communication, we present its full characterization including X-ray and electronic structures, as well as electrochemical and magnetic properties. The thermal decomposition of **1** in hexane leads to a tetranuclear cube-type methylidene complex $[\{VCp^*(\mu_3\text{-}CH_2)\}_4]$, while in benzenic solvents C_6H_5R this treatment produces the formal insertion of a CH fragment into the six-membered ring of a solvent molecule to give $[VCp^*(\eta^7\text{-}C_7H_6R)]$ derivatives with η^7-cycloheptatrienyl ligands.



We thank the financial support of Ministerio de Ciencia, Innovación y Universidades of Spain (PID2023-146287NB-I00) and the Spanish Ministerio de Universidades for a doctoral fellowship (A.C.-M.).

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Iridium Triazolophosphinite Pincer Complexes: Synthesis and Reactivity

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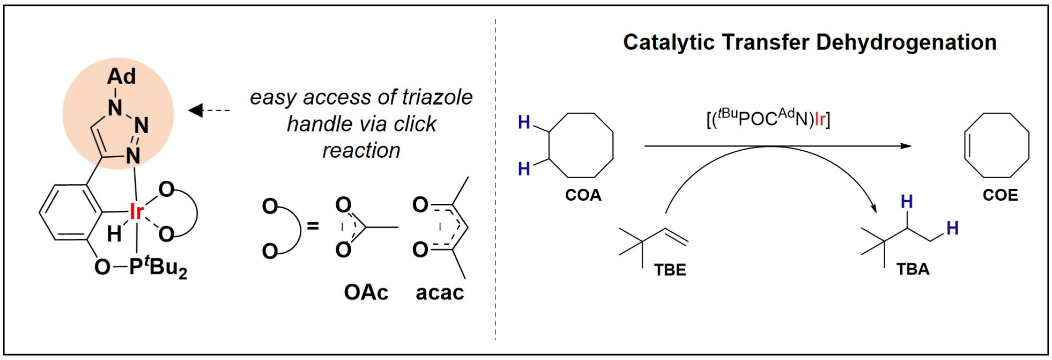
Iridium pincer complexes have been reported as excellent catalysts for transfer dehydrogenation of alkanes to obtain the corresponding alkenes,[1,2] which can be subsequently functionalized to various other derivatives.[3] Herewith, we describe the development of a route to access an iridium pincer catalyst with an unsymmetrical ^{tBu}POC^{Ad}N pincer ligand having an adamantyl (Ad) substituted-triazole arm, that can be accessed via Cu-catalyzed click reaction and a phosphinite handle. The synthesis of Ir-pincer complexes with different ancillary ligands containing oxygen donor atoms was accomplished by employing the appropriate Iridium metalation precursors. The complexes [(^{tBu}POC^{Ad}N)Ir(H)(OAc)] and [(^{tBu}POC^{Ad}N)Ir(H)(acac)] could thus be generated, and were characterized by XRD and NMR spectroscopy. Reactivities of these complexes were also studied, and conversions with carbon monoxide gave further insights into the structure of the pincer backbone. The complexes were also employed for the catalytic transfer dehydrogenation of alkanes and saturated heterocycles using *tert*-butlylethylene as the hydrogen acceptor.



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Selective CO_2 Hydrogenation-Dehydrogenation Catalysis to Formic Acid-Hydrogen Production by NHC-Ru-Cym Complexes with Ionic Liquids

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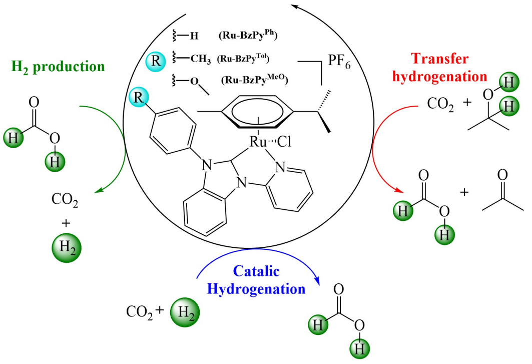
Formic acid (FA) has emerged as a promising hydrogen carrier due to its high hydrogen content, low toxicity, and ease of handling.[1-3] Thus, robust catalysts are essential to enhance FA-based hydrogen storage and its role in clean energy. Here, three new cationic benzimidazole ruthenium derivatives $[RuCl(p\text{-cymene})L]PF_6$ (L = 3-phenyl-1H-benzo[d]imidazole (**BzPy^{Ph}**), 3-(*p*-tolyl)-1H-benzo[d]imidazole (**BzPy^{tol}**), and 3-(4-methoxyphenyl)-1-(4-pyridinyl)-1H-benzo[d]imidazole (**BzPy^{MeO}**)) were synthesized in high yield by the reaction of dimeric $[RuCl_2(p\text{-cymene})]_2$ with 2 equivalents of the desired ligand (**BzPy^{Ph}**, **BzPy^{tol}**, or **BzPy^{MeO}**) in a transmetalation process using 1.1 equivalent of silver oxide, affording **Ru-BzPy^{Ph}**, **Ru-BzPy^{tol}**, and **Ru-BzPy^{MeO}**. The compounds were fully characterized by NMR, FT-IR, UV-Vis, and cyclic voltammetry measurements, and exhibited catalytic activity in antagonistic mechanisms, including CO_2 hydrogenation via catalytic and transfer hydrogenation (TH), as well as FA dehydrogenation. Various additives were assessed, with the ionic liquid BMIm.OAc demonstrating the best performance in CO_2 hydrogenation and TH, and dehydrogenation reactions. **Ru-BzPy^{Ph}** catalyzed the hydrogenation of CO_2 to formic acid, achieving a turnover number (TON) of 6080 (mol of FA produced per mol of catalyst) under optimized conditions. The complexes were also evaluated for TH of CO_2 to formic acid, achieving a TON of 240 after 22 h at 100 ºC for Ru-Bz^{Tol} when BMIm.OAc was used as an additive in a H_2O:*i*PrOH (4:1) solvent mixture. Formic acid dehydrogenation (FAD) reactions were conducted using a FA/cat up to 2000 in presence of 75 mol% of additive. **Ru-BzPy^{Ph}** was evaluated from 85 to 100 ºC in FAD in a FA/cat molar ratio of 1000, obtaining a TOF of 2504 h^{-1} and a conversion of 96% at 100 ºC. The temperature range enabled the determination of thermodynamic parameters, affording a $\Delta S^{\ddagger} = -12.52$ e.u., and an *E*a = 68.36 kJ mol□^{1}. The FA/Ru-BzPyPh/BMIm.OAc system (1:1000:750) remained active for over 20 days without loss in TON.



Funding: This work was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (2021/13128-1).

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Targeting Early Transition Metals for Phosphorus Atom Transfer

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Metal phosphides are an important class of solid-state materials widely used as catalysts and semiconductors. Outside of the stable 3D lattice structures found in solids, molecular phosphide complexes are less stable and are therefore less studied.[1] Transition metal phosphide complexes can be classified into terminal [M≡P] and bridged [M=P=M] phosphide complexes. Transition metal bridging phosphide complexes, featuring [M-P-M] core, are rare compounds with unique reactivities that are different from terminal metal phosphides [M≡P] as well as classical organophosphorus compounds.[2,3] While [M-P-M] complexes involving various transition metals such as W, Mo, Fe, Cr, and early transition metals like Zr and Nb have been reported, complexes featuring vanadium in a [V-P-V] motif have not yet been studied, and their reactivity is unknown. Their potential for direct phosphorus atom transfer makes them attractive targets for the sustainable synthesis of phosphorus-containing chemicals and materials.[4] In this study, we investigate suitable early transition metal platforms that access metal-phosphides using a safe phosphorus source, the phosphaethynolate anion (OCP^-). Low-valent vanadium complexes stabilized by a bulky bidentate N,N-ligand leads to phosphaethynolate complex $[V(PyrNDipp)_2(PCO)]$ (**2**). The complex **2** was characterized by single-crystal X-ray diffraction, confirming the formation of a terminal V–PCO with a P-bound coordination mode. Photolysis of **2** under UV light leads to the formation of a novel μ_2-phosphido-bridged divanadium complex $[L_2V{=}P{=}VL_2]$ (**3**). Single-crystal XRD confirms a near-linear V=P=V geometry (177.0°) and short V=P bond lengths (~2.21 and 2.27 Å), consistent with the bridged V=P=V representation. This transformation likely proceeds through a decarbonylation mechanism in which CO elimination generates a transient V≡P fragment that undergoes dimerization with another V(II) center. The reactivity and stabilization of these transient complexes are being studied further, and the project is in progress towards exploring possible strategies for transferring the coordinated P atom to suitable organic scaffolds.

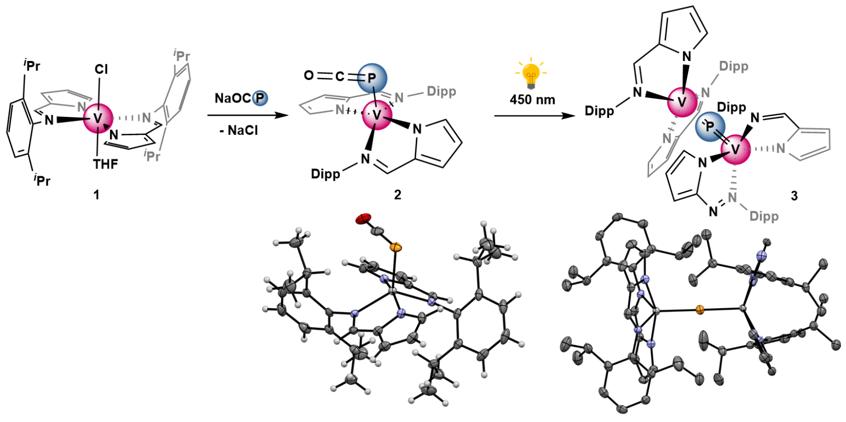

*Figure 1. Synthesis of **2** and **3** and their molecular structures (ellipsoids at 50 % prob. level, hydrogen atoms emitted in **3** for clarity)*

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Influence of the 4*f*-3*d* Metals Pairs on the Synthesis, Structure and Reactivity of Heterobimetallic Siloxide Complexes

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The development of heterobimetallic catalysts has attracted growing interest in recent decades to tackle the challenging activation of inert bonds. The combination of two metal centres with complementary properties and functions, in close proximity, aims to promote cooperativity for original and improved catalytic reactivity, not accessible with monometallic species.[1] For instance, our group recently reported the synthesis of original Ta-Ir and Hf-Ir heterobimetallic complexes, both in solution and grafted on silica solids, exhibiting high catalytic performances for H/D exchange reactions compared to the monometallic analogues.[2] However, the number of heterobimetallic catalysts reported so far is limited and mostly restrained to expensive and rare elements.

The objective of this work is to explore new combinations of non-noble metals, associating lanthanides (Ln) as hard, Lewis-acidic metals, with earth-abundant 3*d* metals such as Mn, Fe, Co, Ni, Cu. Using electron-rich siloxide ligands $(RO)_3SiO^-$, suitable for grafting on solid supports,[3] a promising salt metathesis strategy has been developed and allowed the isolation of new heterobimetallic complexes. Interestingly, by changing the nature of the 4*f* and 3*d* metals, the synthetic routes as well as the structures and properties of the resulting complexes are affected, as will be presented in this poster.

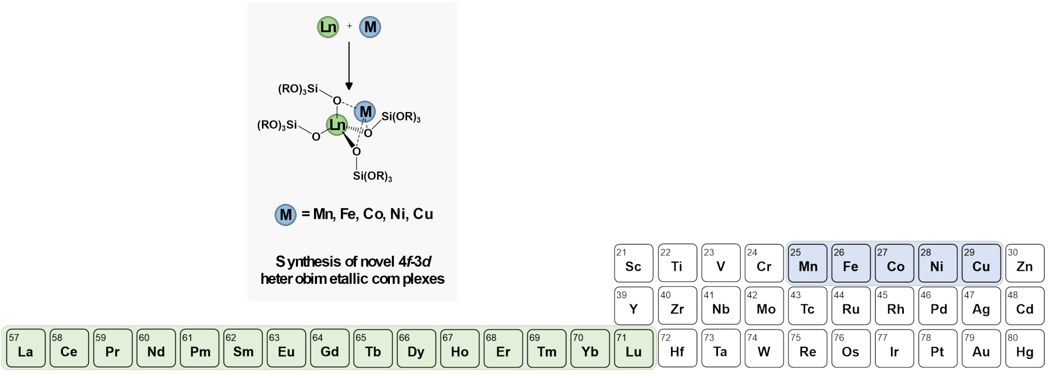

Figure 1 Synthetic strategy to develop novel 4*f*-3*d* heterobimetallic complexes.

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Boron-to-Gold Transmetalation for the Synthesis of mono- and bis-Cyclometalated Gold(III) Complexes

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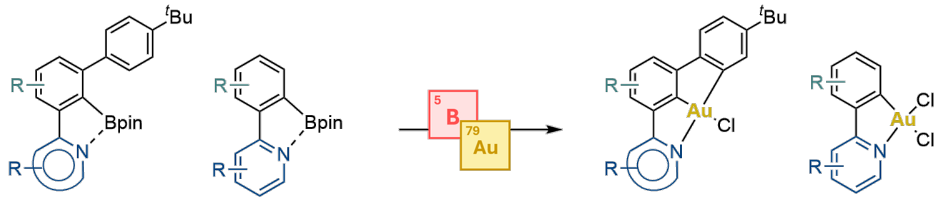
Despite their widespread application in catalysis, material science and biomedical research,[1] the development of gold(III) complexes remains limited by challenges associated with their synthesis. The use of bidentate and tridentate ligands is crucial to prevent the facile reduction to gold(I) or decomposition to elemental gold(0). However, most of the existing protocols to access both, mono and bis-cycloaurated complexes rely on harsh conditions and/or require the use of toxic reagents (e.g. Hg or Sn).[2] On the other hand, organoborane compounds have been efficiently used in stoichiometric and catalytic transmetalation reactions to gold(III),[3] making them an appealing class of functional groups to direct the cyclometalation step.

In this work, we have developed a novel and environmentally-friendly approach to access gold(III) complexes via boron-mediated transmetalation.[4] A late-stage functionalization strategy allows the incorporation of boronic ester groups onto a wide array of (N^C) and (N^C^C) ligands. The X-ray diffraction analysis of the $B(OR)_2$-functionalized ligands reveals the presence of a B-N dative bond, crucial in stabilizing the substrates while promoting the transmetalation. The desired transformation could be achieved under remarkably mild conditions with a broad functional group tolerance, affording mono- and bis-cyclometalated gold(III) complexes in moderate to very good yields. Furthermore, the expansion of this method to the synthesis of (C^N^C)Au(III) complexes has been successfully achieved.

Boron to Gold Transmetalation



- **Late stage ligand functionalization**
- **Functional group tolerance**
- **Mild conditions, no toxic reagent**
- **(N^C) and (N^C^C) templates**
- **Good yield, 17 examples**
- **Crystal structures**

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[2] R. Kumar, C. Nevado, *Angewandte Chemie International Edition*, **2017**, 56, 1994-2015.

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Light-driven Manganese-assisted Carbonylation of Aryl Iodides.

S. Choudhary[1], S. Flesch[1]*, C. S. Horbaczewskyj[1]*, N. T. Hunt[1]*, I. J. Fairlamb[1]*, J. M. Lynam[1]*

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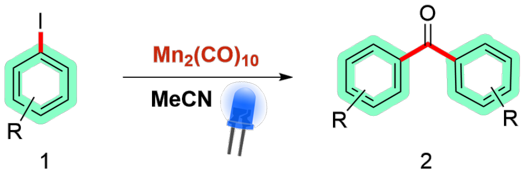
There is considerable interest in the application of manganese carbonyl complexes as catalysts for C–H and C–X bond activation and functionalisation processes.[1,2] Herein, a synthetic protocol for the carbonylation of aryl iodides, assisted by $Mn_2(CO)_{10}$ under visible light, has been uncovered. Photolysis of aryl iodides, 1, in the presence of $Mn_2(CO)_{10}$ affords excellent yields of benzophenone derivatives 2 (Scheme 1).

Detailed mechanistic studies indicate that $Mn_2(CO)_{10}$ serves as a CO source as in operando rapid scan infra-red spectroscopy data demonstrate than it is readily converted to $[Mn(NCMe)]_6[Mn(CO)_5]_2$. The reaction is promoted by electron-rich solvents (e.g. acetonitrile, benzonitrile, and benzyl cyanide) which is consistent with undergoing ligand exchange with the photochemically generated $Mn(CO)_5$ radical, resulting in the in-situ release of CO and disproportionation of $[Mn_2(CO)_{10}]$. A comprehensive substrate scope will be reported as well as other applications of using $[Mn_2(CO)_{10}]$ as a convenient light-activated source of CO.



Scheme 1: Carbonylation of iodoarenes.

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A new series of fluorinated dichloride platinum complexes as promising anticancer agents against orphan tumors

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Glioblastoma (GBM) and pancreatic cancer are both categorized as orphan tumors, for which the only available treatment is the maximal safe surgical resection followed by radiotherapy or chemotherapy with platinum drugs. Nevertheless, the survival rate is still very low (5-6% maximum).[1][2]

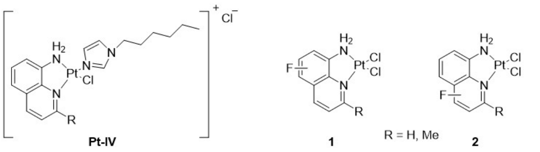
Based on this consideration, the aim of this work is focused on the synthesis, starting from the already published **Pt-IV** complex,[3] of a new series of platinum complexes in which the diamine core is modified by the addition of a fluorine atom in different positions of the ring. In this way, the goal is related to the modification of the solubility and, consequently, of the biological activity of the compound,[4] since one of the main problems for the very low efficacy of these drug is the bioavailability and the possibility to enter the cells.

First of all, two series of dichloride platinum complexes (**1** and **2**) bearing both 8-aminoquinoline and 8-aminoquinaldine with or without a fluorine atom were synthesized (**Figure 1**).

All these new compounds were tested for their ability to bind the DNA using innovative techniques and for their cytotoxicity against tumoral cells, in comparison with cisplatin, the first-in-class drug, and the **Pt-IV**. In fact, this compound has a known IC_{50} of 5.3 ± 0.55 μM against glioblastoma cell line (U87-MG), evaluated in terms of ability to affect cell proliferation.[5]

Is the fluorine atom able to influence the biological activity of the platinum complexes against different tumoral cell lines? Is this influence positive or negative?

Figure 1. The already published **Pt-IV** complex and the two new series of fluorinated compounds (**1** and **2**).



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Pd-Catalyzed Synthesis of Isocyanates without Phosgene: A Computational and Experimental Study.

C. Costabile[1], A. Broton-Rufes[1]*, D. R. Ramadan[2,3]*, M. A. Fouad[2,3]*, G. Galdi[1]*, F. Ferretti[2]*, F. Ragaini[2]*

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Isocyanates are critical commodity chemicals with multi-million-ton annual production and are traditionally synthesized by reducing nitro compounds into amines, followed by reaction with phosgene. [1] However, phosgene’s toxicity and corrosiveness clash with green chemistry principles. [2] Direct reductive carbonylation of nitroarenes has long been proposed as an alternative, yet its mechanism remained unexplored, and no practical application has been achieved. [3-5]

Here we propose the first comprehensive mechanism for the direct reductive carbonylation of nitroarenes catalyzed by palladium–phenanthroline complex, aiming to enable viable, efficient synthesis for industrial use. Extensive calculations revealed key intermediates and transition states governing the reaction; while evaluating alternative pathways, potential side reactions and catalyst decomposition routes are proposed. Experimental validation, using reaction kinetics analysis and potential intermediate reactivity studies, confirmed the model’s accuracy and limits, offering a robust framework for optimization. Complementary computational methods, including natural bonding orbitals and buried volumes, deepened mechanistic insights of the reaction. We propose alternative conditions, and ligand designs to overcome identified challenges, advancing sustainable isocyanate production.

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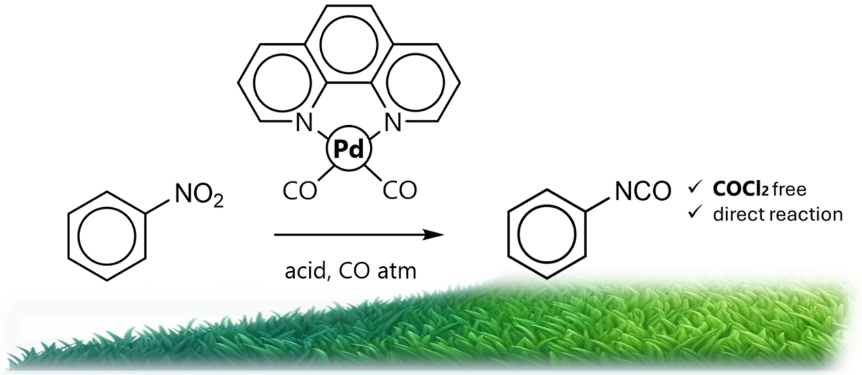

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The iron-catalyzed Miyaura borylation of aryl chlorides and triflates

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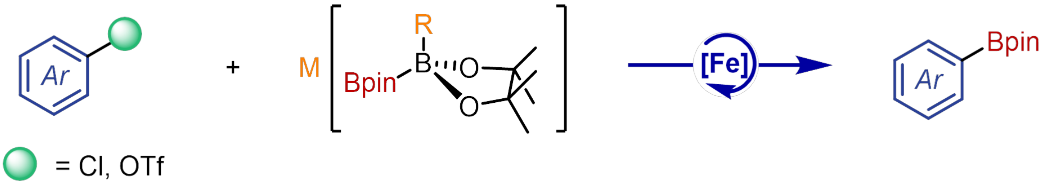
Transition metal-catalyzed borylation is a powerful reaction for the creation of versatile carbon-boron bonds. Traditionally, palladium catalysis are employed which, although highly efficient, are inherently unsustainable and costly.[1] In the synthesis of drug molecules, removal of palladium impurities represents a further challenge due to the stringent requirements for low-level impurities, as does the recovery of palladium catalysts from waste streams.[2] Numerous candidates have emerged as replacements for palladium, with first-row transition metals, particularly iron, being desirable due to its much higher natural abundance, cheaper cost and higher biocompatibility.

With respect to iron-catalyzed borylations, aryl chlorides are a highly appealing, yet challenging class of substrate. Select examples exist within the literature, but suffer from low yields or poor substrate scopes, only performing well for more extensively conjugated aryls (e.g. naphty/biphenyl chlorides).[3,4] We recently reported an improved methodology for the iron-catalyzed borylation of aryl chlorides, offering greater scope and good functional group tolerance, as well as the first example of iron-catalzyed borylation of aryl triflates (Scheme 1).[5]



While these improvements demonstrate that the iron-catalyzed borylation of functionalized aryl chlorides/triflates is achievable, the reaction lacks scalability due to the required pre-activation of B_2pin_2 with the pyrophoric base ^{t}BuLi. Thus, more recent work has targeted the replacement of ^{t}BuLi with more benign, process-friendly 'activators'. To achieve this goal, we have leveraged modern techniques including high-throughput experimentation and design of experiments (DoE) to rapidly identify and optimize early hits, culminating in an improved, safer and more scalable protocol. The scope of the improved methodology is currently under investigation alongside mechanistic studies.

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Mechanochemical Synthesis of a Sodium Anion Complex [Na^+([2.2.2]Cryptand)Na^-]: An Investigation into its Formation and Reactivity

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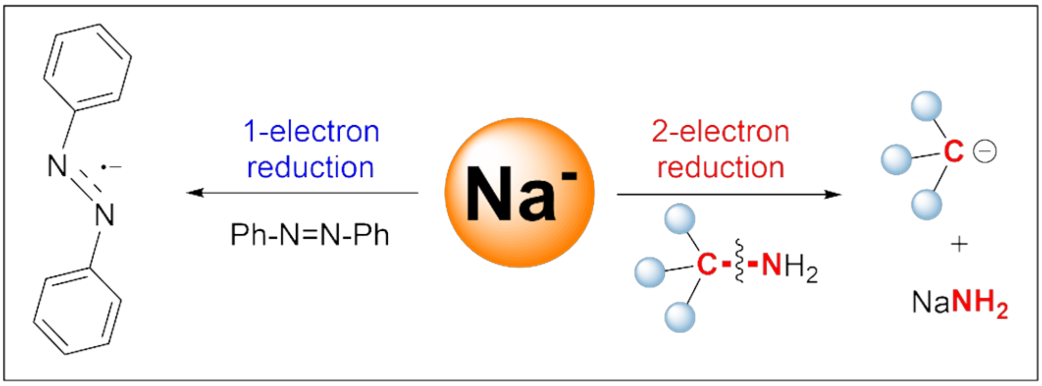
The alkali metals (Li-Cs) are some of the most low-cost and earth abundant metals of all the periodic table. Alkali metal molecular chemistry is dominated by the +1-oxidation state, while a zero valent-oxidation state is widespread in the metals. A more exotic, yet still available, oxidation state of the alkali metals (except lithium) is −1. Complexes containing an alkali metal in the −1-oxidation state are known as alkalides. Reported as early as the 1970s,[1] alkalides appear in modern inorganic chemistry textbooks as an iconic chemical curiosity, yet their reactivity remains largely unexplored. This is due to their synthetic hurdles. Alkalides are traditionally notoriously difficult to synthesise and handle, limiting their use in synthesis.

In this work we demonstrate a facile synthesis of the archetypical alkalide complex, [Na^+([2.2.2]cryptand)Na^-], allowing us to unveil a versatile reactivity profile of this once exotic species. This sodide was found to be stable under an inert atmosphere for hours at room temperature and for months at -35 °C and enabled both one and two-electron reductions of organic substrates.[2] In addition, using a variety of *in-situ* and *ex-situ* techniques we investigated the mechanism of its formation in the solid-state.[3]



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Synthesis and reactivity of a novel trimeric Al(I) species

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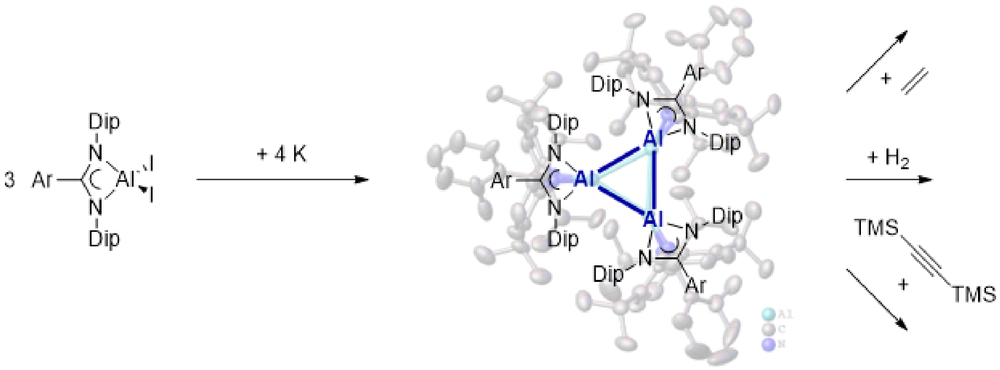
The requirement for humanity to move away from the use of heavy transition metals is well established. As the most abundant metal in the Earth's crust, aluminium represents an attractive alternative but its use in traditionally transition-metal catalysed processes is limited by our still meagre understanding of its reactivity. Interest in the synthesis and reactivity of low-oxidation state aluminium compounds has exploded since the seminal first report of the synthesis of a stable aluminium(I) complex[1], the tetrameric $[AlCp^*]_4$ ($Cp^* = C_5Me_5^-$) and the subsequent report of the monomeric beta-diketiminate (BDI) stabilised BDIAl(I) (BDI = $\{DipNC(Me)\}_2C$, Dip = 2,6-diisopropylphenyl).[2] These species have been utilised for a rich range of reactivity, with applications in transition metal-like bond cleavage, small molecule activation and as stoichiometric reducing agents.[3] Many other monomeric and dimeric aluminium(I) species have been reported subsequently, with some existing in equilibrium between monomeric and dimeric states.[4] Until now, there has been no report of a trimeric neutral aluminium species.

In the Bakewell group, we are interested in the reactivity of amidinate stabilised aluminium hydride species. Their reaction with BDIAl(I) in aromatic solvents leads to an apparent [4+2] cycloaddition, implying the formation of a transient Al^I species.[5,6] Performing this reduction in aliphatic solvents allowed us to isolate this Al^I species for the first time.

From the potassium reduction of a series of bulky amidinate stabilised aluminium diiodides we have isolated a range of novel cyclotrialumane complexes, an unprecedented trimeric structure for aluminium in the +1 oxidation state. In this poster, the synthesis and subsequent small molecule reactivity of a series of novel amidine ligand stabilised cyclotrialumanes is detailed; demonstrating a rare example of ambimeric reactivity. A novel 7-membered heterocyclic mixed oxidation state aluminium complex is also presented, as part of a stepwise reaction with an unsaturated substrate.



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Antibacterial activities and mechanism of action of oxo-rhenium (V) complexes

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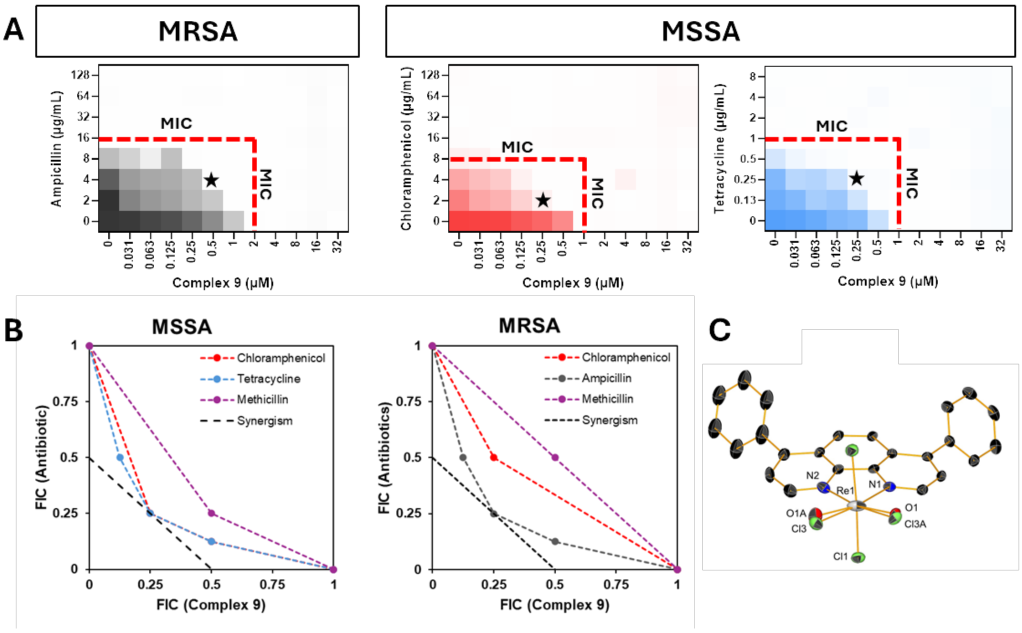
Antibiotic resistance is one of the most serious current threats to global health. The frequent use and misuse of first-line antibiotics have resulted in the increase in multi-drug resistant (MDR) pathogens, such as methicillin-resistant *Staphylococcus aureus* (MRSA). The WHO has flagged the problem as a critical global health concern, with the urgent need to develop new classes of antibiotics. The development of new classes of antibiotics is costly and time-consuming. A parallel strategy is the development and identification of molecules that can act synergistically with already approved drugs. Metal-containing compounds have emerged as a promising alternative to conventional organic antibiotics. Oxo-rhenium (v) complexes have been studied as anticancer agents [1, 2], but little is known about their antimicrobial potential.

In this study, we have prepared a family of Re(V)=O complexes bearing diimine ligands and evaluated them as antibacterial agents against *S. aureus* (MSSA and MRSA), *E. coli,* and *P. aeruginosa* strains (Fig C). From the study, we have identified a compound active at a 2 μM concentration against *S. aureus*, with a therapeutic index of 4.88 (IC50(L929 cells)/MIC(Strains)). From the results of checkboard assays with 6 commonly used classes of antibiotics (Fig B), we determined the synergism of the compound with chloramphenicol and tetracycline in the treatment of the MSSA strain and ampicillin in the treatment of MRSA (Fig A). The checkboard assays showed that, in combination with the antibiotics, the MIC of the molecule dropped to ca. 250 nM and its therapeutic index improved up to 19.5.



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C-H Activation and C_{sp3}-C_{sp3} Coupling Across a Molybdenum Iridium Triple Bond

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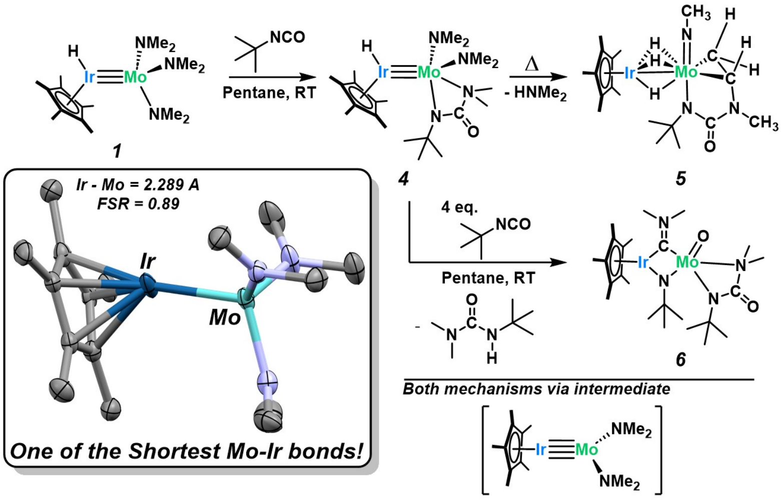
Heterobimetallic complexes have been a near constant source of interesting reactivity as their inherent asymmetry leads naturally to inherent polarized bonding.[1] This bonding can be capable of impressive and difficult substrate transformations if localized in an amenable geometry and with available orbitals for interaction with a substrate.[2] To this end, this oral contribution will detail the synthesis and characterization of an unsupported molybdenum-iridium triple bond, which undergoes an electrophilic insertion with tertbutylisocyanate culminating in an unprecedented triple C_{sp3}-H bond activation and C_{sp3}-C_{sp3} coupling to generate a Mo(VI) metallacyclopropane.



Through computational analysis we show a detailed mechanism showing loss of dimethylamine and formation of an intermediate quadruply bonded system, one of a very few examples of a heterobimetallic quadruple bond. Subsequent α and β hydride abstractions and a C-C coupling eventually yield the hydride bridged complex. Addition of multiple equivalents of isocyanate interrupts this mechanism to undergo a [2+2] cycloaddition from the same intermediate, reorganizing the isocyanate fragment and yielding an aminocarbyne, a bridging imido ligand and a molybdenum(VI) oxo complex. This reactivity is totally unprecedented and represents a novel strategy for bond activation and reorganization.

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Site-Selective Skeletal Metalation of Thalidomide Derivatives

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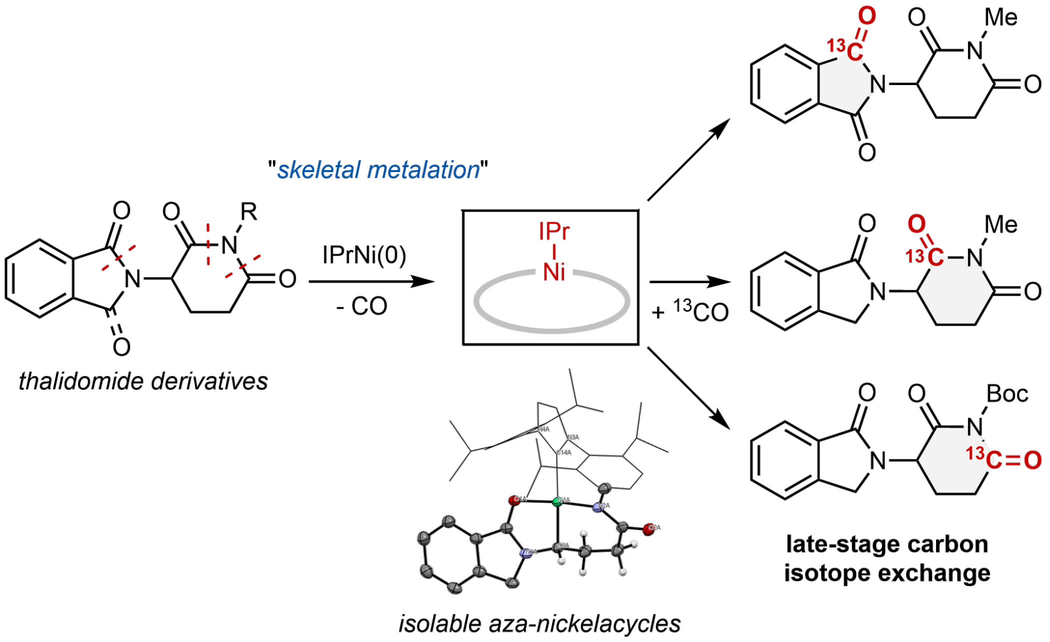
Previously our laboratory reported the Ni(0) promoted C–N bond activation of *N*-Boc protected lactams. Through a formal “carbonyl to nickel” exchange a variety of different azanickelacycles could be isolated in a skeletal metalation approach.[1] Herein we disclose the expansion of this strategy for the chemoselective C–N bond activation in imide scaffolds with several distinct C–N bonds.

Despite its well-known teratogenicity, thalidomide and its derivatives serve as important drugs for the treatment of certain cancers and have gained renewed interest in the context of molecular glue degraders and proteolysis targeting chimeras (PROTACs).[2] We show that depending on the choice of a protecting group or degree of oxidation, different sites in the thalidomide scaffold will undergo skeletal metalation selectively and allow for the isolation of a family of different azanickelacycles. The observed site-selectivity for the metalation process is further rationalized through computational studies. Finally, we demonstrate the applicability of our metalation strategy for the late-stage carbon isotope exchange of all three chemically inequivalent carbonyl positions in the thalidomide scaffold using ^{13}CO gas.



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Unprecedented coordination modes for heteroleptic tetrahedral complexes bearing pnictogen atoms towards Cu^I and Ag^I ions

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In the past decades, research on transition metal complexes bearing pnictogen atoms has witnessed a wide expansion owing to their unusual bonding patterns and rich chemical reactivities.[1] One of our group's contributions to this field was the development of a new approach for the synthesis of homo- $[\{CpMo(CO)_2\}_2(\mu,\eta^2\text{-}E_2)]$ (E = P, As, Sb) (Cp = η^2-C_5H_5) and heteroleptic $[\{CpMo(CO)_2\}_2(\mu,\eta^2\text{-}EE')]$ (E = P, E' = As (**1**), Sb (**2**)) complexes which formally represent E_4 tetrahedranes (E = P, As, Sb) in which two E atoms are replaced by isoelectronic 15 valence electron $[CpMo(CO)_2]$ moieties.[2] These complexes have shown unique coordination behaviour when reacted with Cu^I and Ag^I salts.[3] For example, the reaction of **1** or **2** with CuCl or CuBr using a 1:1 ratio allowed for the facile formation of the neutral oligomeric complexes **3-6**, respectively.[3c] A similar reaction of **2** with CuBr or CuI using however a stoichiometric ratio of 2:3 resulted in the neutral 1D polymers **7** and **8**, respectively. Interestingly, in all supramolecular aggregates **3-8**, the tetrahedral ligand complexes **1** and **2** are found to interact each in a η^2:η^1-coordination mode towards the Cu^I ions. According to DFT computations, this is attributed to a mixed coordination through the lone pair of the P atom and the P-E σ-bond. A summary of the herein mentioned reactions is presented in the following figure.

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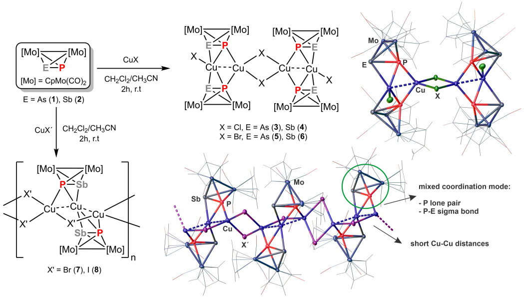
- Selected papers: a) Elsayed Moussa, M.; Shelyganov, P. A.; Seidl, M.; Zimmermann, L.; Scheer, M. *Commun*. **2024**, ***60*, 4703-4706**; b) Shelyganov, P. A.; Elsayed Moussa, M.; Seidl, M.; Scheer, M. *Angew. Chem. Int. Ed*., **2023**, *62*, e202215650; c) Elsayed Moussa, M.; Seidl, M.; Balázs, G.; Hautmann, M.; Scheer, M.; *Angew. Chem. Int. Ed*. **2019**, *58*, 12903-12907; d) Attenberger, B.; Welsch, S.; Zabel, M.; Peresypkina, E.; Scheer, M. *Angew. Chem. Int. Ed*. **2011**, ***50***, 11516-11519.



Nucleophilicity at copper(-I) in compounds with a Cu–Mg bond

N. J. Evans[1], R. Jackson[1]*, D. Babula[1]*, T. Horsley Downie[1]*, R. Charman[1]*, S. Neale[1]*, M. Mahon[1]*, D. Liptrot[1]*

[1]University of Bath

Copper(I) complexes are well known, with extensive use in both synthesis and catalysis due to their ability to activate and functionalise C-H and C-C bonds.[1] Copper(I) catalysis is attractive due to its consistency of reactivity; copper is electropositive and supports nucleophilic boron fragments for example where reactivity can be rationalised as occuring from a $Cu^{\delta+}$-$B^{\delta-}$ element pair. This reactivity is consistent across the vast majority of copper-element bonds, copper almost always shows electrophilic character.

However, a handful of examples do exist where copper shows ambiphilic behaviour, this occurs within Cu-Al bonded systems, whose reactivity towards carbodiimides shows evidence of both $Cu^{\delta+}$-$Al^{\delta-}$ and $Cu^{\delta-}$-$Al^{\delta+}$ bond polarities.[2,3] Whilst this is, perhaps, unsurprising given the high electronegativity of aluminium, the inconsistent reactivity of copper-aluminium bonds has led to their assignment as ambiphilic.

We recently reported the synthesis of a compound containing a copper-magnesium bond. The reaction of (6-Dipp)CuOEt with LMgMgL (6-Dipp = $C\{N(Dipp)CH_2\}_2CH_2$, L = $[\{(Dipp)NC(CH_3)\}_2CH]$, Dipp = 2,6-iPr_2-C_6H_3) results in the formation of (6-Dipp)CuMgL. Exploration of the electronic structure of (6-Dipp)CuMgL via DFT calculations reflects a high charge density at copper, and this is also reflected in its crystallographic structure. The reactivity of (6-Dipp)CuMgL towards substrates from the s-, p- and d-blocks of the periodic table allows us to designate it as an unambiguously nucleophilic source of copper (Figure 1).

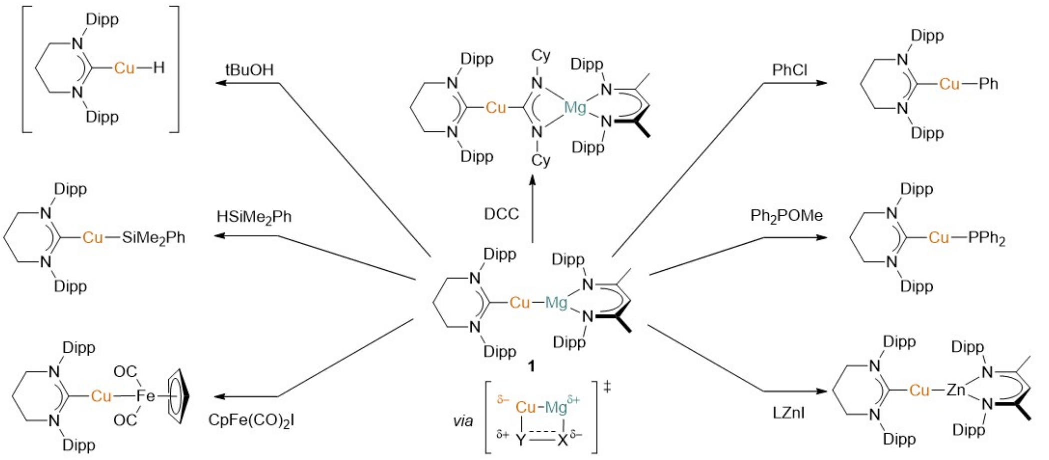


Figure 1. Nucleophilic copper transfer reactivity of (6-Dipp)CuMg(L), with elements from across the periodic table.

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One-pot chemoenzymatic synthesis of enantiopure aryl- and alkyl-azaarenes pharmaceutical intermediates

G. Facchetti[1], G. Coffetti[1]*, L. Arnal[1]*, R. Gandolfi[1]*, I. Rimoldi[1]*

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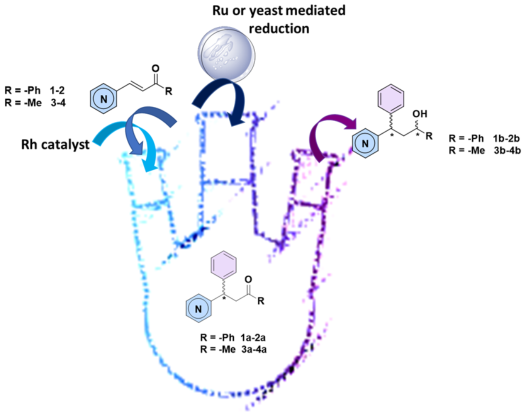
One-pot reactions are distinctive processes in which multiple sequential reactions occur within a single reaction vessel. Crucially, each reaction begins only after the completion of the previous one, ultimately yielding the desired final product without requiring intermediate purification. This approach not only shortens the overall synthesis time but also enhances total yield and minimizes chemical waste, making it a more environmentally sustainable strategy [1,2]. Following this successful approach, a one-pot reaction was designed and set up in two steps for the preparation of enantio-enriched 3,3-azaaryl-1-aryl-propanols and 3,3-azaaryl-1-alkyl-propanols containing a pyridine core. The first step of the one-pot protocol provided the addition of phenyl boronic acid to a carbonyl-activated alkenyl azaarenes (**1-4**) using [Rh(coe)(*S*)-TetraMeBITIANP] as catalyst [3] reaching up to 80% e.e. and quantitative conversion, a prerequisite to perform in the same reactor the second step, *i.e.* the asymmetric reduction of the prochiral keto group. In the case of propanones **1a** and **2a** the enantioselective reduction was realized by a ruthenium diamine complex under ATH (Asymmetric Transfer Hydrogenation) conditions in aqueous media, affording the *anti*-diasteromers in up to 90% e.e. Meanwhile, a biocatalytic approach for the reduction of carbonyl group of the products **3a-4a** in *R* configuration was realized screening different yeasts. In this case, *Torulopsis molischiana* CBS 837 provided the products in *anti* -configuration with a molar conversion up to 95% and excellent enantiopurity (up to 99% e.e.) in 24h [4].



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Detailed comparison of different phosphine ligands in the palladium-catalyzed isomerizing methoxycarbonylation of alkenes

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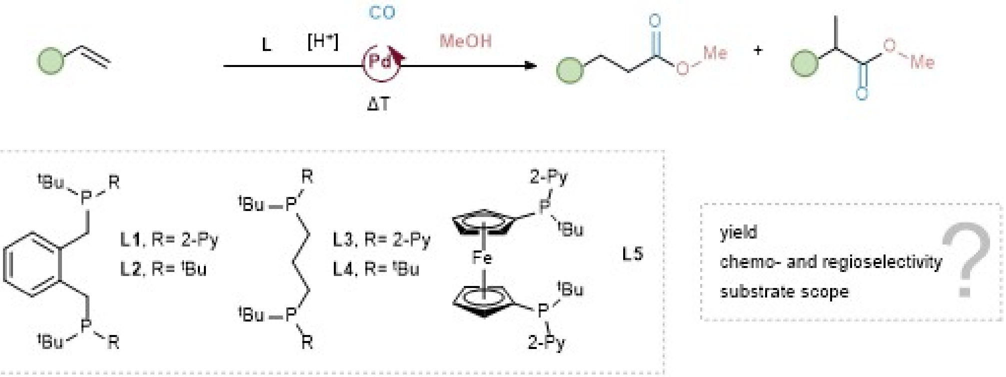
The carbonylation of widely available unsaturated compounds is an indispensable method for producing compounds such as esters. For this type of reaction, metal-ligand systems are used to catalyze the reaction in the presence of an alcohol and carbon monoxide (CO).[1, 2] Phosphine ligands are suitable for many different desired products due to their electronic properties and their adaptability, for example the customization of their backbones.

Various palladium catalyzed systems in combination with phosphine ligands are already established due to their outstanding performance. These include phosphine ligands with xylene (**L1**, **L2**) as well as with ferrocenyl backbones (**L5**). Phosphine ligands with aliphatic backbones, on the other hand, are not yet fully established.[3] However, these have a high potential due to their wobbly backbone, which can lead to the development of more complex substrates.[4] In this work, differences in performance, selectivity and versatility between these and analogous ligands with C3 backbones (**L3**, **L4**) are illustrated for the methoxycarbonylation of various substrates.



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NHC Metal Peptide Conjugates for Abiotic Catalysis

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N-heterocyclic carbene (NHC) ligands have fundamentally transformed homogeneous catalysis, with impact in particular on catalysis with first row transition metals and precious platinum group metals. Considering these advances, it is remarkable that only few attempts have been demonstrated to incorporate NHCs into artificial metalloenzymes.[1–4] We therefore sought to develop non-canonical amino-acids (ncAAs) for site-specific incorporation into a peptide chain. For example, we have demonstrated the introduction of the NHC-like ncAA Hum into a small peptide to produce a minimalistic iridium peptide conjugate for hydrogenation reactions as a miniaturized prototype of an artificial hydrogenase.[5] Here, we will present our latest advances in developing NHC precursor ncAAs and their scope in binding a diverse set of transition metals for new-to-nature catalysis.

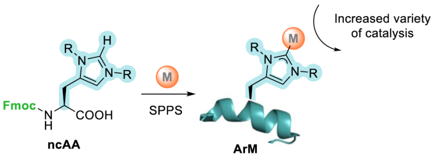

Figure Non-canonical amino-acids with a NHC-like side-chain which can be site-specifically included into a peptide sequence through Solid Phase Peptide Synthesis (SPPS).

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Gold(I)-Catalyzed Intramolecular and Intermolecular Hydroarylation Reactions for the Direct Synthesis of Coumarins

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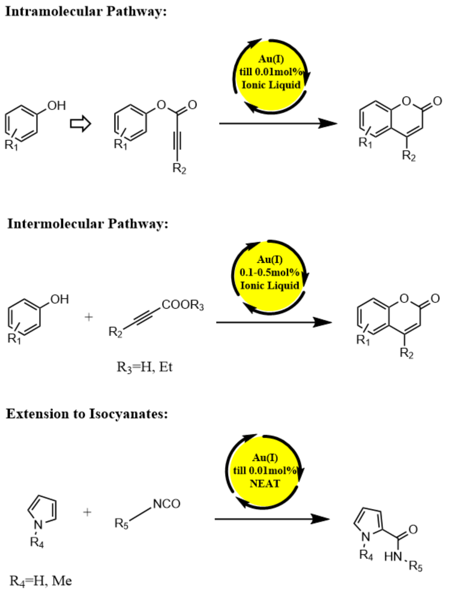
The combination of gold(I) complexes bearing N-heterocyclic carbene (NHC) ligands with ionic liquids (ILs) has led to the development of two distinct catalytic systems for the efficient synthesis of coumarin derivatives. In a first approach[1], an intramolecular hydroarylation of suitably designed alkynyl phenols is promoted under gold catalysis in ILs, enabling high catalytic activity at very low Au loadings (down to 0.01 mol%), using either commercial catalysts such as IPrAuNTf□ or tailor-made NHC-gold(I) complexes for less reactive electron-deficient substrates. In the second strategy, an intermolecular hydroarylation between phenols and alkynoic acids/esters is catalyzed by gold(I) complexes employing ILs as solvent, followed by an intramolecular thermal or acid-catalyzed cyclization, leading to coumarin formation. Both processes operate under mild conditions, with high atom economy, short reaction times, and catalyst loadings <1% Au, and prove particularly efficient for electron-rich phenols. In both systems, the IL medium enables catalyst recovery and recycling, offering sustainable and efficient routes to functionalized coumarins. Building upon these results, our we are currently investigating the gold-catalyzed hydroarylation of isocyanates, expanding the scope and synthetic potential of this methodology.



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Transition Metal-Catalyzed Reductive Cyclization of Nitroarenes Using CO or Its Surrogates as Reductant: It Takes Two to Tango!

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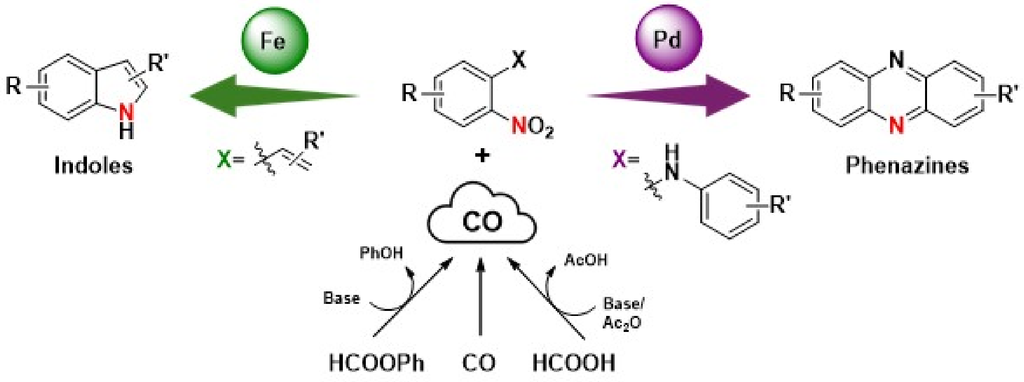
N-Heterocycles are essential building blocks in medicinal and material chemistry, driving synthetic chemists' efforts to develop innovative and efficient synthetic strategies.[1] Our group pioneered catalyzed reductive cyclization of nitroarenes using carbon monoxide (CO) as a potent and cheap reductant.[2] However, the handling of gaseous CO presents safety challenges, requiring specialized precautions. To address this, we explored safer and more convenient CO-releasing agents such as formic acid and phenyl formate. In this context, we report a Pd-catalyzed reductive cyclization of 2-nitro-*N*-phenylanilines to phenazines, achieving high selectivity under two optimized conditions: Method A, utilizing phenyl formate (HCOOPh) as a CO surrogate, and Method B, employing gaseous CO. Both methods operate with exceptionally low Pd-catalyst loading (substrate/[Pd] = 2000:1). Building on our previous success with the Pd-catalyzed reductive cyclization of 2-nitrostyrenes,[3,4] we further explored more economical catalysts and broadened our approach by investigating the reductive cyclization of 2-nitrostyrenes to indoles using iron as a catalyst. Here, CO and its *in-situ* surrogates proved to be effective, economical reductants, yielding promising results thus far. These advancements highlight the potential of our approach as a practical, selective, and scalable strategy for *N*-heterocycle synthesis.



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Al-Fe complexes supported by *o*-Phenylenediamido redox-active ligands: synthesis and reactivity

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The development of sustainable homogeneous catalytic systems is one of the most important fields of research during the last years. The growing interest in green chemistry and environmental protection, particularly concerning metal-based catalysis, necessitates the replacement of precious metals with earth-abundant elements, which are cheaper and more biocompatible.[1] Among these earth-abundant metals, aluminum has garnered significant interest due to its high natural abundance, low cost, and reduced toxicity compared to most transition metals.[2]

In terms of catalytic activity, the enhancement of catalytic systems can be achieved through the design of novel ligands that control the reactivity of the metal center in the catalytic cycle or by combining the properties of first-row transition metals (such as Fe, Mn, Ni, and Co) with aluminum-based metalloligands.[3] A promising strategy for advancing metal-based catalysis involves the incorporation of redox-active ligands. These ligands enable cooperative interactions between the metal and ligand, potentially bypassing the need for metals to adopt unusual oxidation states during the catalytic cycle. Among the variety of redox-active ligands, o-phenylenediamido (o-PDA) systems have demonstrated remarkable flexibility in coordination modes and the ability to support one- or two-electron redox processes.[4] Given these properties, redox-active ligands in combination with aluminum present an ideal platform for catalysis in redox transformations. However, their application in electrophilic activation and redox transformation reactions remains underexplored.[2]

Building on these principles, herein we describe the synthesis and characterization of aluminum complexes supported by o-PDA ligands, as well as the preparation of PDA-based heterobimetallic aluminum-iron complexes. Additionally, we explore their reactivity with small molecules, highlighting their potential application in catalysis.

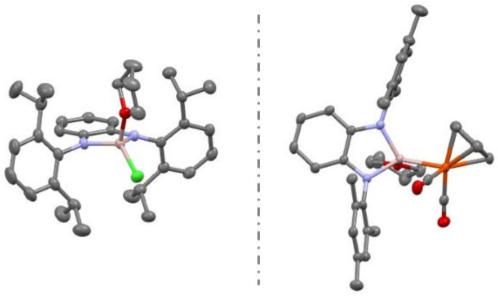

Figure 1. Structures of aluminum-based complexes supported by o-PDA ligand.

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Synthesis of Low Oxidation State Tantalum Phosphinine Complexes

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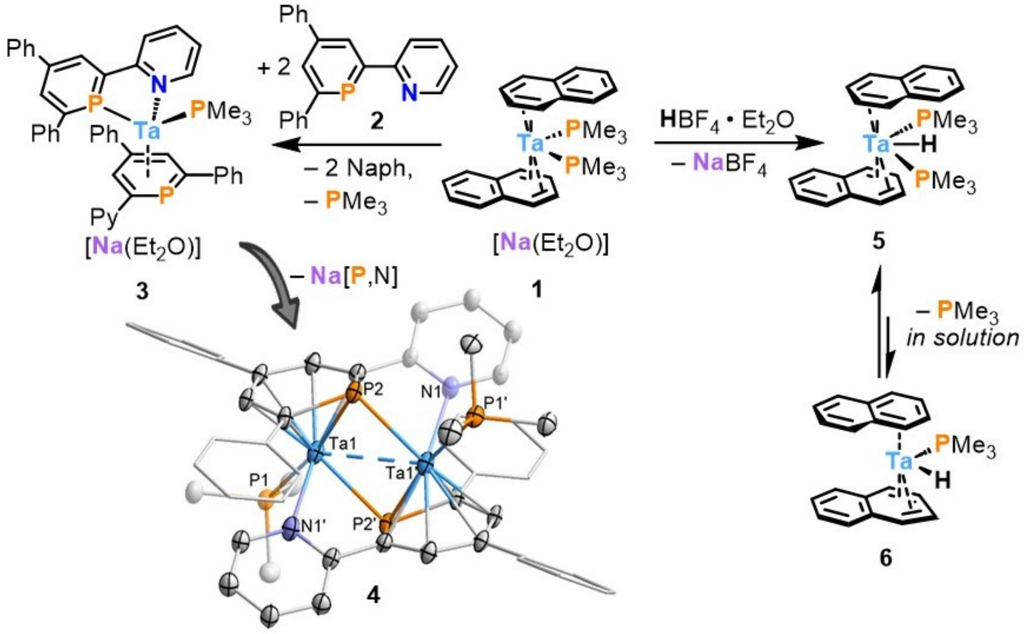
Phosphinine ligands form reactive and catalytically active transition metal complexes, due to their beneficial σ-donor and π-acceptor capabilities.[1] We are interested in using phosphinines to stabilize low oxidation state transition metalate anions.[2] While this has given access to phosphinine complexes of late transition metals, such as Fe and Co,[3] the reactivity of early transition metalates towards phosphinines remains largely unexplored.

This poster presents the synthesis and reactivity of the anionic tantalate salt **1**, which serves as a precursor for phosphinine complexes. Reaction of **1** with 2-pyridyl-phosphinine **2** leads to the formation of complexes **3** and **4**, depending on the solvent used. The latter is a bimetallic complex featuring two bridging phosphinine ligands in a previously unreported η^6/η^1 coordination mode. Additionally, **2** is cleanly protonated by $HBF_4 \cdot Et_2O$, affording the hydride species **5** and **6**, which can also serve as precursors to new phosphinine complexes.



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Exploring the Impact of Metallacycle Size in Tantalum-Catalyzed Hydroaminoalkylation: A Computational Study

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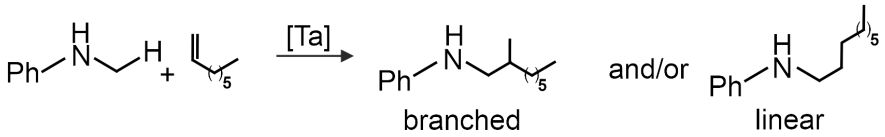
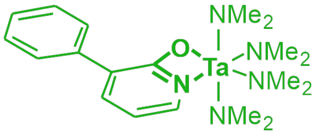
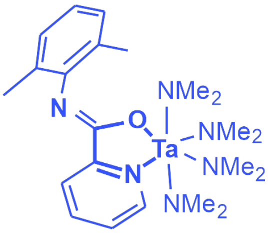
Hydroaminoalkylation (HAA) is a highly efficient catalytic method for the direct functionalization of alkenes and alkynes with amines that has attracted considerable attention in recent years [1] (Scheme 1). Tantalum complexes with N,O-donor ligands forming 4-membered metallacycles [2] have proved to be effective catalysts in this transformation. Although key steps of the reaction mechanism have been studied [3], the impact of ligand design, particularly the size of the metallacycle, has not been fully explored.



In this study, we present a computational analysis of the tantalum-catalysed HAA reaction, comparing the energy profiles of catalysts with 4-, 5- and 6-membered metallacycles (Scheme 2). By using additional computational tools, we were able to clarify the observed trends and provide a rational explanation for the experimental results. These findings provide a comprehensive understanding of the catalytic systems and contribute valuable knowledge for the future development of more efficient catalysts in this field.



Ta-1



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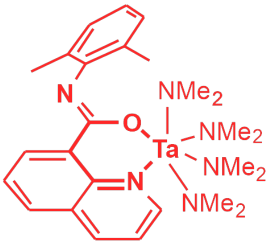

Ta-3

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Cross-Coupling Reactions of Aryl Iodides with Nitriles: A comparative DFT Study on the different selectivity of Au and Pd complexes.

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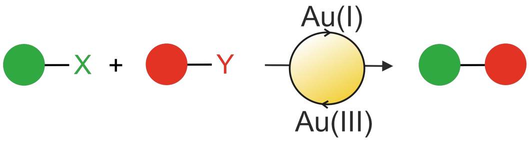
Gold catalysis is a promising approach for cross-coupling reactions, although is limited by the redox potential of the Au(I)/Au(III) couple. Innovative strategies - such as Bourissou's bidentate MeDalPhos ligand (P^N) - have proven effective in stabilizing Au(III) species, thus enabling a wide range of gold-catalyzed transformations (Scheme 1) [1].

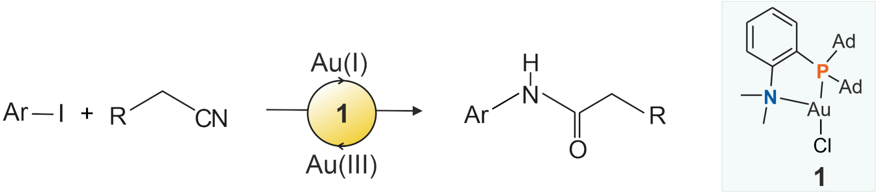


Recently, we performed a DFT study on the 1,2-oxyarylation of ethylene mechanism showing rationally designed ligands of high interest for the stabilization of Au(III) species involved in the reaction [2].

In this framework, we aim at expanding our findings to challenging reactions as the synthesis of aryl amides and aryl carbamates through selective C-N cross-coupling of aryl iodides with nitriles catalyzed by MeDalPhosAuCl (1 in Scheme 2) [3]. These compounds are crucial substrates in various fields, including organic and medicinal chemistry, as well as in agrochemical production [4].

Although it is widely accepted that Au(III) species play a role in the catalytic cycle, the mechanism of this reaction remains unclear. Above all, the selectivity of gold in promoting the C-N coupling is in contrast with the C-C coupling catalyzed by palladium starting from the same substrates. [5]

Here we propose the mechanism of aryl amide formation, including key rate-determining intermediates and transition states, highlighting the main differences between gold and palladium selectivity as well as the central role of water during the reaction.



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Surface-Bound Photoredox Heterogeneous Organometallic Catalysts

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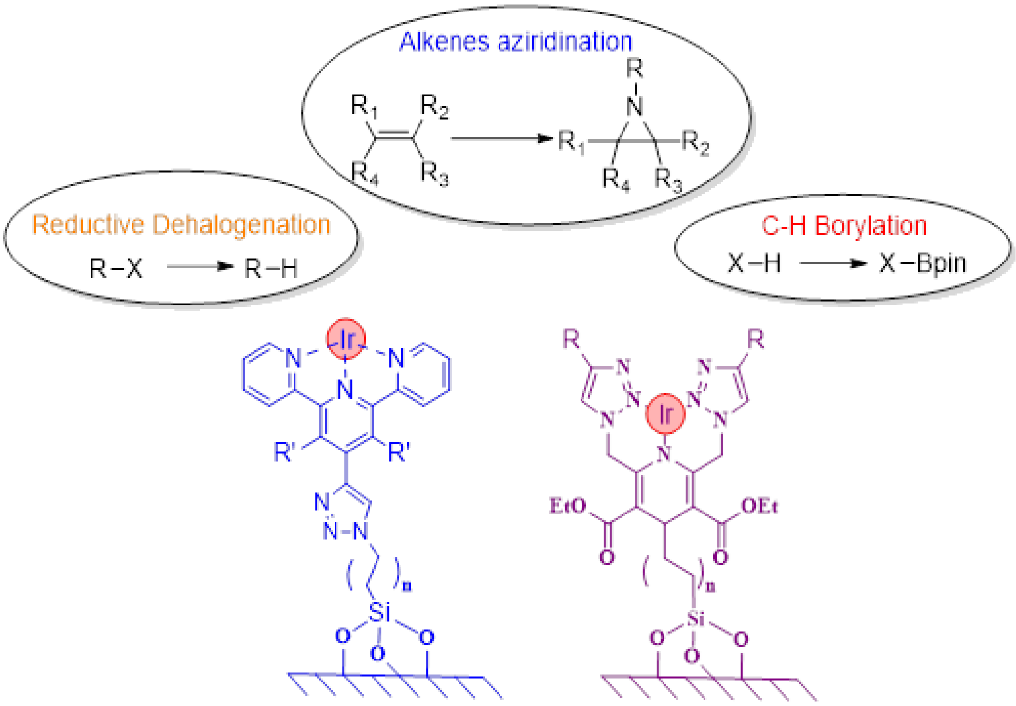
Photocatalysis, particularly with iridium(III) complexes, is a powerful tool in organic synthesis, offering enhanced versatility, specificity and recyclability through catalyst heterogenization via surface immobilization. Understanding how the surface environment affects the catalytic mechanism is vital for effective catalyst design.

This study reports the successful development of surface-immobilized Ir(III) complexes demonstrating efficient and recyclable photoredox catalysis. Specifically, the complexes facilitated C-H borylation with a yield of 72%. Furthermore, we observed a 68% yield in aziridination reactions catalyzed by these immobilized complexes. Insights gleaned regarding surface interactions and their consequential effects on reaction kinetics and selectivity will inform the rational design of future heterogeneous photoredox catalysts. Current efforts are directed toward expanding the substrate scope and exploring additional organic transformations, including reductive dehalogenation.

Ir(III) complexes were synthesized and characterized by NMR, UV-Vis, and electrochemical methods. Immobilization on silica was achieved via silanol and phosphonic acid linkages, with surface coverage quantified by contact angle and XPS.



Pendant-base catalysts for homogeneous hydrogenation of CO_2 to MeOH

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[1]Homogeneous and Supramolecular Catalysis, Van 't Hoff Institute for Molecular Sciences, University of Amsterdam

The hydrogenation of CO_2 and CO_2-derivatives using a homogeneous, molecularly defined catalyst has been widely explored in recent years, but most examples are limited to low TONs, which limit their applicability compared to heterogeneous catalysts for the same reaction. This is mostly due to slow steps in the catalysis, one of the most relevant being the H_2 splitting. In this project, this slow step is tackled using metal-ligand cooperation. In the case of H_2 splitting, Ir- and Co-based homogeneous catalysts bearing a pendant base in the ligand backbone were synthesized, using the commercially available and air-stable terpyridine ligand, but affording a dynamic bidentate coordination. The dynamicity of the coordination allows for a proton shuttle behavior that can aid H-H splitting by metal-ligand cooperation, which allows for facile hydride formation.

Development of cooperative late transition metal complexes for Dehydrocoupling of amine boranes

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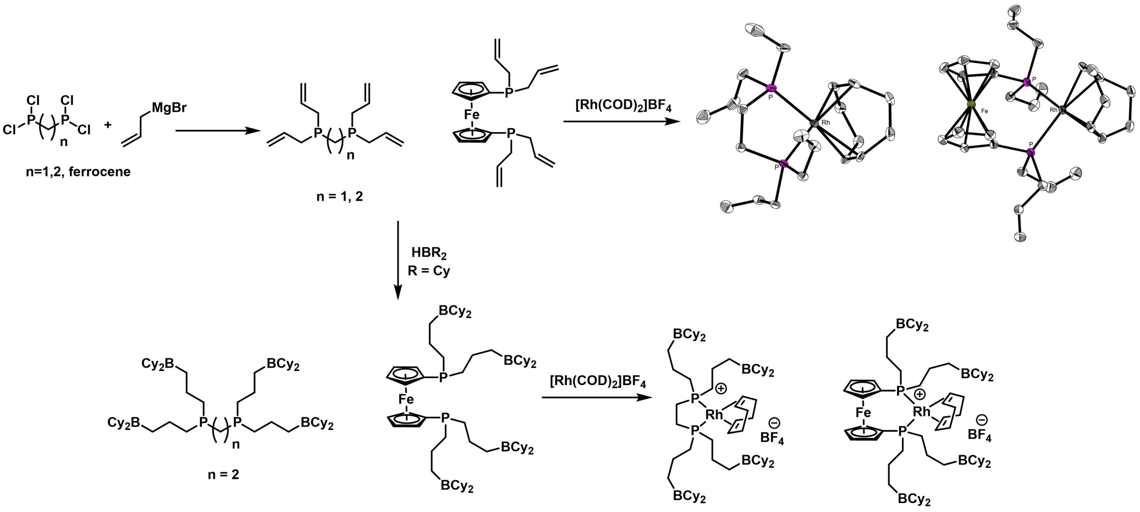
The analogy between B-N and carbon-based compounds and the expanding interest in polymeric materials based on main-group elements makes boron-nitrogen based polymers interesting targets. B-N polymers are promising compounds for applications as preceramics or as non-linear optical materials.[1] Catalytic dehydropolymerisation of primary amine boranes provides a promising atom efficient route to access these polymers. Compared to traditional methods such reductive coupling or high temperature condensation this method allows to adjust polymer properties.[2] Several groups have demonstrated that primary amine-borane adducts can be dehydrocoupled using various transition metal complexes to afford a linear poly(aminoboranes).[3] In recent years, our group focused on group 8/9 complexes bearing phosphorous based pincer ligands. Recently, we reported the use of Rh(I) PNN pincer complexes for dehydrocoupling of amine boranes.[4] Cationic Rh(I) diphosphine complexes were first studied by the Weller group and showed good activity for the dehydropolymerisation of methylamine borane.[5]



Here, we report the synthesis new phosphine ligands with introduction of Lewis acidic borane units in the secondary coordination sphere, as well as their complexation with Rh, producing a set of new Rh(I) complexes that could be used as catalysts for the dehydrocoupling of amine boranes. The role of the borane functionality for the activity and selectivity of the systems is discussed.

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Fe(III) complexes as photocatalysts for photopolymerization reactions, hydrogels preparation and copolymerization

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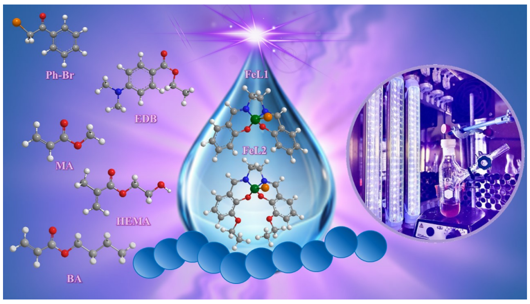
Light-activated polymerization is transforming industries by offering a more sustainable alternative to traditional thermal processes. By reducing energy consumption and minimizing the release of volatile organic compounds, this technology is driving innovation and expanding its impact across a wide range of applications[1].

Iron-based catalysts are highly sought after for their low toxicity, affordability, and biocompatibility. Their widespread availability makes them an excellent choice for sustainable catalytic processes[2]. Therefore, this study focuses on the synthesis and evaluation of Fe(III) complexes with symmetric Schiff base ligands as photocatalysts in the controlled radical photopolymerization of methyl acrylate (MA).

Additionally, Fe(III) complexes are water-soluble and were explored for the fabrication of polymerized hydrogels from 2-hydroxyethyl methacrylate (HEMA). With their soft texture and high water content, hydrogels offer exceptional permeability and biocompatibility, closely mimicking human tissues. These qualities make them highly desirable for a wide range of biomedical applications[3].

Furthermore, Fe(III) complexes were investigated for the synthesis of block copolymers (PHEMA-β-PBA). Theses systems utilizes three components, including photocatalysts and additives (Fe(III)/Ph-Br and EDB) under 365 nm LED irradiation.



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Acknowledgements

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Selective activation of aromatic C-H bonds by a new (PSiP)Ni complex

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The selective functionalization of aromatic C-H bonds represents an important challenge in the pursuit of sustainable synthetic processes.[1] Given that a wide range of pharmaceuticals contain fluoroaromatic moieties, there is a specific interest in the activation of C-H bonds of fluorinated molecules. For some transition metal complexes, however, competing C-F activation can lead to undesired byproducts.[2] This competition has been extensively studied in the oxidative addition of aryl fluorides by nickel(0) complexes.[3,4] Whereas oxidative addition of the C-H bonds can be observed in solution, the isolation and complete characterization of the respective products remains extremely rare.[4] This can be attributed to the highly reversible C-H activation, combined with a thermodynamic preference for C-F activation.[3] Therefore, stoichiometric studies have been limited to a narrow scope of highly fluorinated substrates.

Herein, we present a new (PSiP)Ni complex, designed to promote the selective cleavage of aromatic C-H bonds in presence of C-F bonds. Due to their unusual stability, a series of C-H activation products could be isolated and characterized. Investigation of the mechanism via DFT studies sheds light into the supporting role of silicon during the C-H activation and in the stabilization of the product.

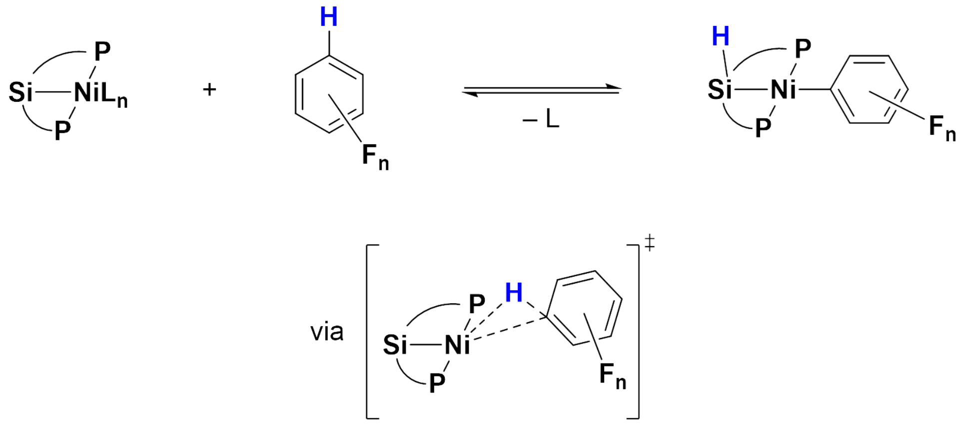

Figure 1. Simplified scheme showing the product resulting from C-H activation of a fluoroarene by the (PSiP)Ni complex.

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About the versatile Rh(I) aminophenol chemistry

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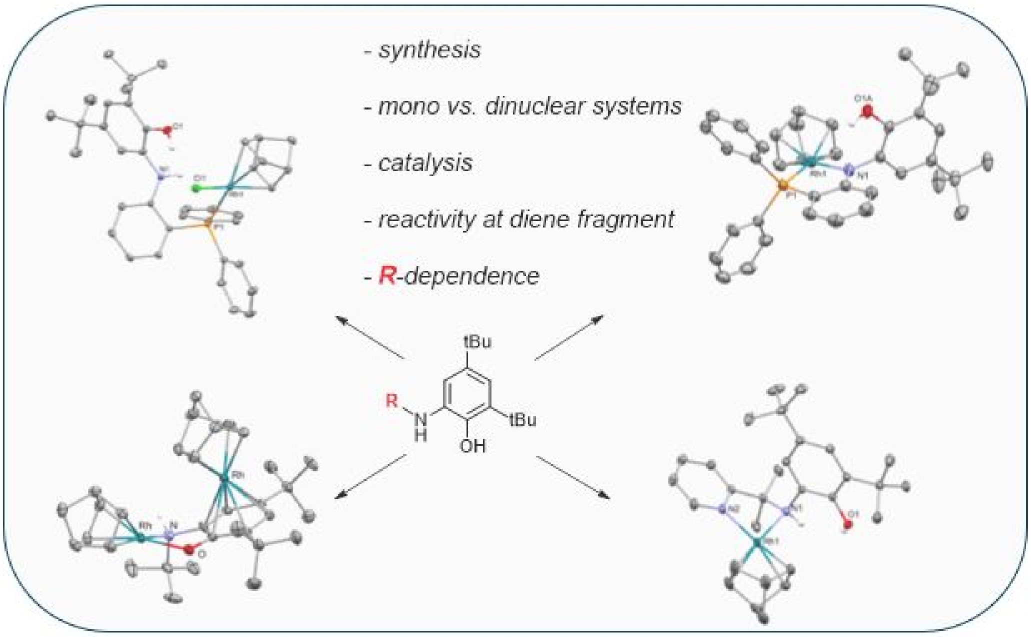
Combining redox-active, non-innocent ligands with transition metals gives the complexes unique properties. Of particular note is the access to new reaction pathways for the selective preparation of a broad spectrum of synthetically useful compounds.[1] Our group exploited tridentate PNO^{H2} and NNO^{H2} ligands with a $Pd^{\mathbf{II}}$ platform for homolytic bond activation of disulfides or the aminocyclization starting from organic azides, mediated by Pd^{II}.[2,3] Inspired by these results we currently focus on isoelectronic $Rh^{\mathbf{I}}$ complexes, including radical diene/π-system complexes and their intrinsic redox chemistry. The investigated Rh(I) complexes show considerable differences in their structure and subsequent reactivitiy depending on the precursors and substituted aminophenol ligands used.

We will report on their synthesis, characterization using multinuclear NMR spectroscopy, UV-Vis absorption spectroscopy, cyclovoltammetry, EPR and XRD analysis supported by DFT calculations. In addition, first avenues regarding catalytic applications will be discussed.



- *synthesis*
- *mono vs. dinuclear systems*
- *catalysis*
- *reactivity at diene fragment*
- ***R**-dependence*

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Heavy Alkali Metal Complexes of N-Heterocyclic Carbenes

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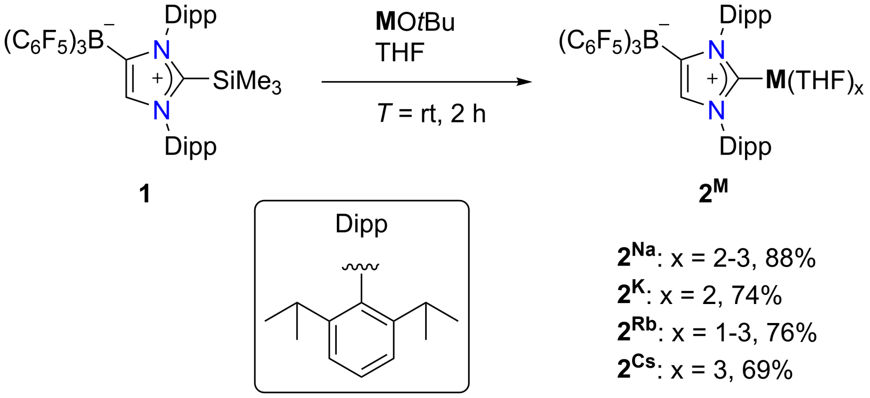
The strong σ-donating N-heterocyclic carbenes (NHCs) stabilize elements spanning almost the entire periodic table. The heaviest alkali metals represent one of the few exceptions, and no rubidium or cesium containing NHC complexes are reported.[1]

Most well characterized alkali metal NHC complexes involve lithium, while significantly fewer examples are known for sodium and potassium.[2] A common strategy to stabilize such heavier alkali metal complexes involves the use of NHC ligands bearing anionic functionalities to obtain overall charge-neutral species. These complexes are typically accessed via deprotonation of the NHC precursor with suitable alkali metal bases, with monomeric forms often stabilized by additional coordinating moieties.[3] In our group, Schlosser-type base combinations were employed to access the sodium complex $\mathbf{2}^{\mathbf{Na}}$; however, attempts to synthesize the potassium analog $\mathbf{2}^{\mathbf{K}}$ instead resulted in the formation of mixed lithium-potassium salts.[4]

To avoid the use of multiple metals, we now report the synthesis of alkali metal complexes *via* desilylation of the trimethylsilyl (TMS)-protected NHC **1**. Treatment with alkali metal *tert*-butoxides M(O*t*Bu) (M = Na, K, Rb, Cs) affords well-defined complexes $\mathbf{2}^{\mathbf{Na\text{-}Cs}}$ as tetrahydrofuran (THF) solvates. These compounds have been fully characterized by NMR spectroscopy, single-crystal X-ray diffraction, and elemental analysis.



$\mathbf{2}^{\mathbf{Na}}$: x = 2-3, 88%
$\mathbf{2}^{\mathbf{K}}$: x = 2, 74%
$\mathbf{2}^{\mathbf{Rb}}$: x = 1-3, 76%
$\mathbf{2}^{\mathbf{Cs}}$: x = 3, 69%

Scheme 1: Synthetic route to alkali metal complexes $\mathbf{2}^{\mathbf{Na\text{-}Cs}}$, with the solvent content as determined by X-ray diffraction analyses.

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Reactivity studies of heterobimetallic Fe-Cu complexes supported on dipyrrin and tpa

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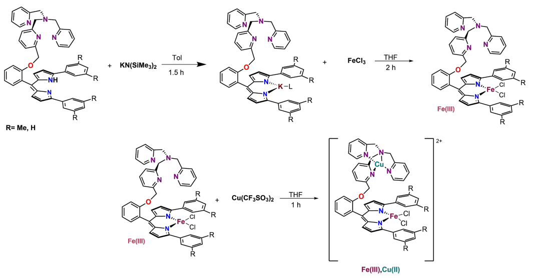
style="text-align: justify;">Heterobimetallic Fe-Cu complexes with Fe-porphyrin tethered to a Cu-tpa have been studied by Karlin for their use as cytochrome C oxidase analogues that mimic the activity of the active site (tpa = tris(2-pyridylmethyl)amine).[1] While the majority of work on this kind of Fe-Cu complexes has been focused on the use of porphyrin as the platform for Fe, we have focused on the use of dipyrrin moiety as an open version of the porphyrin to simplify the purification, enhance the yield, and increase the scale.[2] In this poster, we will discuss the synthesis of two binucleating ligands and their Fe-Cu complexes, having variations in the aryl group of the dipyrrin fragment (Scheme 1). Preliminary work on electrocatalytic reduction of CO_2 will be included, along with DFT calculations of possible adducts of C_2 products. Additionally, the synthesis of mononuclear Cu(I), Cu(II) and Fe(III) complexes on dipyrrin ligands was developed to compare their activity on electrochemical CO_2 reduction.[3]

Scheme 1. Synthesis of complexes.



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Design and synthesis of triazole based macrocycles for AFM studies

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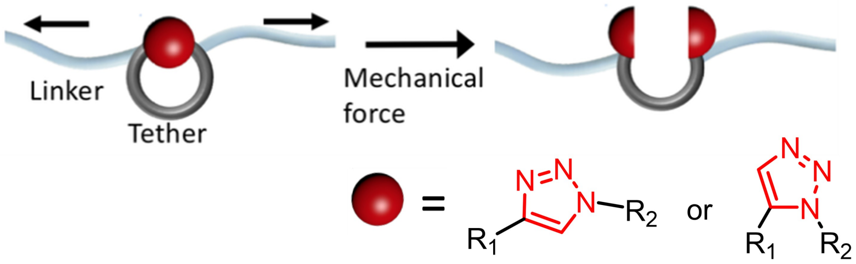
The 1,3-dipolar cycloaddition between an azide and an alkyne, commonly known as the "click chemistry" reaction, is a powerful synthetic tool that forms 1,2,3-triazole compounds.[1] These triazoles are highly versatile building blocks with wide applications in various fields, including biology,[2] polymer science, and materials science.[3]

The cycloaddition process to form the 1,2,3-triazole motif is strongly favoured thermodynamically. As a result, the triazole product is stable towards most thermal and chemical treatments. It can tolerate high-temperature treatment and normal-light irradiation. The mechanical reversibility of click reactions is largely unknown.[4] Single-molecule force spectroscopy (SMFS) has contributed to developments in mechanochemistry by enabling the mechanical activation of covalent bonds,[5] with applications in irreversible bond scission and opening of mechanophores.[4,6]

To address the potential mechanochemical cycloreversion of 1,2,3-triazoles, we designed tethered ring-opening mechanophores that allow the investigation of the mechanochemical activation of a triazole on the single-molecule level. Herein, we present the multistep synthesis of a ring-opening mechanophores which will be studied by single-molecule force spectroscopy (SMFS).



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Design of Bis(amino)silane Ligands: Synthesis, Structure, Reactivity with Organolithium Compounds, and Activation of Polar Substrates

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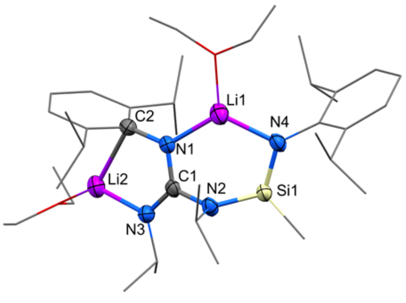
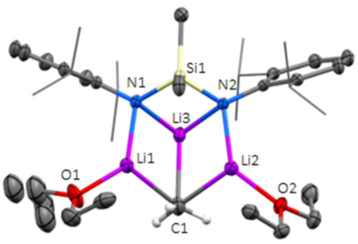
Sterically hindered lithium bis(amino)silanes were synthesized and structurally characterized to evaluate their potential as highly reactive polar organometallic intermediates. Employing stepwise lithiation with n-BuLi under inert conditions, mono- and bis-lithiated species were obtained and analyzed via multinuclear NMR (^{1}H, ^{13}C, □Li) and single-crystal X-ray diffraction (SC-XRD).

The introduction of bulky aryl substituents on nitrogen significantly influenced coordination geometries and aggregation states. Reactions with ethers such as diethyl ether demonstrated unprecedented C–O bond cleavage, yielding well-defined lithium alkoxide clusters.

In addition, reactivity with N,N′-diisopropylcarbodiimide afforded lithium amidosilylguanidinates, providing new insights into nucleophilic addition pathways involving polar metal-ligand frameworks. These findings open new perspectives on ligand behavior in main-group element chemistry and the design of controlled synthetic routes to low-valent compounds. The results represent a step forward in the development of reactive, low-coordinate main-group complexes for small molecule activation and novel bond-forming processes.





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

From Zirconium to Iron: Activation of Transition Metal Catalysts with the SiHB System

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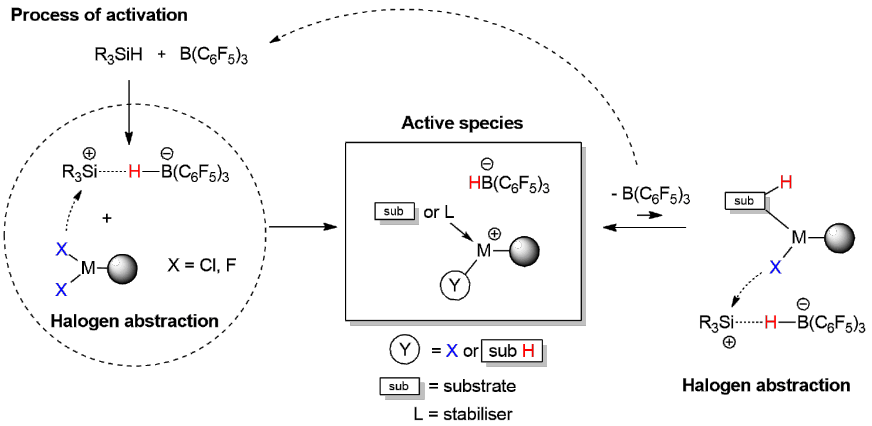
The transition metal/hydrosilane/borane adduct (SiHB) system offers a novel approach to the activation of transition metal catalysts. This method involves the sequential reaction of hydrosilane with a Lewis acid borane, typically $B(C_6F_5)_3$, and a transition metal-halogen complex. The SiHB system represents a valuable alternative to traditional activators such as methylaluminoxane (MAO) or alkylaluminium/borate salts in catalytic carbon-carbon bond formation reactions, where the structure of the transition metal complex is critical in determining activity and selectivity towards specific product configurations. In general, the proposed mechanism involves hydride transfer from hydrosilane to $B(C_6F_5)_3$ and subsequently to the transition metal, which directly activates readily available halide complexes by forming a metal-hydride bond essential for catalytic performance.

Proposed activation mechanism of the SiHB system



Since 2016, we have reported the study of the SiHB system for the activation of early transition metal halide complexes (Ti, Zr, Cr) in the catalytic (co)polymerisation of olefins and hydrodehalogenation reactions. In 2024 we extended the application of the SiHB system to the activation of late transition metal halide complexes, specifically Ni and Fe. In the selected examples, the activation led to an unprecedented synthesis of hydrosilyl-terminated polyethylenes, opening new avenues for the development of functionalised polymeric materials. The talk will highlight these recent advances in catalytic applications of the SiHB system using some earth-abundant transition metals.

This work was supported by the AMULET project (No. CZ.02.01.01/00/22_008/0004558).

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Amino derivatives of cyclophosphazenes: interesting ligands with fluorescent properties

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Cyclophosphazenes are inorganic ring compounds consisting of phosphorus and nitrogen atoms. They have found many applications over the years (flame resistance, catalysis, fluorescent sensors, OLEDs, nanomaterials or biomedicine)[1] due to their properties, such as chemical stability, solubility in organic solvents, variable coordination modes or optical and magnetic properties.

In this contribution we report on extending the family of amino derivatives of cyclotetraphosphazenes (see examples in Figure 1) and investigating their properties in solution and in the solid state. These derivatives exhibit significant fluorescence behaviour on its own, however, these properties can be possibly influenced (and tuned) by protonation of the amino groups or by coordination of metal ions of inorganic salts to the substituent groups and/or by interaction of the anion with the amino groups.

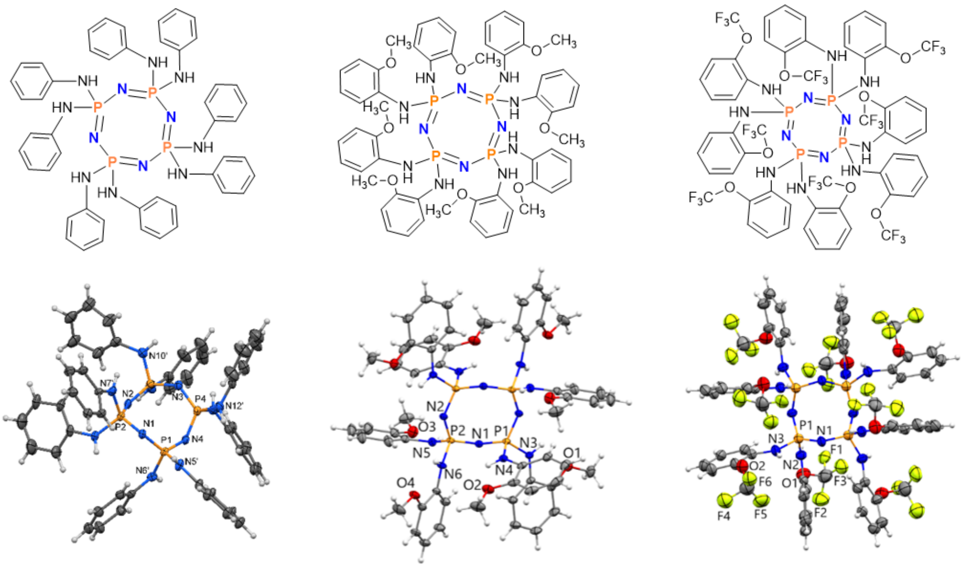

Figure 1: Examples of prepared anilino derivatives of cyclotetraphosphazenes.

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Enhancing Reactivity with Caesium Amides

T. M. Horsley Downie[1], P. Ferguson[1]*, P. A. Macdonald[1]*, S. D. Robertson[1]*, R. E. Mulvey[1]*

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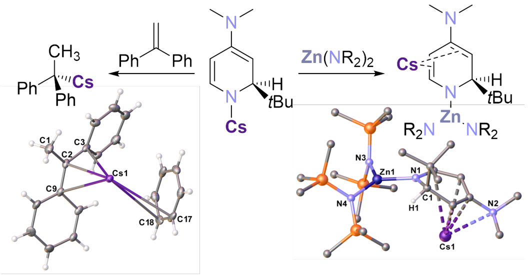
The role of alkali metal complexes as synthetic workhorses is longstanding,[1] but over the past two decades their capabilities as catalysts and pre-catalysts in their own right for a series of transformations has gradually emerged.[2] Our recent studies have established that the heavier alkali metals in particular can exhibit much greater capabilities in certain mediating applications than their lighter congeners.[3,4]

Herein, we report the synthesis and reactivity of a range of caesium complexes. In particular, facile synthetic methodologies allow generation of an array of different amide species. Despite straightforward isolation, the most extreme of these readily react with most solvents. However, though careful tuning of the electronics, moderation can be achieved. This yields species displaying significantly enhanced reactivity than that of common utility amides, while more conveniently handled. Our investigations show that these complexes offer potential in both synthesis and catalysis, as well as in the formation of novel bimetallic species.[5]



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Two-Coordinate Anionic N-Heterocyclic Carbene Zinc Complexes for the 1,2-Regioselective Hydroboration of N-Heteroarenes, and Catalytic Hydroboration of Ketone, Ester, and Nitrile

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N-heterocyclic carbenes (NHCs), by having strong σ-donating properties and steric tunability, are effective ligands that provide remarkable stability to (NHC)Zn complexes.[1-3] Among these, anionic NHCs bearing weakly coordinating anions (WCA), specifically $[(C_6F_5)_3B–NHC]Li(solv)$, demonstrate significant efficiency in forming neutral, low-coordinate complexes with high solubility.[4] Hence, [(WCA-IDipp)ZnHMDS] (**2**) and $[(WCA\text{-}IDipp)Zn(CH_2SiMe_3)]$ (**3**) were prepared from [(WCA-IDipp)Li(tol)] (**1**) through one-pot method (Figure 1). These neutral complexes **2** and **3** display high solubility, and the enhanced Lewis acidity at the zinc atom due to low coordination of Zn(II), increases the electrophilic character. The monomer structure of complexes **2** and **3** feature a linear C–Zn–C arrangement with sp-hybridized Zn(II) center and two low-lying vacant p orbitals available for substrate activation.

Zinc complexes have attracted significant attention for applications in catalysis due to the abundance, low cost, and low toxicity of zinc. In this context, we utilized the high catalytic activity of complexes **2** and **3** for the regioselective 1,2-hydroboration of N-heteroarenes. Additionally, complex **2** displays excellent performance in the catalytic hydroboration of ketone, ester, and nitrile showing its versatility and efficiency in organic transformations.

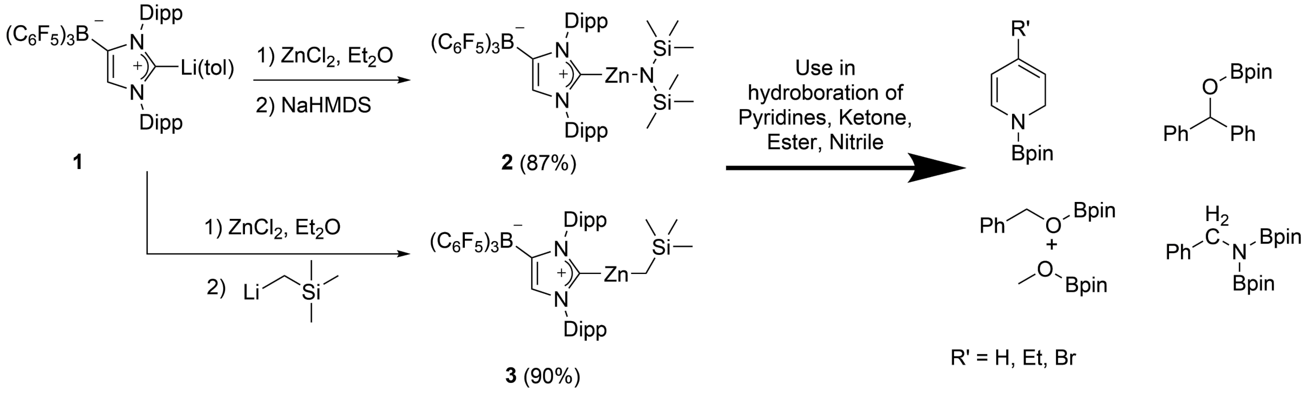

Figure 1. Preparation of complexes **2** and **3**, and their application in hydroboration of pyridines, ketone, ester, and nitrile; Dipp = 2,6-diisopropylphenyl.

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From N2–methylated Triazoles to β-diketiminate–like Complexes: A Route via Selective Triazolium Ring Cleavage

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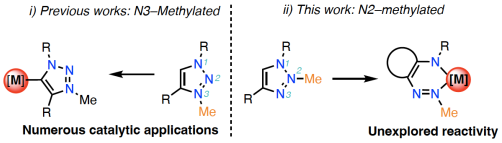
1,2,3–substituted triazoliums are a prominent class of ligand precursor in carbene chemistry, serving as versatile NHC precursors and being applied to a myriad of catalytic reactions.[1] Typically, methylation of 1,2,3–triazoles proceeds exclusively at the N3–position. Here we demonstrate for the first time that it is possible to selectively methylate 1,2,3–triazoles at the N2 position, in contrast to this central dogma of triazolium chemistry. Even more striking, our investigations reveal “hidden” reactivity in the corresponding 1,2,4– triazolium. Metalation with various metal precursors leads to cyclic N–N bond cleavage and complexes that are analogous in structure to common β-diketiminates.[2,3] This unique pathway broadens the synthetic scope of triazolium chemistry and opens opportunities for novel metal complexes and their catalytic transformations.



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Alkali Metal Complexes of a Phosphine− Functionalized Cyclooctatetraene

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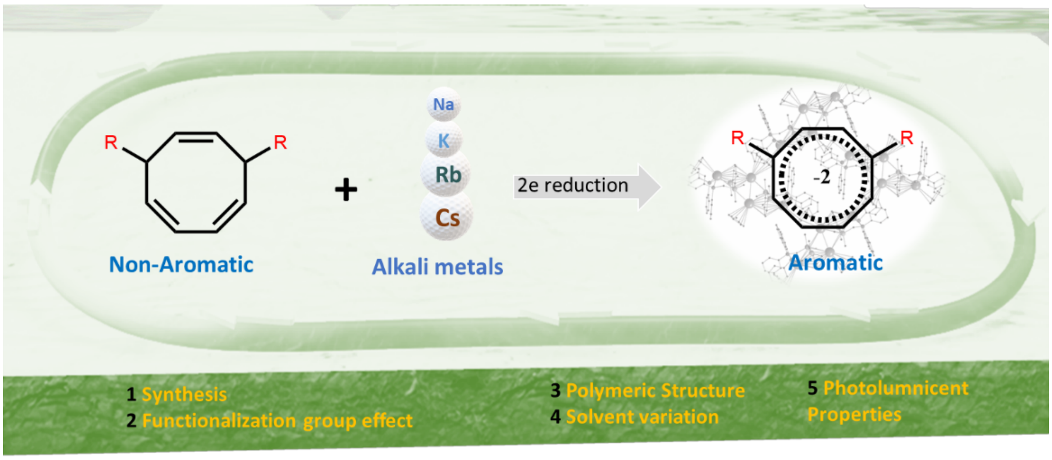
We reported the synthesis and characterization of a novel phosphine-functionalized cyclooctatriene (COT) ligand, (1,4-bis(dimethylsilylmethyl)diphenylphosphinecycloocta-2,5,7-triene), and its alkali metal complexes, $M_2[C_8H_6\text{-}1,4\text{-}(Me_2SiMePPh_2)_2]$ (M = Na, K, Rb, Cs). Structural analyses reveal polymeric architectures influenced by crystallization solvents, with the rubidium complex forming an eight-membered polymeric structure in benzene. UV-vis and photophysical studies highlight luminescent properties, while reactivity with alkali metal tert-butoxides demonstrates efficient metal exchange, enabling synthesis of analogous complexes. These are the first structurally characterized alkali metal complexes featuring a functionalized cyclooctatetraene ligand.



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Bis(Boryl) and Triply Bridging Borylene Complexes of Ruthenium

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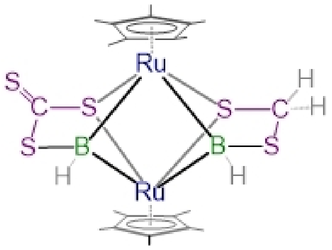
Recent years have witnessed significant growth in the field of transition metal (TM) boron chemistry. Among them, the TM-boryls and borylene complexes have gained extensive attention due to their unique structures, ability to undergo interconversions and their applications in various organic transformations.[1] TM-boryl complexes are found to be the key intermediates in many catalytic cycles, for example, diboration, hydroboration and C–H borylation reactions.[2] In this regard, a new synthetic route for the synthesis of diruthenium boryls has been established by performing the reaction of $[Cp^*RuCl_2]_2$ with $[LiBH_4{\cdot}THF]$ followed by the addition of $[S_2CPPh_3]$ that resulted in a diruthenium bridging bis(boryl) complex, $[(Cp^*Ru)_2(\mu\text{-HBS(C=S)S-}\kappa^2B{:}\kappa^2S)(\mu\text{-HBSCH}_2\text{S-}\kappa^2B{:}\kappa^2S)]$ (**1**) consisting of two unsymmetrical boryl ligands.[3] On the other hand, when the reaction of $[Cp^*RuCl_2]_2$ was carried out with $[NaBH_4]$, this led to the formation of a triruthenium triply bridging borylene cluster $[(Cp^*Ru)_3(\mu\text{-H})_5(\mu_3\text{-BH})_2]$ (**2**) having trigonal bipyramid geometry in which both the {BH} fragments occupy the axial positions.[3] Further, to synthesize similar type of borylene clusters, we treated $[Cp^*RuCl_2]_2$ with $[LiBH_4{\cdot}THF]$ followed by the addition of $[M_2(CO)_{10}]$ (M = Mn and Re) which resulted to the isolation of group-7 trimetallic $[(Cp^*Ru)_2\{M(CO)_3\}(\mu\text{-H})(\mu\text{-CO})_3(\mu_3\text{-BH})]]$ [M = Mn (**3**) and Re (**4**)] clusters featuring triply bridging hydrido(hydro-borylene) moiety.[4] The key results of this work will be presented.



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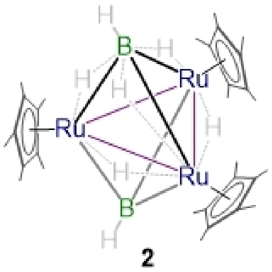

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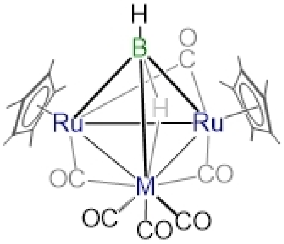

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Catalytic Conversion of Amino Acid-derived Oxetanes and CO_2 for Optically Active Polycarbonate Production

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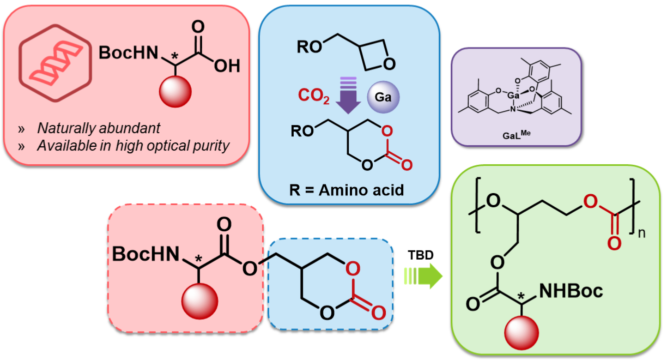
Bio-derived plastics, or polymers made partially from renewable sources, are becoming more popular as a sustainable alternative for standard plastics. Polycarbonates are a specific class of thermoplastic polymers that have found a variety of uses. Ring-Opening Co-Polymerization (ROCP) of oxiranes with carbon dioxide (CO_2) is a promising approach for the synthesis of these polycarbonates. Previously, a gallium-based catalyst system reported by our research team has been studied using epoxides,[1] however, oxetanes (4-membered oxiranes) have received less attention. When highly functionalized oxetanes are involved, direct ROCP faces limitations. An alternative approach involves the Ring-Opening Polymerization (ROP) of six-membered cyclic carbonates, enabling more diverse monomers. This strategy is preferrable since an organocatalyst like triazabicyclodecene (TBD) can promote the ROP under mild reaction conditions.[2] Using our gallium-based catalyst system, we will prove how it is possible to synthesize the six-membered cyclic carbonates with an amino acid functionality incorporated into the structure. In this study, we will show that the inherent stereochemistry of these amino acids may be transferred to final polymer products through preparation of oxetanes with amino acid functionality, formation of the corresponding six-membered cyclic carbonate and then, subsequent ROP of these cyclic carbonate monomers.[3] As a result, new optically active polycarbonates were achieved.



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A Versatile Pyridonate-NHC Ligand Platform in Iridium Coordination Chemistry and Catalysis

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N-Heterocyclic carbene (NHC) ligands continue to generate great interest, as these platforms exert significant control over the reactivity, selectivity and catalytic efficiency of both homogeneous and heterogeneous systems. The functionalization of these ligands enables, for instance, the introduction of coordinating groups that allow polydentate coordination, increasing the stability of the metal species involved in different stages of the catalytic cycles. Moreover, the introduction of specific functional groups with acid/base properties can promote external sphere mechanisms, which are highly relevant in catalysis.[1]

In this regard, the incorporation of hydroxypyridine fragments into the NHC structure gives rise to proton-responsive ligands that show promising potential. Metallic complexes with these ligands have enhanced hydrophilicity due to the high polarity and protic character of this group, whereas the hemilability of the N/O moieties may lead to easier generation of vacant coordination sites during catalysis.[2] Under this premise, Ir-NHC complexes containing one or two 2-hydroxypyridine fragments in the ligand's structure have been prepared (Figure 1). The chosen auxiliary ligands were Cp* or cyclooctadiene, the latter remarkably appearing in an unsual κ^1,η^3 coordination mode in some compounds what means that such a reaction should be initiated by an intramolecular C-H activation of the COD ligand and followed by either inter- or intramolecular insertion, or reductive elimination and further C-H activation elementary steps. Deprotonation of the 2-hydroxypyridine fragment leads to the pyridonate functional group, forming anionic NHC ligands that allow modulation of the charge, solubility and catalytic activity of the complexes.[3] Because of their interesting properties, the reactivity of these complexes towards several small molecules such as molecular hydrogen and oxygen, and carbon monoxide or alkynes has been explored. These complexes have proven to be efficient and versatile catalyst in several processes, including the acceptorless dehydrogenation of primary alcohols and formic acid, as well as water oxidation.

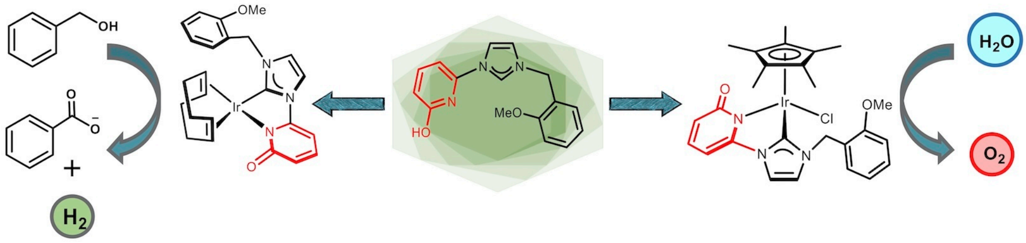

Figure 1. Iridium complexes with pyridonate-functionalized NHC ligands active in acceptorless dehydrogenation of benzyl alcohol and water oxidation catalysis

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Regioselective Direct Cobaltation of *N*-heterocyclic Molecules Mediated by a Super Basic Co(II) Amide

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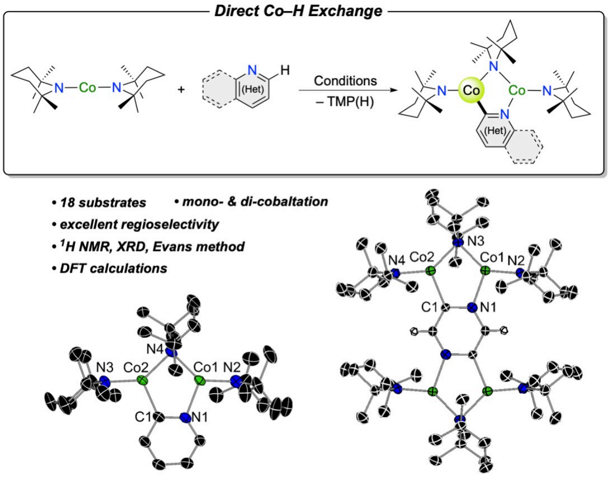
Exemplified by pyridine and pyrimidine, azines and diazines are among the most important *N*-heterocyclic motifs ubiquitous in pharmaceuticals and materials.[1] Despite their synthetic relevance, their metalation using traditional alkali metal bases has numerous drawbacks including harsh conditions and low selectivity.[2] When it comes to cobalt-catalysed C–H functionalisation of pyridines and diazines, many literature reports have hinted at a C–H activation mechanism via oxidative addition,[3] although very few have been structurally authenticated.[4] Recently our group reported the synthesis and characterisation of a novel cobalt(II) bis-amide Co(TMP)$_2$ (TMP = 2,2,6,6-tetramethylpiperidide) and its ability to promote direct Co–H exchange reactions with a range of fluoroarenes.[5]Expanding this reactivity to *N*-heterocycles, here we report the deprotonative metalation of pyridines and diazines with Co(TMP)$_2$ to afford mono- and di-metalated species without changing the oxidation state of the metal centre. Structural elucidation of the products confirmed the formation of new Co(II)-C$_{\text{het}}$ bonds. DFT calculations were employed to shed light on the unique *ortho*-N regioselectivity in these transformations.



- *18 substrates*
- *mono- & di-cobaltation*
- *excellent regioselectivity*
- *^{1}H NMR, XRD, Evans method*
- *DFT calculations*

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Reduction of Nitrite in an Iron (II)-nitrito Compound by Thiols and Selenol Produces Dinitrosyl Iron Complexes via an $\{FeNO\}^7$ Intermediate

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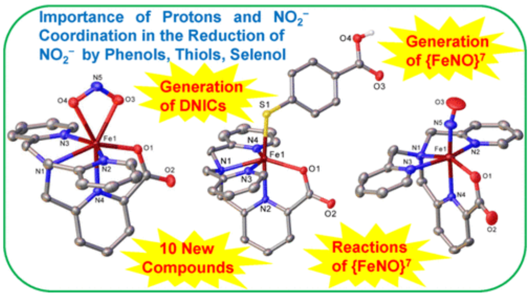
Reaction of a Fe (II) complex, [Fe(6-COO$^-$-tpa)]1+ (1) with PhE$^-$ and NO2$^-$ produced [Fe(6-COO$^-$-tpa) (EPh)] (E = S, 2a; Se, 3) and [Fe(6-COO$^-$-tpa) (κ2-O, O′-NO2)] (4), respectively (6-COOH-tpa is bis(2-pyridylmethyl) (6-carboxyl-2-pyridylmethyl) amine). Treatment of 4 with 2 equiv of PhEH (E = S, Se) produced NO in ~ 40% yields, respectively, along with 1 and the DNICs, [Fe(EPh)2(NO)2]1$^-$ (E = S, Se). Treatment of 4 with excess PhEH produced NO in similar yields while 4 was converted to the same DNICs and 2a/3 (instead of 1). The DNICs have been proposed to generate via the reaction of PhE$^-$ with an in situ generated, unstable {FeNO}7 intermediate, [Fe(6-COO$^-$-tpa) (NO)]1+ (6), which has also been sythesized separately. Compound 6 reacts with PhS$^-$ to generate [Fe(SPh)2(NO)2]1$^-$, thus supporting the proposed reaction pathway. Finally, while the treatment of two unique compounds, featuring inbuilt proton sources, [Fe(6-COO$^-$-tpa)(S-C6H4-p-COOH)] (7) and [Fe(6-COO$^-$-tpa)(S-C6H4-o-OH)] (8), with 0.5 and 1 equiv of NO2$^-$ could produce NO only in 8-26% yields, treatment of 4 with HS-C6H4-p-COOH and HS-C6H4-o-OH produced NO in much higher yields (65-77%). The combined results delineated the importance of the coordination of NO2$^-$ for the proton-assisted reduction of NO2$^-$ to generate NO.



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From tellurophene-containing porphyrinoid to organoosmium macrocycles with variable geometries

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Porphyrin is an excellent four-donor ligand, capable of binding almost all metal ions. In the classical porphyrin complex - metalloporphyrin - the metal ion is bound in the 4N coordination cavity. A new type of metal binding in porphyrins is the formation of *metallaporphyrins* in which the transition metal ion replaces the NH group, forming a metal-carbon bond. In such organometallic porphyrinoids, the pyrrole ring is replaced by a metalacyclopentadiene ring. The metallaporphyrins obtained and described so far were formed by replacing a tellurium atom(s) in 21,23-ditelluraporphyrin with Pd^{II}, Pt^{II}, Pt^{IV} or Rh^{III} [1-4]. Metalation of an expanded telluraporphyrinoid composed of four pyrroles and four tellurophenes, tetratelluraoctaphyrin, with $[Ru_3(CO)_{12}]$ resulted in the formation of an organometallic diruthenium compound with two 1-ruthena-2-telluracyclohexadiene units [5].

We will show investigations whether 26,28-ditellurapentaphyrin(1.1.1.1.0) **1**, which consists of three pyrroles and two tellurophenes, would be a suitable platform for the formation of expanded metallaporphyrins. The metalation of **1** with $[Os_3(CO)_{12}]$ was carried out. Depending on the reaction conditions, mono- and bis-osmium(II) complexes **2** and **3** were obtained. The reaction also resulted in the removal of one or two tellurium atoms from the macrocyclic skeleton, yielding organoosmium(II) complexes of annulene-porphyrinoid hybrids **4**, **5** and **6**, which exhibit a variety of macrocyclic skeleton geometries.

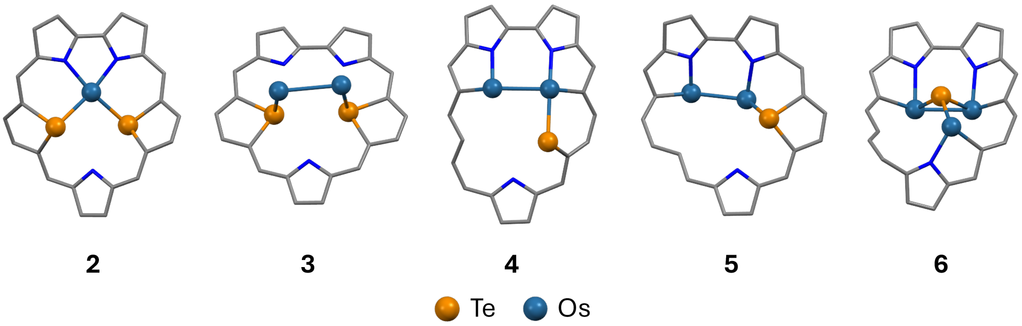

*Figure 1. X-ray structures (**2**,**3**,**5**,**6**) and DFT model (**4**) of osmium(II) complexes of expanded porphyrinoids. Hydrogen atoms, additional ligands and peripheral substituents are not shown.*

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Prussian White $K_2MnFe(CN)_6$–Carbon Nanotube Electrode Materials for Energy Storage Applications

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This study is focused on a composite material consisting of the Prussian white analogue $K_2MnFe(CN)_6$ (K-MnHCF) with modified carbon nanotubes (CNTs), used as a promising high-energy cathode for potassium-ion batteries (PIBs). The incorporation of the carbon network to the Prussian white analogue prepared through a facile chelating agent-assisted precipitation method provided control over the particle features, crystallization defects, and lattice moisture compared with the material prepared without it. Thus, at low current rates of 0.1 and 0.5 C in a given voltage window of 2.7–4.4 V vs K/K^+, the K-MnHCF–CNT cathode showed a high reversible capacity of 119 mAh g^{-1}, while the material without a CNT backbone delivered a capacity of 108 mAh g^{-1}, exhibiting a capacity loss during cycling. Operando X-ray diffraction analysis demonstrated the stability of the K-MnHCF–CNT cathode, showing a reversible two-phase structural transition from monoclinic to tetragonal via an intermediate cubic phase. Moreover, the operando analysis revealed that the incomplete phase conversion from the intermediate cubic to tetragonal phase, related to the Mn^{2+}/Mn^{3+} transition during charging in the K-MnHCF material without a carbon backbone, can be responsible for its structural instability. Ex-situ findings with the recovered active electrode supported the findings of the operando analysis. Thus, the K-MnHCF–CNT composite appears as a promising candidate for the development of suitable cathodes of PIBs for energy-storage applications.

Accessing the Synthesis of Dihydropyridine Derivatives through a Nucleophilic Organosodium Compound

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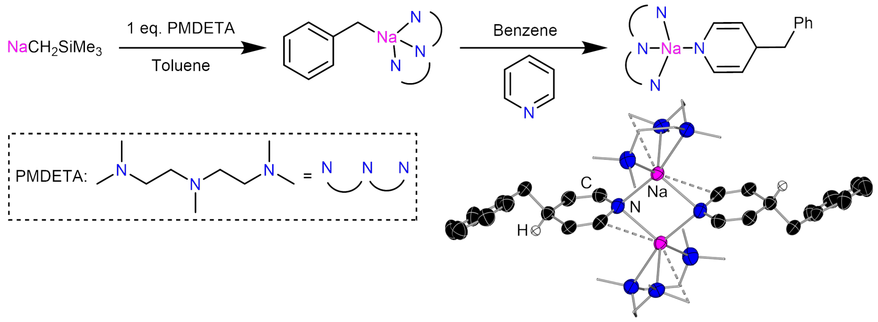
The availability and high reactivity of organolithium compounds combined with the great solubility in hydrocarbon solvents enabled their widespread use in organic synthesis.[1] Trying to find more sustainable alternatives, the much more earth-abundant and highly reactive sodium congeners have recently been found to be a powerful alternative.[2] Yet, the advantages of those compounds are undermined by their low solubility in hydrocarbon solvents and the challenge in handling. Previous work in our group has shown that N-donor PMDETA can be used to solubilize organosodium compounds, which increases their reactivity and opens new roads for C-H formation or deuteration reactions.[3-5]

Advancing the work in this field, we report the use of organosodium compounds for the formation of C-C bonds through nucleophilic attack on pyridines. This enables the formation of dihydropyridines, which are relevant in biological chemistry or in transfer hydrogenation.[6-7] We show how those reactions can be performed in a one-pot process, starting from the *in-situ* formation of benzyl sodium, followed by the addition of pyridine. Further, we investigate the different reactivities of the benzyl sodium compound by systematically changing pyridine to 3- and 4-picoline, where we show that changing the substrate leads to a change in reactivity. Lastly, we explore how the addition of the boron compound $B(CH_2SiMe_3)_3$ affects the selectivity of the reaction.



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Synthesis and complexation of tridehydro[12]annulene and tetradehydro[16]annulene fused with cyclohexene

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The versatility of dehydro[n]annulenes as ligands in transition metal complexes has been well documented, particularly with respect to their ability to coordinate metals within their central cavities. The cavity size of these π-conjugated systems is a critical factor, influencing whether they can accommodate first-row or heavier second-row transition metals [1-4]. Building upon our ongoing research into catalytic alkyne metathesis using molybdenum and tungsten alkylidyne complexes [5], we have synthesized tridehydro[12]annulene (**2**) and tetradehydro[16]annulene (**3**) via efficient one-pot reactions. Structural characterization by X-ray diffraction revealed that compound **2** adopts a planar geometry with an average triple bond-to-center distance of 2.05 Å, while compound **3** exhibits a tub-shaped conformation with an increased average distance of 2.65 Å, indicative of a larger and more flexible cavity. These findings have guided our strategy for selective metal complexation: compound **2** is being investigated for coordination with low-oxidation-state first-row transition metals (e.g., Ni(0), Cu(I)), whereas compound **3** is being explored for complexation with second- and third-row metals such as Pd(0), Ag(I), and Au(I). Notably, the reaction of compound **2** with Ni(COD)$_2$ in benzene afforded complex **4** in 95% yield. This complex was thoroughly characterized by XRD, NMR spectroscopy, and elemental (CHN) analysis. Ongoing studies aim to expand this series of complexes and further elucidate the coordination behavior and electronic properties of these novel dehydroannulene ligands.

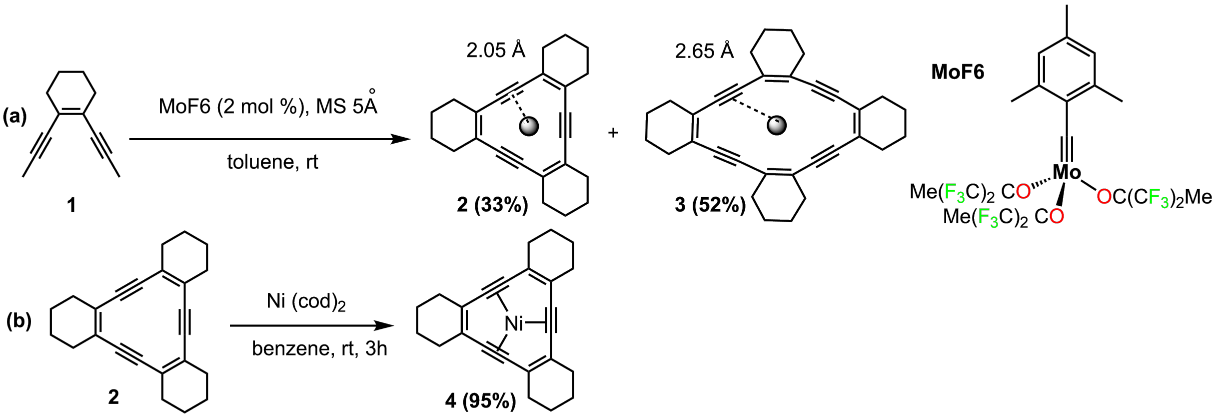

Figure 1. One pot synthesis of tridehydro[12]annulene (**2**) and tetradehydro[16]annulene (**3**) by alkyne metathesis (a); preparation of nickel complex of tridehydro[12]annulene (**2**) (b).

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Heavy Pnictogen Dipyrrins for Photochemical Applications

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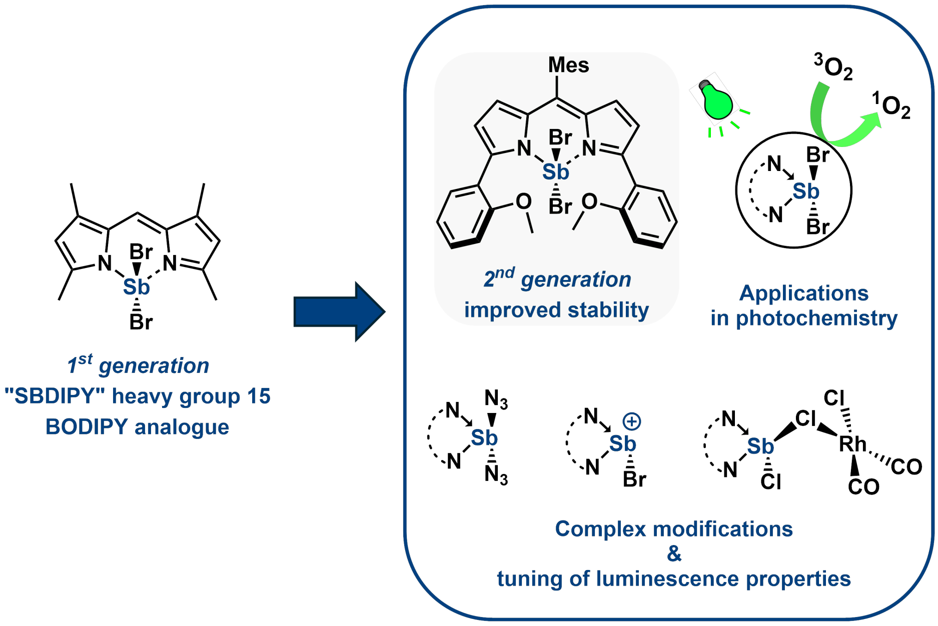
Boron-based dipyrrin chromophores (BODIPY) have found widespread applications in fields beyond synthetic chemistry due to their highly tuneable emissive features.[1] Despite advances in the field, dipyrrin complexes with different central atoms are considerably less studied. Recently, we reported the synthesis and characterization of novel chromophores based on the heavy pnictogens antimony and bismuth.[2] Spectroscopic studies through VT-UV/Vis and fluorescence spectroscopies revealed a temperature dependent decomposition event. Unfortunately, the resulting low stability of these chromophores has hindered any further applications. The current work highlights a new generation of heavy pnictogen dipyrromethene complexes with improved stability thanks to changes in the ligand design.[3] The most stable Sb-complex was found to perform especially well as a photosensitizer for singlet oxygen ($^1O_2$), achieving $^1O_2$ quantum yields as high as Φ_Δ = 0.76. Furthermore, methods for complex modification through halide substitution and metal coordination are described, along with their effects on photoluminescence properties.



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An N-Heterocyclic Germylene with a Versatile Metal-Binding Pocket: Insights into Heterodinuclear Bonding and Reactivity

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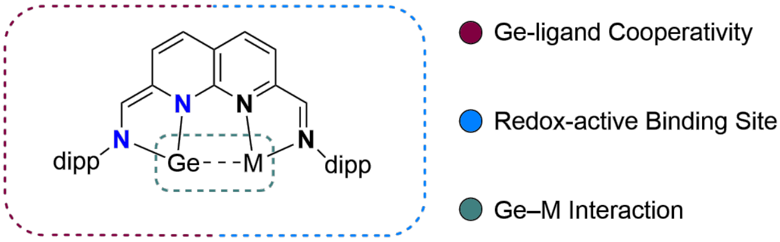
Germylenes are a promising class of complexes due to their versatile reactivity, including examples such as redox-reactivity arising from the Ge$^{II/IV}$ manifold,[1] or Ge-ligand cooperative activation of bonds.[2] Germylenes are also frequently used as ligands on transition metals and, combined with their ambiphilic nature, this can give rise to Ge–M cooperative activation of chemical bonds.[3] In contrast, Ge-main group combinations are underexplored. We report the synthesis, isolation, and characterisation of an N-heterocyclic germylene (NHGe) derived from a two-electron reduced Mg-synthon of the redox-active $^{\mathbf{dipp}}$**NBA** ligand.[4] This NHGe features a vacant binding pocket capable of coordinating various metals, which enables the formation of heterobimetallic Ge–Zn and Ge–Mg complexes. Electronic structure calculations reveal that the Ge–Zn interactions are weak, whilst the interactions between the metals found for the heterodinuclear Ge–Mg complex are stronger. These findings highlight how the nature of the Ge–M interactions adapts to the electron density requirements of the metal occupying the redox-active binding pocket flanking the Ge^{II} centre. Notably, the Ge–Mg complex undergoes a 'Metallo-Diels–Alder' reaction with unsaturated C–C bonds, activating these bonds over the Ge centre and the ligand backbone – a transformation that does not proceed without Mg. This provides a compelling example of indirect cooperativity, where the Mg centre electronically stabilises a quadruply reduced ligand, upon which Ge engages in metal-ligand cooperative activation of C–C unsaturated bonds.



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The first ferrocene-containing depsipeptides: antiproliferative activity and conformational preferences

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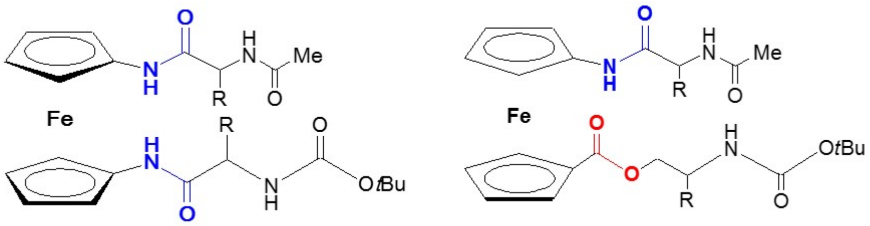
It is well known that natural depsipeptides are an important source of pharmacologically active compounds, as the ester bond replacing at least one amide bond, allows greater resistance to enzymatic degradation, increases biological activity and contributes to conformational changes to obtain stable secondary structural elements [1].

Since ferrocene-containing depsipeptides have not been previously described, the main objective of this work was to investigate the effects of replacing an amide bond in ferrocene peptides **I** with an ester bond in ferrocene depsipeptides **II** on (*i*) the hydrogen bonding pattern and formation of secondary structural elements and (*ii*) biological activity.

Therefore, we prepared six depsipeptides **II** (**1-6**) as analogues of previously described peptides **I** [2] to deduce the pattern of intramolecular hydrogen bonding and to investigate their antiproliferative activity (Figure 1). As expected, replacing an amide bond with an ester reduces the number of available hydrogen bond donors, which affects the conformational patterns. Of several cancer cell lines tested, MCF-7 cells were sensitive to treatment with depsipeptides **1-6**.



I **II**

Figure 1. Ferrocene peptides **I** and ferrocene depsipeptides **II**

[R = $–CH(CH_3)_2$, $–CH_2CH(CH_3)_2$, $–CH_2Ph$]

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Sulfanilic acid-capped Ru-Nanoparticles for enhanced HER activity in neutral media

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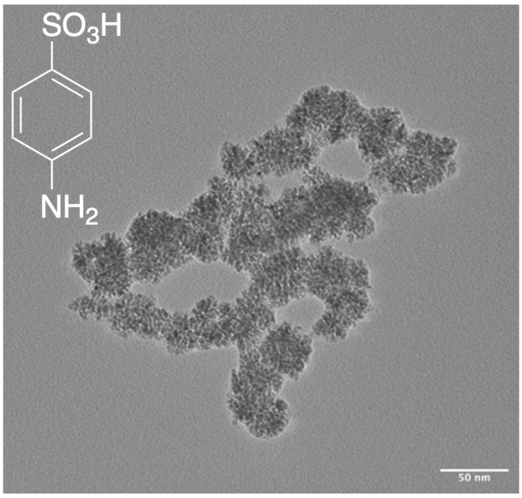
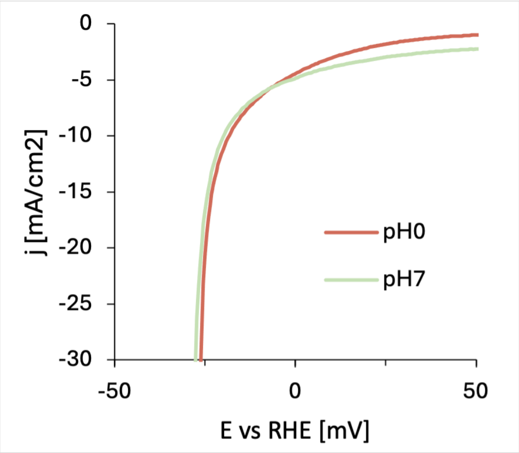
Metal-based nanoparticles (NPs) have experienced rising popularity due to their unique properties compared to their corresponding bulk metals or molecular metal complexes. They are now utilized in a broad range of applications, such as electrocatalysis, photo(electro)catalysis, and medicine. The advantage of NPs lies in their high surface-to-volume ratio, due to their small size. As a result, the availability of potential active sites on the surface is increased, which can lead to higher activity in catalytic reactions.[1] In our group, nanoparticles are synthesized via the organometallic approach, which allows for a clean modification of the surface and a narrow size distribution of the particles. By decomposing an organometallic precursor with hydrogen under mild conditions in the presence of the ligand of interest, the nanoparticle contains only the chosen ligand on the surface, with no contaminants or by-products that could alter the activity (**Fig. 1**).[2]



In particular, the hydrogen evolution reaction (HER) requires new materials that can maintain high activity in seawater or wastewater.[3] To work towards this objective, in this contribution we report sulfonate-capped Ru-based NPs where the negatively charged ligand is intended to repeal chloride anions from seawater. This catalyst has been preliminary tested in freshwater at pH 0 and pH 7 showing comparable activity in both media (**Fig. 2**).



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A Comprehensive Study of the Alkaline Metal Catalysed Hydrophosphination of C–C Double and Triple Bonds

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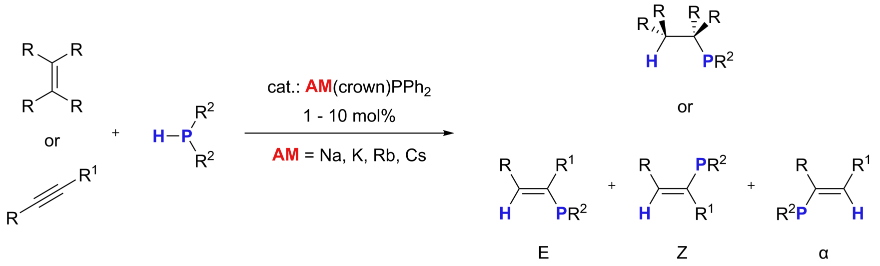
Alkali metal organic compounds, particularly of lithium, and to a more limited extent of sodium and potassium, have long been one of the most widely used classes of substances in the history of synthetic chemistry. Surprisingly, though organosodium and organopotassium compounds were the first such compounds to be reported, in 1858 by Wanklyn,[1] organolithium compounds, are by far the most commonly utilized organoalkali reagents, introduced later by Schlenk and Holtz in 1917.[2] Until recently nearly all of these applications have been in reactions within the limits of stoichiometric conversions.[3] On the other hand, *d*-block metal complexes have dominated the world of catalysis for many decades. With the advantage of high earth abundance (especially sodium and potassium), low cost, environmental benignness, and relatively low toxicity compared to some of their *d*-block counterparts, alkali metal-based compounds could become a valuable alternative commodity for catalysis.[3]



Scheme 1. Reaction scheme of the alkaline metal catalysed hydrophosphination of C – C double and triple bonds. R/R^1 = H, alkyl, aryl; R^2 = alkyl, aryl; AM = Na, K, Rb, Cs; crown = 15-crown-5 (Na), 18-crown-6 (K-Cs).

Recently we reported about designing donor-supported sodium phosphides such as [Ph$_2$P][Na·15-crown-5] as effective and fast catalysts for the hydrophosphination of alkynes (Figure 1).[4] The benchmark conditions for sodium are 10 mol% [Ph$_2$P][Na·15-crown-5] and a concentration of c = 0.5 M were full conversion is reached after 30 min using 1,1-Diphenylethylene and Ph$_2$PH as the substrates. Descanting the group, the loading as well as the concentration can be decreased significantly to 1 mol% and c = 0.01 M in the case of cesium. Hydrophosphination of un- or poorly-activated unsaturated bonds with alkyl phosphines is a key challenge in the field. So not only Ph$_2$PH, by far the most frequently used phosphine in the literature, is applied as a substrate, but also alkyl phosphines such as *i*-Pr$_2$PH, *t*-Bu$_2$PH and the mixed alkyl Ph*t*-BuPH.

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Synthesis of luminescent polymers using calcium complexes as catalysts

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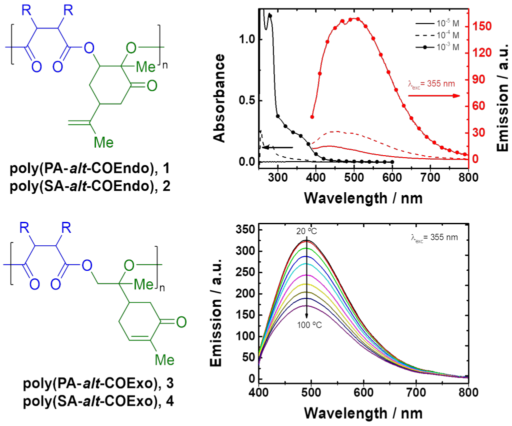
Nowadays, the use of molecules derived from biomass waste to produce new polymers is becoming an emerging new frontier to material science.[1] Stimulus-responsive polymers, better known as ‘‘smart’’ polymers, are a type of material designed and synthesized to respond by altering their structure, function, or stability when a slight external stimulus is produced.[2] The development of smart polymers, whose luminescence properties are sensitive to several single stimulus, have gained importance. However, most smart luminescent polymers suffer from low biocompatibility and biodegradability which hampers their use in fields like biosensing or diagnosis as well as their environmental long-term effect is also compromised by their associated waste. In this context, ring-opening copolymerization of epoxides and cyclic anhydrides has emerged as a valuable methodology for producing polyesters.[3] Herein, we detail the synthesis of novel calcium complexes and their application as catalysts for polyester production.[4] Notably, these compounds exhibited good performances, high selectivity, and effective polymerization control under mild reaction conditions, even with bio-sourced substrates included. In this study, different polyesters have been synthesized from monomers derived from biomass that present a non-traditional intrinsic luminescence that depends largely on their folding structure and their environment (Figure 1), highlighting their great potential as sensors, especially when the temperature is modified. Therefore, this study demonstrates the implementation of these materials in promising fields as thermosensitive smart polymers.



poly(PA-*alt*-COEndo), 1
poly(SA-*alt*-COEndo), 2

poly(PA-*alt*-COExo), 3
poly(SA-*alt*-COExo), 4

Figure 1

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The Bioorganometallic Chemistry of Osmium Carbonyl Clusters: From Imaging and Sensing to Therapeutics

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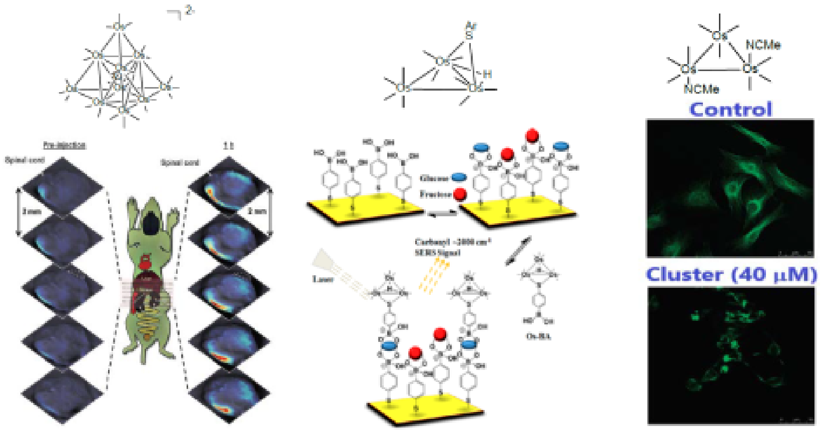
Almost a quarter of a century ago, we began looking at the potential application of osmium carbonyl clusters in the biomedical sciences. This has taken us through the use of clusters in bioimaging – mid-IR[1], SERS[2], and photoacoustics[3] – to sensing[4] and finally as therapeutics for cancer[5] and Parkinson's.

In this talk, I hope to be able to show you the path which we have taken and demonstrate the breadth of this direction of research.



Photoacoustic imaging **Glucose sensing** **Disruption of microtubules**

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