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Photo-responsive Luminescent Single-Molecule Magnets Based on Lanthanide-Anthracene Complexes

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Photo-responsive magneto-optical bifunctional complexes are attractive due to their potential applications in information storage, molecular sensors and devices. Lanthanide complexes are ideal candidates for constructing such materials, but how to realize the synergistic modulation of their magnetic and luminescent properties through external stimuli is still a challenge. Considering that anthracene derivatives are not only rich in optical properties but also may undergo reversible photoinduced [4+4] cycloaddition reactions when the anthracene groups are face-to-face π - π interacted, we synthesized a series of lanthanide-anthracene/dianthracene complexes and realized the synergistic modulation of their single-molecule magnet and luminescent properties by light and/or heat.

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Hyperpolarising Metal Complexes through SABRE

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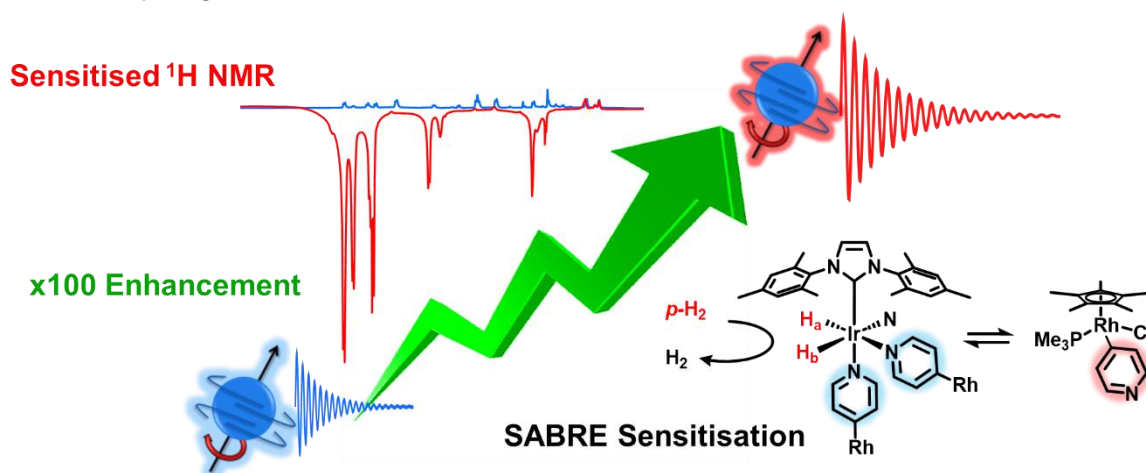
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Widely accessible nuclear magnetic resonance (NMR) spectroscopy is a cornerstone of chemistry where its unmatched diagnostic power delivers precise insights into product identification, structural architecture, reactivity, and dynamic interactions between and within species. However, despite all this power, it suffers from low intrinsic sensitivity as the nuclear spins it probes interact weakly with magnetic fields, meaning only a small fraction of the sample contributes constructively to the detected signal. This research uses the catalytic process Signal Amplification by Reversible Exchange (SABRE) to improve NMR sensitivity without chemical change (Scheme 1).¹ Here a series of organometallic complexes are synthesised and examined under SABRE for use in subsequent high-sensitivity reaction monitoring and mechanistic studies.

SABRE operates in seconds by reversibly binding the polarization source *parahydrogen*² to an iridium complex alongside the substrate whose improved NMR sensitivity is targeted. Heteroaromatic species such as pyrazine have been employed, and their ¹H, ¹³C and ¹⁵N NMR signals amplified by several thousand-fold. This project focuses on designing and synthesizing heteroaromatic analogs of Cp*Rh(PMe₃)(C₆H₅)Br, a groundbreaking precursor that led to Cp*Rh(PMe₃)(C₆H₅)H and revolutionized our understanding of C-H bond activation.³ The ¹H and ³¹P SABRE NMR-sensitization of these complexes is discussed, and their use as probes of reactivity targeted.⁴



Scheme 1: SABRE Sensitization leading to enhanced inverse ¹H NMR Signals.

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Dual-responsive phosphorus-based fluorescent sensors: synthesis and selective metal sensing of pyrazolyl phosphine oxides

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The development of novel fluorescent sensors for metal ions remains an active area of research.¹ Such sensors typically rely on coordination of a fluorophore to a metal centre *via* donor atoms, inducing either a 'turn-off' or 'turn-on' response. However, there have been very few examples of phosphorus-based fluorophores being used in metal sensing applications. Such systems may take advantage of the well-established coordination abilities of phosphorus, in combination with a robust fluorescent backbone.²

Here, we report the synthesis and characterisation of pyrazolyl-phosphine oxides and their use in metal sensing applications.³ The sensor is dual-responsive, with both 'turn-off' and 'turn-on' fluorescent responses observed for different metals, with the 'turn-on' response arising due to coordination of the pyrazolyl-phosphine oxide to the metal centre. These responses allow pyrazolyl-phosphine oxides to act as selective phosphorus-based fluorescent sensors for certain metals.

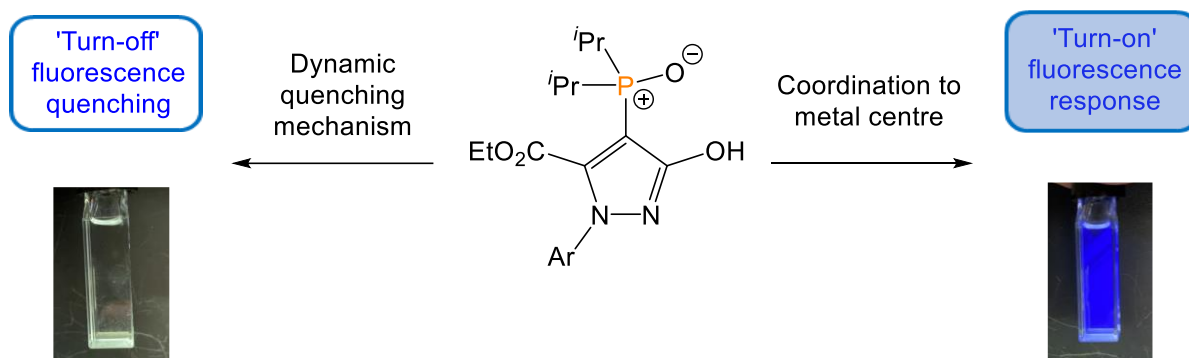


Figure 1: 'Turn-on' and 'turn-off' fluorescence responses of pyrazolyl-phosphine oxides to metals.

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Solution vs. Solid-state: Reactivity of an Iridium(I)/(III) System Featuring a New Adamantyl Pincer Ligand

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Single-Crystal to Single-Crystal (SC-SC) transformations can be used to isolate highly reactive complexes in the absence of solvent, such as σ -alkane complexes.¹ Recent work in the Weller group involves the application of SC-SC techniques to Brookhart's [(^tBuPONOP)Ir(Me)(H)][BAR^F₄] system.² When placed under high vacuum (5×10^{-5} mbar) at 80 °C, [(^tBuPONOP)Ir(Me)(H)][BAR^F₄] liberates methane to yield an operationally unsaturated iridium(III) cyclometalated complex, which undergoes SC-SC reactivity with methane, ethane, CO and N₂.³ Methane loss and subsequent cyclometallation occurs *via* a transient 14-electron intermediate, [(^tBuPONOP)Ir][BAR^F₄]. Such complexes are key intermediates in alkane dehydrogenation catalysis, although they have yet to be observed experimentally.⁴

This work (Fig 1) presents the synthesis and reactivity of an iridium system which features an adamantyl substituted pincer ligand, ^{Ad}PONOP, that is less likely to undergo cyclometallation. The ability of [(^{Ad}PONOP)Ir(Me)(H)][BAR^F₄] to liberate methane in the solution and solid-state is compared to the ^tBuPONOP analogue. Steric interactions between the closely packed cations within the crystal have a profound impact on reactivity, demonstrating the influence of the crystalline microenvironment. The C–H activation of 1,2-difluorobenzene is also reported, which suggests that the corresponding 14-electron complex is accessible in solution.

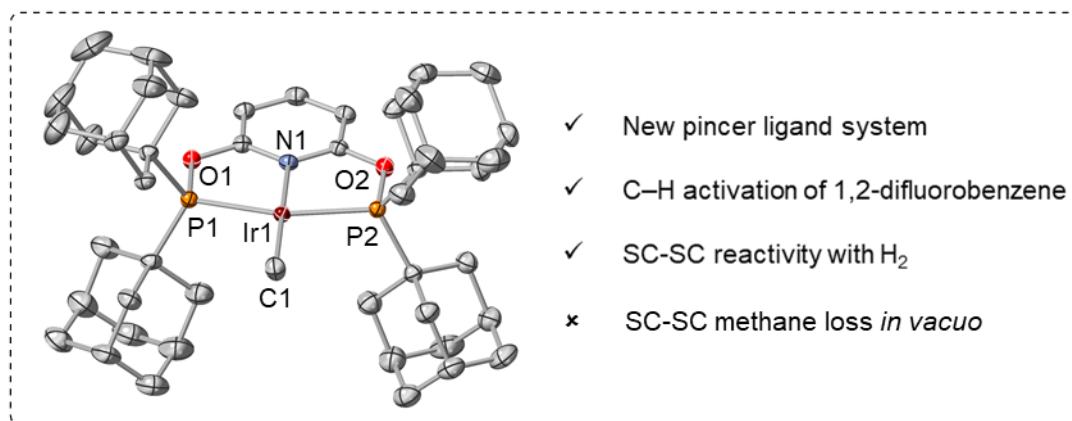


Figure 1. Molecular structure of the isolated cation of [(^{Ad}PONOP)Ir(Me)(H)][BAR^F₄] and a summary of the work to be presented. Displacement ellipsoids are set at 50% probability. Hydrogen atoms, lattice solvent and [BAR^F₄][−] anion are omitted for clarity.

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Plasma Assisted Deposition of Metal Inks on Flexible Substrates

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The move toward low-cost flexible electronics is one of the standout advancements of this century. However, there is a gap between the industrial requirements for the development of these electronics and the manufacturing processes available. Thermal deposition techniques involving the patterning of molten metals are incompatible with affordable flexible materials due to the high melting point of metals which is in stark contrast to the deformation temperatures of a range of plastic, paper or fabric materials.

Currently the production of printed electronics involves the use of time-consuming and expensive multi step-techniques as well as toxic chemicals.¹ The atmospheric-pressure and room-temperature printing of metal-organic decomposition (MOD)^{2,3} inks followed by plasma treatment for conversion to metal is a convenient alternative to current techniques.⁴ It compresses the manufacturing process into two steps- printing and sintering. The low temperatures associated with this process also allow the easy usage of substrates such as paper and plastic. It is a simple and scalable method with the potential to fulfil the unmet needs of the ever-growing printed electronics market.

The low cost, high abundance and low resistivity of copper makes it an appealing metal for use in these printed electronics. This research looks at a range of copper(II) MOD inks for the synthesis of conductive circuits for printed electronics via plasma sintering onto a range of flexible substrates including various types of paper and plastics.

Inks using copper as the metal of choice that have successfully been deposited *via* thermal sintering techniques have been utilised in this project.⁵ These inks have then been deposited onto a range of flexible substrates such as photo paper, parchment paper, tracing paper and acetate sheets. Subjecting these inks to atmospheric pressure plasma yields conductive deposits of the copper metal. These have been analysed by GIXRD, SEM and EDX. Thermal resistivities have been measured using a two-point probe.

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Probing Local Structure of Ag and Bi in AgBi-Mixed-Metal Thiolate coordination polymers

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Metal n-alkanethiolates (MTs) with long hydrocarbon chains are self-assembling two-dimensional (2D) coordination polymers (CPs) that benefit from their organic-inorganic hybrid structure constructed by metal and chalcogen bonds within an organic matrix. A subclass of this family of compounds is mixed-metal thiolates (MMTs) which are otherwise similar to MTs but hetero-metallic and usually contain two or three hetero-metals.^{1,2} A few of their structures were revealed by single-crystal X-ray diffraction (SCXRD) where single crystals could be isolated^{3,4}, but most of them do not produce crystals of suitable size for SCXRD studies, driving the researchers search for other advanced techniques⁵. The nature of the atomic level connectivities within the metal and chalcogen play crucial role in directing their self-assembly nature thus their solubility, stability, reactivity etc. and are very important to be investigated.

In this work, we have synthesized a novel MMT AgBi(SR)₄ (R=C₁₂H₂₅) and probed the local structure of metals using X-ray absorption spectroscopy. With support from theoretical study, our study revealed an Ag-Bi metallophilic interaction at 2.71 Å in this compound (**Figure1**) that brings extra stability compared to that of its respective MTs [*viz*; AgSR and Bi(SR)₃] and results in the formation of an MMT.

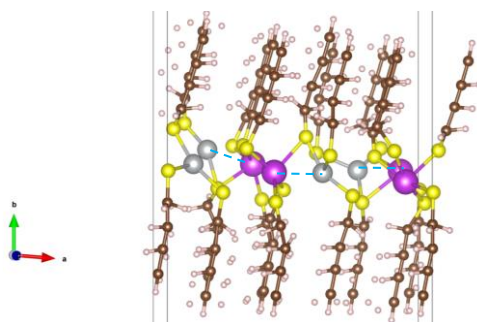


Figure 1: AgBi(SR)₄ structure showcasing Ag-S-Bi bridging and Ag-Bi metallophilic interactions (blue bonds) at 2.71 Å, directing the formation of an MMT complex. Ag-silver, Bi-pink, yellow-S, brown-C.

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[B(O₂C₂(CF₃)₄)₂][−] (FPB): Repurposing This Weakly Coordinating Anion for Solid-State Molecular Organometallic Chemistry.

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Weakly coordinating anions (WCA) have been instrumental in the development of synthetic and catalytic organometallic and main-group chemistry of reactive cationic species.¹ One example of this is the use of the [BAR^F₄][−] (Ar^F = 3,5-(CF₃)₂C₆H₃) anion in single-crystal to singlecrystal (SC-SC) reactions for the isolation of stable σ-alkane-complexes.² The framework of [BAR^F₄][−] anions support metal-centered reactivity, the CF₃ groups promote substrate diffusion, and provide stability from non-covalent interactions.³ Different anions, such as [Al(OR^F)₄][−] or [B(3,5-Cl₂-C₆H₃)₄][−] do not support SC-SC reactivity. However, the multistep in-house synthesis of Na[BAR^F₄] creates a need for alternative anions that can facilitate SC-SC reactions. New anions should be cost competitive, easily prepared from commercial sources on the gram scale and be solvent free. The perfluoropinacol borate-based anion [B(O₂C₂(CF₃)₄)₂][−], [FPB][−] (Figure 1) offers these advantages. While this anion has been exploited as a battery electrolyte, its use as an anion in organometallic or main group chemistry has not been reported on outside of a single patent disclosing its use in alkene polymerization.⁴ We report now that the [FPB][−] can be used as a WCA in organometallic chemistry through its use in the synthesis of a σ-alkane complex using SC-SC methods.

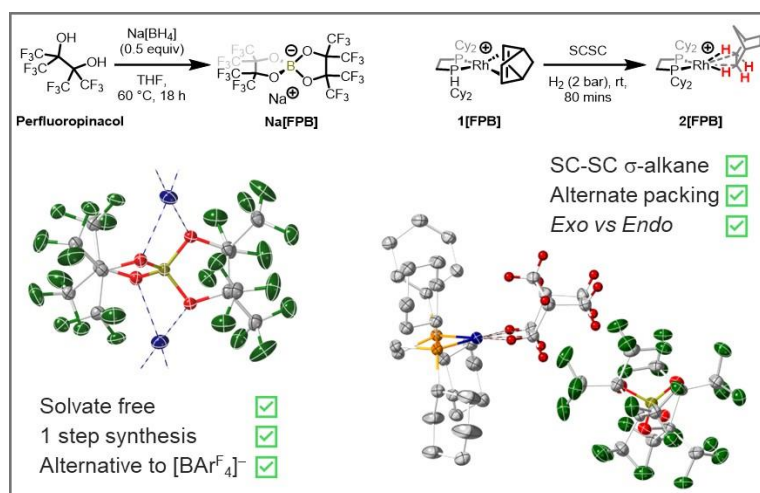


Figure 1. Synthesis and X-Ray structures of Na[FPB] and rhodium σ-alkane complex.

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Achieving site selectivity in Suzuki-Miyaura cross-coupling reactions using earth abundant Ni based catalytic systems

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Suzuki-Miyaura cross-coupling (SMCC) has been the leading choice for C-C bond-forming reactions for several decades, especially in the pharmaceutical industry.¹⁻² However, the heavy dependence on Pd to carry out these reactions has become an area of concern due to its high cost and scarcity. Ni has become a leading choice as an alternative to Pd mainly due to its affordability and abundance. To illustrate further, Pd (on a per mole basis) is nearly 3 times more expensive than Ni while at the same time having an almost 600 times greater global warming potential (3880 kg equivalents of CO₂ in comparison with 6.5 for Ni).³⁻⁴ Dihalosubstituted heteroarenes hold great synthetic potential due to their multiple sites enabling connectivities and thus increasing the scope for molecular complexity (Figure 1). C2-arylation (2-Ar in Figure-1) is the conventional path for these types of couplings due to several electrochemical factors. The focus in our group has been to achieve the atypical selectivity at the C-X bond at a distal position to the heteroatom (4-Ar in Figure 1). Although literature reporting such site-selective cross-couplings of dihalopyridines is available, most of them are focused on Pd catalysis.⁵ This project is focused on mechanistic insights into the site-selective SMCC reaction by different Ni based catalysts.

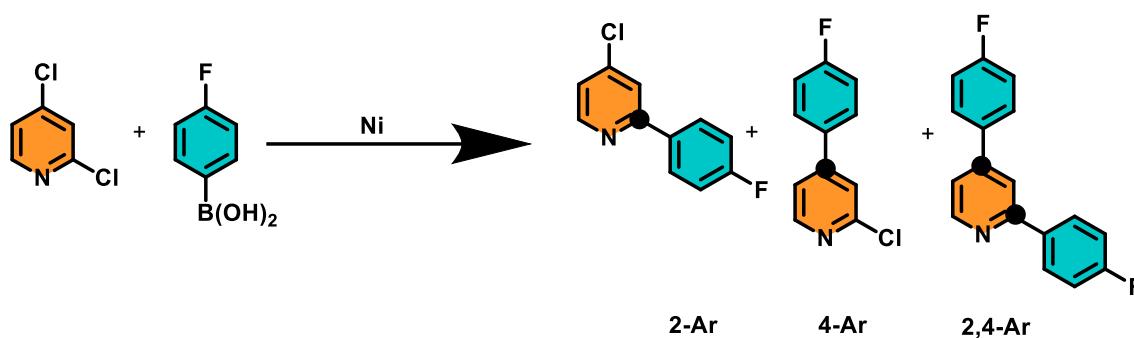


Figure-1. Ni-catalysed SMCC reaction of dihalopyridines with three potential products

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Advancing Self-Cleaning Photovoltaics with Lanthanide Oxide Thin Films

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Soiling across solar modules by dust and dirt particles remains a major obstacle for the use of solar photovoltaics. There is a critical need for self-cleaning solar utilities in order for these to replace the current unsustainable fossil fuel-based energy generation systems. To that effect, we present the design, synthesis and application of inorganic rare Earth oxide layers (Ce_2O_3 , Er_2O_3) deposited by aerosol assisted chemical vapour deposition (AACVD) with intrinsic hydrophobicity. There are very few reports of lanthanide oxide complexes for hydrophobic coatings using AACVD within the literature. This prompted our investigation into such coatings. Water contact angles of up to 103° were established across the thin films deposited using these complexes, demonstrating their self-cleaning potential.

As a new approach to self-cleaning solar modules, we investigated the synthesis of volatile lanthanide β -diketonate precursors. Notably, inorganic rare Earth (Ce, Y, Er, Lu) oxide layers have been shown to be durable, UV-stable, oxidant resistant with intrinsic hydrophobicity, with a water contact angle range of 110 - 125° .^{1,2} Likewise, β -diketone ligand complexes have been proven to serve as effective and stable precursors. Compounds of the type $[\text{X}(\text{Y})_{3,4}]$ have been synthesised via adaption of a known synthetic route to $[\text{Ce}(\text{thd})_4]$ and $[\text{Er}(\text{thd})_3]$,^{3,4} where X = lanthanide metal (Ce, Er) and Y = thd (dipivaloylmethane), dbm (dibenzoylmethane).

AACVD of the synthesised complexes yielded lanthanide oxide films on fluorine tin doped (FTO) glass under a constant flow of nitrogen. Thermogravimetric analysis of these compounds indicated suitable deposition temperatures ranging from 400 - 600°C . The most hydrophobic coatings, with contact angle of 101° , were obtained by the deposition of cerium oxide onto FTO at temperatures between 400 and 500°C . These rare oxide thin films were intrinsically analysed using surface analysis and characterisation techniques. X-ray photoelectron spectroscopy confirmed the presence of a mixed phase system of Ce(III) and Ce(IV) across the surface. Further analysis of the deposited thin films was conducted using SEM and XRD to determine the surface morphologies of these hydrophobic coatings.

Further research on the synthesis of mixed ligand lanthanide systems has also been investigated for thin film deposition, holding further promise for the synthesis of self-cleaning photovoltaics.

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Designing an automated electrochemical flow platform to remove the harmful effects of toxic metals in industrially relevant metal-catalysed processes

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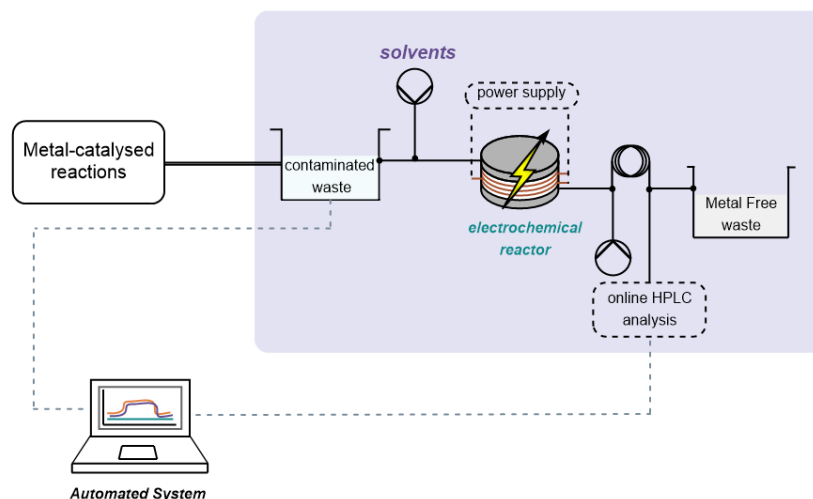


Figure 1. Platform for the electrochemical removal of toxic metals from catalytic wastestreams.

Metal-catalysed reactions have changed the face of chemical synthesis, with applications across the academic and industrial sectors.¹ However, these reactions require the use of often toxic, expensive and unsustainably sourced transition-metal catalysts. While cheaper and more sustainably sourced metals such as nickel have now started to pique the interest of the scientific community, the toxicity of the nickel species is of significant concern.² An ability to recover metals from catalytic waste streams would address many issues associated with their use in the chemicals industry; removing and recycling transition metals would not only reduce chemical costs but also improve both the environmental and health concerns linked to these metals.

Recently, work has been focused on using electrochemistry to clean chemical wastestreams.^{3,4} This research looks to design a closed-loop automated flow platform for the sequential synthesis of metal catalyst, catalytic reaction, and catalyst recovery, enabling traditional metal-catalysed reactions with none of the drawbacks. A selection of Schiff bases have been explored for their use as sensors for metal ions, allowing for quantitative analysis of reaction mixtures in-line. Using artificially generated Ni wastestreams, we have successfully demonstrated >70% recovery in both batch and flow.

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Aerosol-Assisted Chemical Vapour Deposition of α -Fe₂O₃ and BiFeO₃ as effective Photoanodes for Photoelectrochemical Water Splitting

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PEC water splitting shows promise for green hydrogen production but lacks commercial viability due to material limitations, especially in developing scalable photoanodes. α -Fe₂O₃ and BiFeO₃ are promising PEC photoanode materials, but face charge carrier issues linked to phase purity and morphology¹. Developing a scalable fabrication method is crucial for advancing this technology, with aerosol-assisted chemical vapour deposition (AACVD) as a relatively underexplored technique that holds great potential. AACVD is advantageous as it avoids volatile precursors and enables the fabrication of tailored, high-performance photoelectrodes². Herein, we report some of the first instances of depositing phase pure α -Fe₂O₃ and BiFeO₃ via a 'Universal' precursor approach, in which a common ligand framework based upon an amino-tris alcohol was utilised on various metal centres.

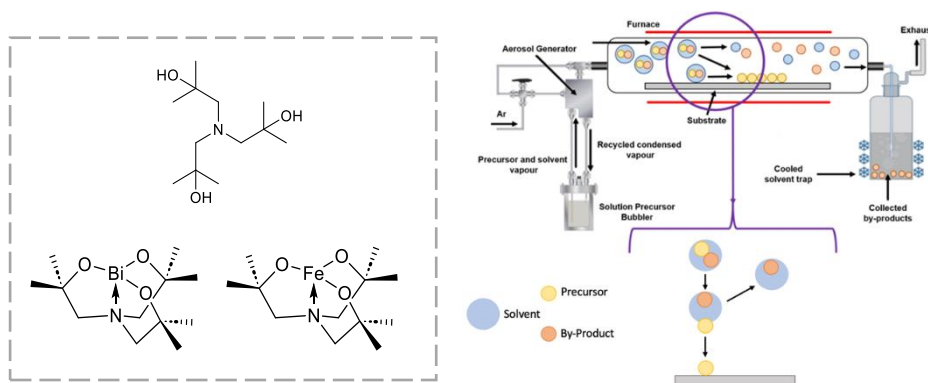


Fig. 1. Left: 'Universal' ligand and precursors utilised in this study. Right Schematic Diagram of an AACVD setup and theorised deposition mechanism³

By aligning precursors at molecular level, complementary decomposition pathways could be achieved, enabling the development of dual-source precursors to deposit single and mixed metal oxides of high phase purity. Each precursor's structure was confirmed via single-crystal X-ray diffraction, ¹H NMR, ¹³C NMR, and elemental analysis. The suitability of each compound as an AACVD precursor was assessed using thermogravimetric analysis (TGA). Successful deposition of phase pure films of α -Fe₂O₃ and BiFeO₃ was confirmed using powder X-ray diffraction, Raman spectroscopy, and energy dispersive X-ray spectroscopy. In addition, scanning electron microscopy revealed favourable morphologies: α -Fe₂O₃ formed as nanoflakes, while BiFeO₃ grew as high-surface-area nanorods. Our materials matched the highest reported values for photoactivity from literature. Notably, this is the first instance in which BiFeO₃ has successfully been grown via AACVD using dual-source precursors.

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Ru-H bond activation by means of x-ray radiation : how it might work

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Some time ago G. Nikonov et al. reported NHC carbene supported half-sandwich hydridosilyl complexes of ruthenium, and found evidence for interaction between the Ru-H and the Si atoms.¹ More recently, we reported the results of low temperature, high resolution x-ray structural QTAIM analysis combined with detailed DFT calculations.² However, this did not explain the proposed Ru-H ... Si interaction.

One of the problems in x-ray crystallography is the exact location of hydrogen atoms next to heavier elements, in particular transition metals. We wanted to expand our initial reported investigation to LCpRu(H)₂SiH(Me)(Ph) (**1**) as we had suitable crystals for neutron diffraction. During our low temperature (100 K) x-ray diffraction measurement on the Diamond x-ray synchrotron facility of **1**, we not only observed the expected structure of **1** but also the Ru-H activation product, the result of a Ru-Si and Ru-H bond breakage, concomitant with the generation of the free silane HSiH(Me)(Ph) (**2**). **2** is trapped within the unit cell and makes up to around 10% of the observed structures. Due to the free coordination side on the Ru atom, the phenyl ring of **2** is filling this vacancy in an *agostic* type of interaction (cf. Figure 1).

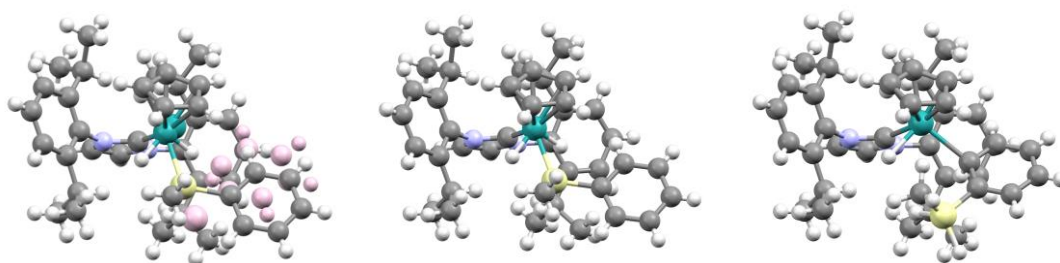


Figure 1: observed x-ray structures. Left: full structures, middle major product **1**, right minor product **2**.

In this presentation, we are discussing the outcome of our investigations, both experimentally and theoretically, of this unusual Ru-H bond activation by means of x-ray radiation. Specifically, we not only report the results of NBO, QTAIM and ETS-NOVC DFT calculations of **1** and the observed product **2**, but also put forward a possible explanation why this activation was not observed in the previously investigation¹, why only using QTAIM might be insufficient, and why using different functionals might be beneficial for the understanding of the nature of these interactions.

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Detailed DFT calculations of a hetero-carbene Ru₂CPt complex

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We recently reported the results of detailed DFT calculations of a [LL'Ti-C-AlMe₂][AlMe₃]₃ compound with a penta-coordinated carbon.¹ Our results indicates the AlMe₃ moieties are coordinated to the Ti-C triple bond, rather than having a penta-valent carbon. Here we are reporting detailed DFT calculation (QTAIM, NBO, ETS-NOCV) at the PBE0-D3 level of theory of a bimetallic Ru₂CPt compound [(Cp*Ru)₂(μ²-NHPH)(μ²-H)(μ³-C)(PtMe(PMe₃)₂)[OTf] (**1**) with a trigonal-planar μ³ carbon bridging the bis-ruthenium moiety with the Pt one.²

These results are compared with the model compound [(NHC)'-PtMe(PMe₃)]⁺ (**2**) where the bis-ruthenium moiety has been replaced with a more traditional carbene. This way, we can compare the C-Pt interaction of **1** and **2** directly and elucidate the bonding mode to see if the μ³-C could be better described as a carbene and not a carbido carbon.

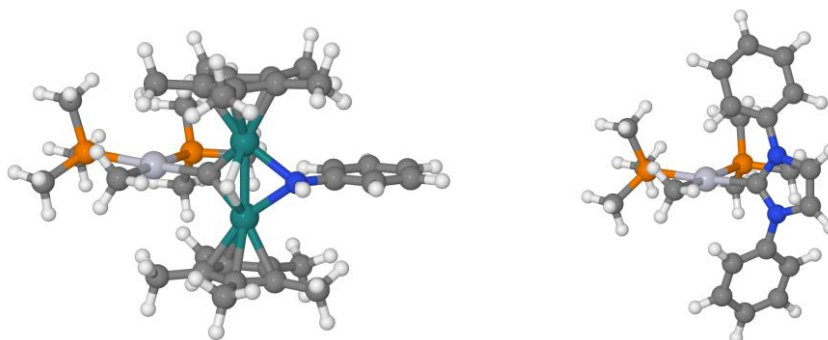


Figure 1: Left: compound **1**, taken from ref. 2; right: hypothetical compound **2** for comparison.

The poster describes the similarities of the electronic structure between both compounds. Instead of describing the C-Pt bond in **1** as a carbido carbon, we suggest a better description would be of a carbido-carbene, highlighting the similarities between both compounds.

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Phosphinoaryloxyde-based Rare Earth Complexes Towards Frustrated Lewis Pair (FLP) Activity

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Since the ground-breaking research by Stephan et al. in 2006,¹ Frustrated Lewis Pair (FLP) chemistry has been a rapidly developing area of research. This is due to the potential economic and environmental benefits of using cheap and abundant p-block elements in small molecule activation and catalysis. There has been a lot of interest in exploiting the Lewis acidity of metal cations for developing novel FLP systems.² In this respect, rare earth (RE) cations display high Lewis acidity. However, examples of FLP-type reactivity with these metals remain scarce.^{3–5} Wass and co-workers exploited the Lewis acidity of Group 4 metals combined with the use of bulky phosphinoaryloxyde ligands to develop complexes that can exhibit FLP-type reactivity.^{6,7} Group 4 cations Ti^{4+} , Zr^{4+} and Hf^{4+} are isoelectronic to RE^{3+} (RE = Sc, Y and La) cations, thus providing us with the inspiration to develop analogous systems that could be intriguing candidates for metal-based FLP activity. We recently reported the synthesis of novel homoleptic phosphinoaryloxyde-based RE^{3+} complexes, which ultimately proved to be unreactive towards small molecule activation.⁸ Building on this work, we present herein the synthesis and reactivity of novel, heteroleptic RE^{3+} complexes containing bis-cyclopentadienyl and phosphinoaryloxyde ligands.

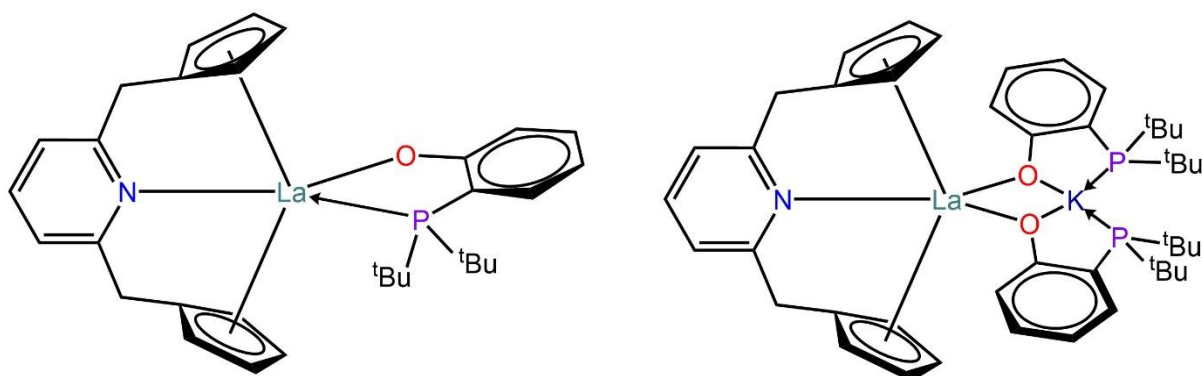


Figure 1: Selected examples of complexes synthesized in this work. Left: targeted complex. Right: 'ate' complex observed as a side-product.

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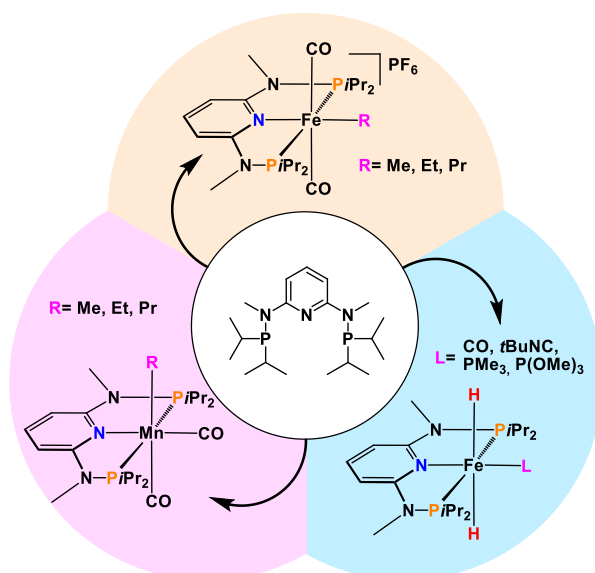
Synthesis and application of novel alkyl and hydride iron and manganese PNP pincer complexes

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Iron PNP pincer complexes have demonstrated high catalytic efficiency for hydrofunctionalization and hydrogenation reactions. However, their low air and moisture stability is the primary shortcoming of these highly active catalysts.¹ In contrast, manganese bisphosphine (PP) complexes have shown that stable alkyl carbonyl complexes can undergo migratory insertion, resulting in the formation of highly active Mn(I) hydride catalysts.² Therefore, it was the goal to synthesize stable iron PNP alkyl complexes, as well as manganese PNP alkyl complexes and compare their catalytic activities with one another and manganese PP systems.



Scheme 1. Overview of new alkyl and hydride Fe(II) and Mn(I) PNP pincer complexes

Herein, the synthesis of new manganese and iron complexes (**Scheme 1**) as well as their applicability as catalysts is reported. The dicarbonyl alkyl complexes were examined for the hydrofunctionalization of alkynes. Furthermore, new dihydride complexes could be obtained that showed an increased catalytic activity for the hydrogenation of aldehydes in comparison to our previously described bis-hydride complex $\text{Fe}[(\text{PNP}^{\text{Me-}}/\text{Pr})\text{H}_2(\text{CO})]$.³ Additionally, these complexes showed a catalytic activity for aldol condensation and Tishchenko-type reactions, as well as for the selective deuteration of α -carbons of ketones.

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Small Molecule Activation Inside Extended Cryptands

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Cryptands are (roughly) spherical three-dimensional macrocyclic ligands which are commonly used to sequester cations such as K^+ . Expanding cryptands in one dimension results in the formation of a capsule-shaped ligand which has two internal metal binding sites with a gap between them. The size of the gap, which correlates to the $M \cdots M$ distance, can be controlled by varying the spacer (see Figure) used during the ligand synthesis.¹ This enables the ligand to be tuned to perfectly fit a small molecule (such as N_2 or CO_2) between two metal centres, activating it towards further reaction.

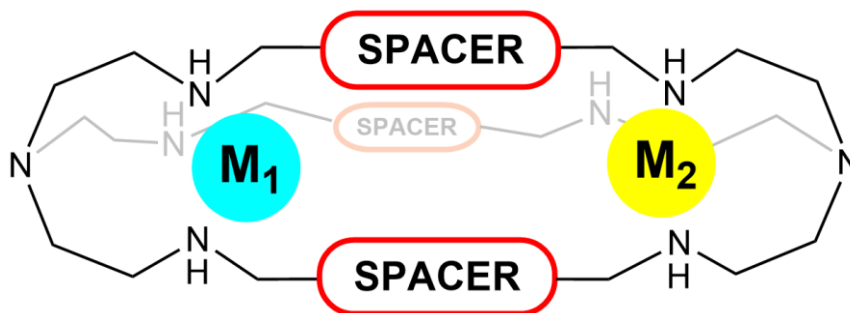


Figure: the extended cryptand ligand architecture. $M_1 = M_2 = Cu^I, Ag^I$; spacer = m-xylyl, p-xylyl

Here we present homobimetallic complexes of Group XI metals in the +1 oxidation state. Several examples of dicopper(I) and disilver(I) complexes with various weakly coordinating anions have been structurally characterized, allowing us to study the effect of varying the spacer length, anion type and the ionic radius of the metal on the $M \cdots M$ distance. We have discovered that the inherent flexibility of the ligand allows the $M \cdots M$ distance to expand and contract, which is advantageous for small molecule activation within these systems. Whilst the Group XI complexes are unreactive towards N_2 or CO_2 , the dicopper(I) compounds with m-xylyl spacer bind dioxygen from the atmosphere, forming a dicopper(II) species with two coordinated superoxides.²

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Electrostatics in metal carbonyl bonding: computational analysis of late transition metal pincer complexes

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An unexpected blue shift of the carbonyl stretching frequency across a homologous series of metal pybox carbonyl compounds was recently rationalised by conformational changes of the tridentate ligands, which alters the magnitude of the local internal electric field projected along the M–CO bond.¹ This physical phenomenon is known as the internal Stark effect,² but is often overlooked when describing the metal–carbonyl interaction. To gauge the role of electrostatics in metal carbonyl bonding more generally, we have investigated a computational dataset of 62 pincer complexes featuring carbonyl ligands.³ These complexes have been analysed using density functional theory methods and correlations of the carbonyl stretching frequency with the extent of π -backbonding, as determined by energy decomposition analysis, and the dipole of the pincer–metal fragment, as a proxy for the local electric field projected over the ligand, are discussed.

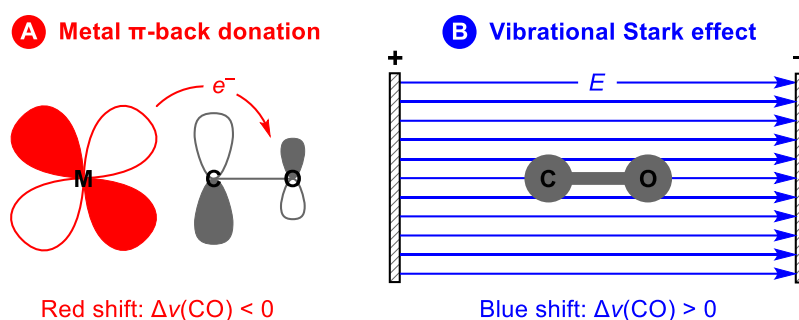


Figure 1. Orbital (A) and electric field (B) interactions with carbon monoxide and their effect on carbonyl stretching frequency.

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Synthesis, characterization and catalytic activity of iron, cobalt and nickel complexes of a N-heterocyclic carbene-based PCP ligand

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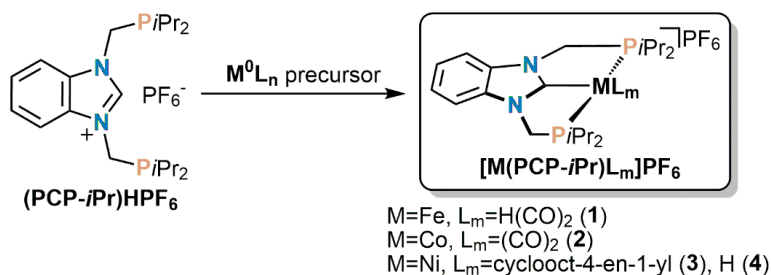
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The high tunability of pincer ligands allows for the isolation of wide varieties of transition metal complexes and thus probe their stoichiometric and catalytic reactivities.¹ Picking up on previous synthetic efforts,² a hexafluorophosphate benzimidazolium salt with two $\text{CH}_2\text{P}i\text{Pr}_2$ side arms (**(PCP-*i*Pr)HPF₆**) and the respective N-heterocyclic carbene-based PCP-*i*Pr manganese complexes have been previously reported, with catalytic applications in hydrogenation.³ In this work, the coordination chemistry of the **(PCP-*i*Pr)** ligand has been extended to other late transition metals.

The reaction of the zerovalent precursors $[\text{Fe}_3(\text{CO})_{12}]$, $[\text{Co}_2(\text{CO})_8]$, $[\text{Ni}(\text{COD})_2]$ and $[\text{Ni}(\text{PPh}_3)_4]$ with (**(PCP-*i*Pr)HPF₆**) respectively led to the formation of the cationic iron, cobalt and nickel complexes $[\text{Fe}(\text{PCP-}i\text{Pr})\text{H}(\text{CO})_2]\text{PF}_6$ **1**, $[\text{Co}(\text{PCP-}i\text{Pr})(\text{CO})_2]\text{PF}_6$ **2**, $[\text{Ni}(\text{PCP-}i\text{Pr})(\text{cyclooct-4-en-1-yl})]\text{PF}_6$ **3** and $[\text{Ni}(\text{PCP-}i\text{Pr})\text{H}]\text{PF}_6$ **4**, by oxidative addition of the benzimidazolium CH bond in (**(PCP-*i*Pr)HPF₆**) (Scheme 1). All complexes were characterized by NMR and FTIR spectroscopies, high-resolution mass spectrometry and selected cases by single-crystal X-ray diffraction. The cobalt complex **2**, in the presence of KO^tBu , was catalytically active in the hydroboration of several terminal alkenes in high yields, in THF at 70 °C for 18 h.



Scheme 1: Synthesis of the iron, cobalt and nickel PCP-*i*Pr complexes **1-4**.

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Small Molecule Activation and Redox Chemistry of Divalent *bis*-(tethered)arene Rare Earth Complexes

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The divalent oxidation state has been known in non-aqueous molecular systems for Sm^{2+} , Eu^{2+} , and Yb^{2+} for over 40 years,^[1] but it has only been in the last two decades that molecular examples have been isolated for the rest of the rare earths (save radioactive Pm). Tris-(substituted)cyclopentadienide (Cp^{R}) complexes remain the most explored (**Fig. 1A**)^[2], where the *pseudo*- D_{3h} ligand framework results in the additional electron populating a non-bonding d_{z^2} -like molecular orbital. While Cp^{R} ligands have been crucial to developing rare earth redox chemistry, exploring alternative frameworks is particularly interesting to unlock new reactivities and electronic structures. Previous works have used sterically demanding ligands that enforce metal-arene π - and δ -interactions to access rare earth and uranium complexes in low formal oxidation states with varying degrees of arene reduction (**Fig. 1B**).^[3-6]

Rare-earth *bis*-(tethered)arene complexes have more recently been explored for the isolation of room temperature stable formally divalent rare-earth complexes (**Fig. 1C**).^[7-9] In these complexes, the highest occupied molecular orbital resembles a $\text{d}_{x^2-y^2}/\text{d}_{xy}$ atomic orbital engaged in M-arene δ -bonding interactions. We have shown that the electronic structure of these complexes is particularly sensitive to the nature of the M-arene interaction which was quantified by spectroscopy and calculations.^[7] Here, the electronic structures, electrochemistry, and small molecule activation of several rare-earth *bis*-(tethered)arene complexes will be discussed, highlighting differences that arise as the series is traversed.

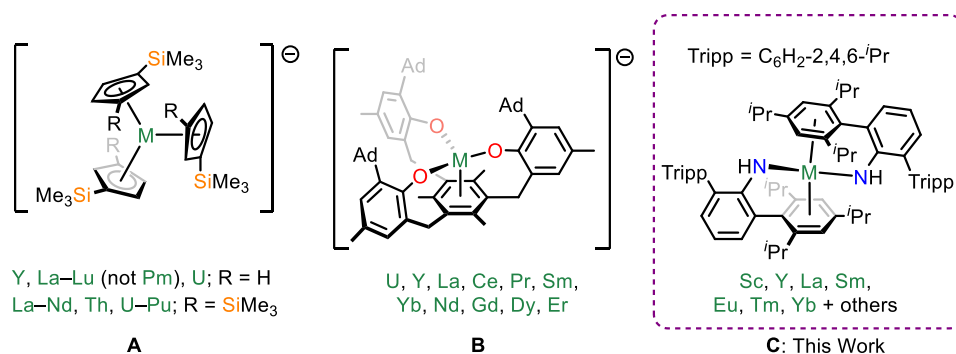


Figure 1. (A) Tris-cyclopentadienyl divalent complexes; (B) Arene supported divalent complexes; (C) This work: *bis*-(tethered)arene environment.

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Lithium polysulfides for the deposition of battery materials through aerosol-assisted chemical vapour deposition

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Conversion-type cathode materials are some candidates for future generations of secondary Li and Li-ion batteries. Compared to intercalation-type materials, they have the potential to be safer, more environmentally friendly and incorporate cheaper, more abundant materials.¹ One such cathode material is lithium sulfide (Li_2S). This boasts a theoretical specific capacity of 1166 mAh g^{-1} , approximately three times that of the current state-of-the-art intercalation-type materials.² However, these systems require over-charging prior to use, due to the high activation voltage of 3.5 V required to overcome the high lattice enthalpy of Li_2S .

Aerosol-assisted chemical vapour deposition (AA-CVD) offers a route to generate Li_2S that could reduce this activation voltage, possibly eradicating it completely, as seen with other vapour-deposition techniques.³ Single-source precursors for AA-CVD are used to alleviate any volatility requirements, expanding the pool of precursors to select from, such as the lithium polysulfide species seen in Figure 1, whilst reducing the potential energy requirements to produce the films.⁴ The work entailed highlights generation of lithium polysulfide compounds for use as precursors to generate battery materials via AA-CVD. Deposition is being optimised with the aim of depositing on a suitable host material to produce coin cells to assess the resultant electrochemistry.

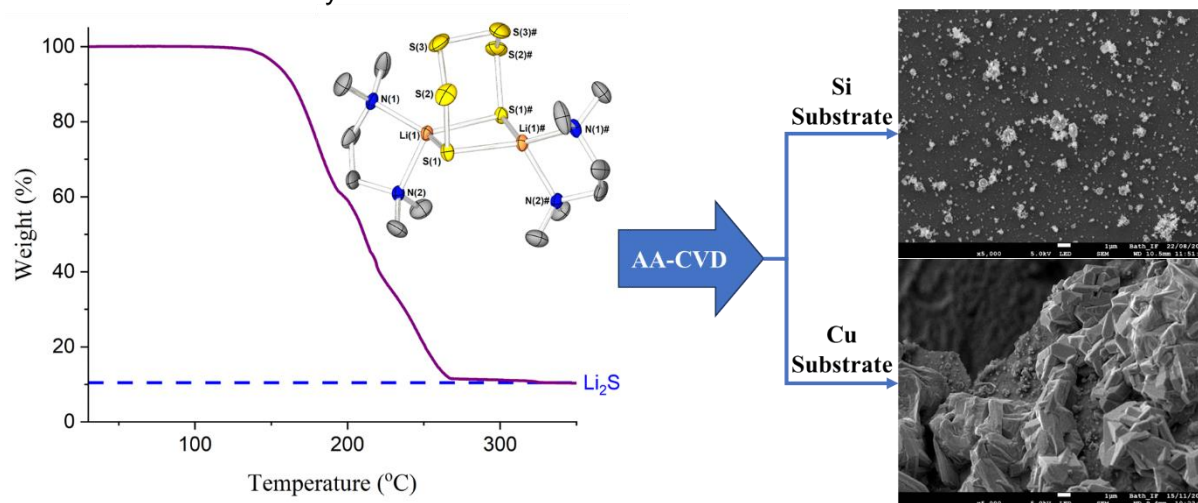


Figure 1. TGA plot of lithium polysulfide precursor (Crystal structure inserted in plot. Thermal ellipsoids are shown at 50% probability. Hydrogens are omitted for clarity). Dotted lines highlight calculated weight % associated with Li_2S . This transitions to SEM images of resultant deposition using this precursor on both silicon and copper substrates.

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Synthesis and Reactivity of Zinc-Fluoride Coordination Complexes

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Zinc fluoride coordination complexes represent an under-explored compound class with only a few fully characterised examples in the literature.^[1-5] Their synthesis often requires use of toxic reagents such as Me₃SnF, while their reactivity as fluorinating agents have not been researched extensively. The aim of this work is the synthesis of novel zinc fluoride coordination complexes and their investigation as novel fluorinating agents.

A series of zinc fluoride complexes were synthesised by defluorination of various fluorine sources (pentafluorobenzonitrile, HFCs, HFOs). While dimeric in the solid-state coordination of 4-dimethylaminopyridine (DMAP) at room temperature forms monomeric zinc-fluoride complexes with a terminal fluoride ligand. The structure and bonding of four isolated compounds has been investigated by NMR spectroscopy (¹H, ¹⁹F, DOSY), X-ray crystallography and calculations (DFT, AIM). When compared to other molecular main group fluoride reagents,^[6,7] preliminary studies show a good scope of reactivity towards electrophiles, including silanes, benzoic anhydride, haloaryls and haloalkyls – likely due to relatively weak nature of Zn–F bonds. Mechanistic studies (isolation and rational synthesis of an intermediate, computational studies) suggested that an ionic mechanism is in operation.

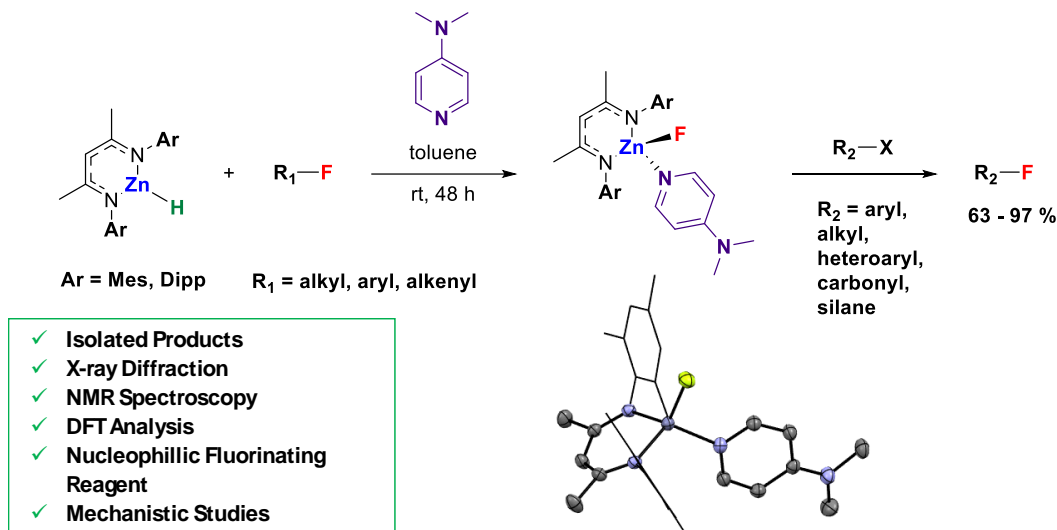


Figure 1. Synthesis of zinc-fluoride complexes and subsequent reaction with substrates.

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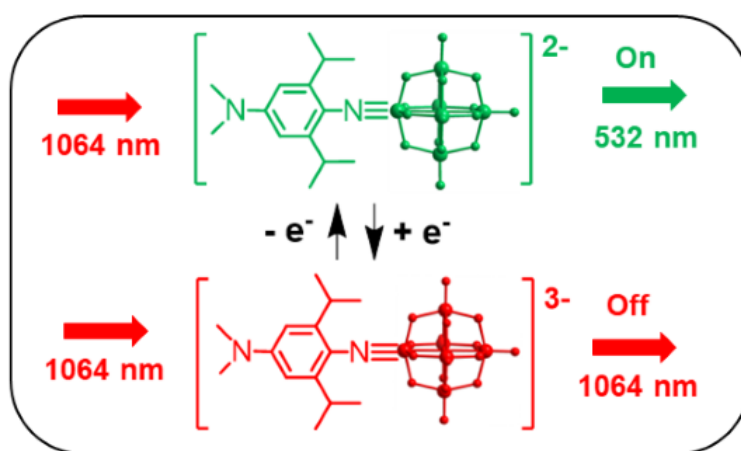
“Laser-Focused” Polyoxometalate Hybrid Chemistry

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Arylimido polyoxometalates (a-POMs) connect organic π -systems to electronically delocalised metal-oxo clusters, across a highly conjugated imido-bridge.¹ This can produce materials with new properties, emerging from the strong communication between organic and inorganic subunits. Our focus is on charge-transfer (CT) systems constructed from a-POM electron acceptors, and donor or acceptor units, and their non-linear optical (NLO) properties – for example laser frequency doubling,² two-photon absorption.³



Redox-switched 2nd order non-linear optical response in an a-POM charge transfer chromophore

This talk will discuss the development of a range of a-POM based CT chromophores: both 1D linear² and multidimensional systems,^{3,4} organic and organometallic donors, and their linear and non-linear optical properties including redox-switching.⁵

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Photophysical properties of lanthanide coordination complex-based ionic liquids as security inks for anticounterfeiting applications

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Counterfeiting has been a persistent issue for the worldwide economy and this research aims to address the challenges in the synthesis and formulation of security inks in complexity, solubility, miscibility, and tuneability.¹ Here we report three luminescent lanthanide coordination complex ionic liquids, that have characteristic and tuneable photophysical properties. Anionic nine coordinate complexes of Eu, Dy, and Tb are reacted with cations known to promote ionic liquid properties, to make transparent, viscous, and luminescent ionic liquids. Upon illumination of short wave UV light, red emission for Eu, green emission for Tb, and aqua blue emission for Dy can be observed. All ionic liquids have been characterised using IR spectroscopy, thermogravimetric assay, and pXRD. Lanthanides owe their emission to f-f transition, due to low molar absorptivity, they need to be sensitised using an organic ligand. The resulting ionic liquids can be mixed in equimolar ratios to make ionic liquid mixtures with characteristic peaks of all constituent lanthanides present, and specific excitation wavelengths can activate each. This tunability, homogeneity, and complexity in the ionic liquid mixtures make it a good candidate for the security ink industry.

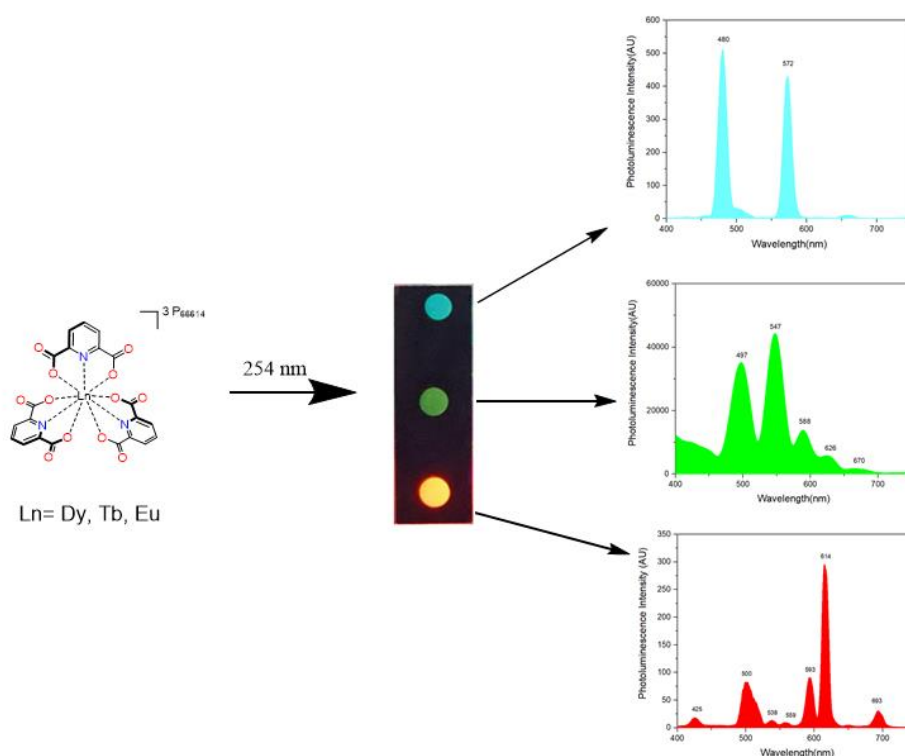


Figure 1: Demonstration of ionic liquids as security inks

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Optimising Polarisation Transfer through SABRE for Pyrazine

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Nuclear Magnetic Resonance (NMR) is an important analytical technique which assists in the characterisation and fingerprinting of known and unknown molecules thereby allowing their chemical and physical properties to be investigated. However, the insensitivity of this technique has always been a major hurdle compared to other analytical methods with better sensitivity¹. For NMR spectroscopy the low sensitivity is tied to the population difference between spin states, this population difference is dependent on the applied external magnetic field. Therefore, the sensitivity of NMR can be increased by using a stronger magnet but this method is not always available due to increased cost². The hyperpolarisation technique Signal Amplification by Reversible Exchange (SABRE) addresses the sensitivity issue of NMR by creating a more readily detectable non-Boltzmann population distribution through molecular catalysis.

The SABRE polarisation, of pyrazine is shown in Figure 1. It involves the addition of the singlet spin isomer of hydrogen gas, *para*-hydrogen (*p*-H₂), to a metal catalyst through an oxidative addition reaction. This causes the symmetry of *p*-H₂ to break and allows magnetisation to transfer from the newly formed hydride ligands of the complex to pyrazine via the scalar coupling pathway³. Signals for both free and bound pyrazine are detected. This project aims to optimise the pyrazine signal enhancement by using various organometallic complexes.

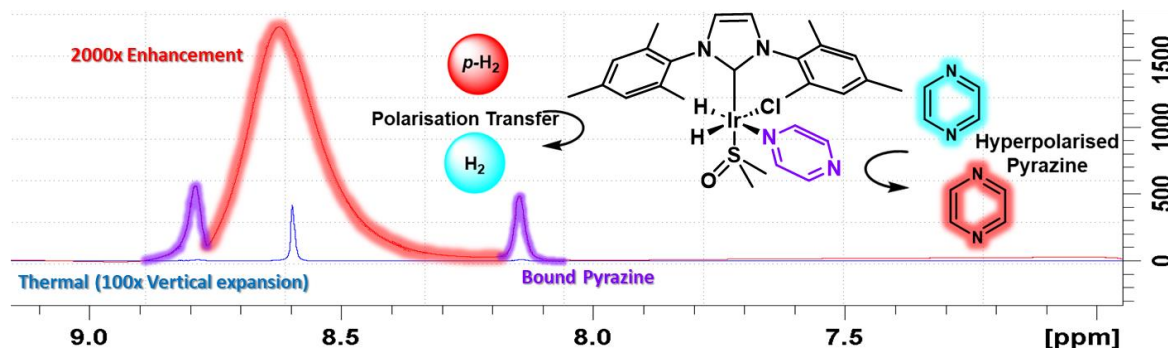


Figure 1: Pyrazine binds reversibly to the SABRE catalyst thereby allowing polarisation to transfer from *p*-H₂ to increase the NMR sensitivity of pyrazine by 2000-fold at 9.4 T.

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Synthesis of Poly(olefin-co-esters) by Switching Catalysts

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In 1963, Ziegler and Natta were awarded the Nobel prize for their discovery of well-controlled catalysts for olefin polymerisation.¹ Since then, commodity polyolefins have become a ubiquitous part of everyday life, and the demand is increasing every day. However, these polymers have significant disadvantages. They are typically synthesised from depleting fossil fuel feedstocks, have bioaccumulated throughout the natural ecosystem and are persistent (rather than degradable) in the natural environment. To mitigate these challenges, chemists across the globe are currently developing greener environmental solutions such as sustainable alternatives to conventional polyolefins.² However, replacing polyolefins is challenging as many bioderived and biodegradable polymers exhibit poorer material properties. The synthesis of block copolymers combining olefins with bioderived polar monomers is an interesting solution, as block copolymers can provide the 'best of both' in terms of material properties.³ Yet switching between these two mechanisms is highly challenging, due to the different monomer classes thus different polymerisation mechanisms required.

This presentation will describe an unprecedented synthetic route to prepare poly(olefin-co-esters), enabled through careful control of the catalyst metal-coordination environment. This strategy exploits a cationic titanium catalyst to prepare the polyolefin block, with the subsequent addition of a metal-based switch reagent to instigate cyclic ester polymerisation and generate the polyester block. Notably, the synthesis of these nonpolar-polar block copolymers was achieved utilising a simple one-pot strategy based on sequential monomer addition (Fig-1). The synthesis of copolymers is evidenced through a combination of techniques including NMR spectroscopy, DOSY NMR, size-exclusion chromatography and microscopy, and materials characterisation studies reveal the potential applications of these novel copolymers.⁴

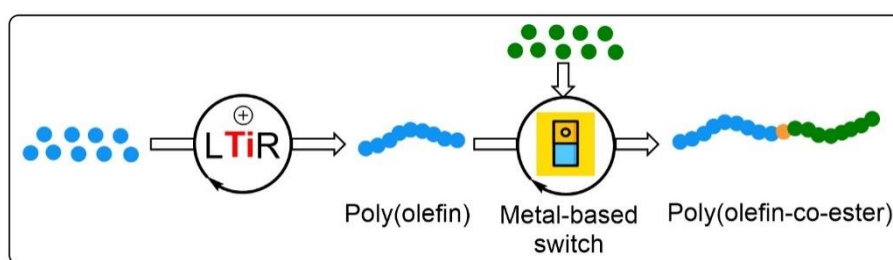


Figure 2: One pot synthesis of nonpolar-polar block copolymers

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Earth Abundant Bimetallics: Synthesis, Structure, and Applications in Sustainable Catalysis

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Complexes based on inexpensive, Earth-abundant lighter transition metals and main group elements are ideal candidates for more sustainable catalysis. Cooperative reactivity between multiple metal centres is well-known in heterogeneous catalysis, and many metalloproteins (such as Photosystem II) use ensembles of metals in their active sites. The principle of cooperativity is increasingly being embraced in molecular catalysts, where pairs of metals can be used to direct reactivity or selectivity.^[1]

The β -diketiminato ligand, $\text{CH}[\text{C}(\text{R}^1)\text{N}-\text{R}^2]_2$ has initiated numerous breakthroughs in molecular chemistry, catalysis and in mimicking of metalloproteins.^[2] This research aims to develop cooperative catalysts using these dinucleating ligands as a template,^[3] to provide two active sites within a single molecule to enable selective, sustainable and scalable functionalisation of small molecules.

Bimetallic magnesium complexes are presented, featuring macrocyclic frameworks with two anionic binding sites.^[4] These systems show entropically improved stability due to the chelate effect and offer the possibility of fine tuning the topological properties like bite angle, chirality and steric hinderance. Preliminary investigations into their reactivity toward unsaturated small molecules and applications in catalytic hydroboration of alkynes and ketones are also reported.

Additionally, recent results are presented using an alternative anilido-oxazoline ligand platform to prepare titanium complexes that efficiently catalyse the cycloaddition of CO_2 and bio-derived feedstocks, under mild conditions.

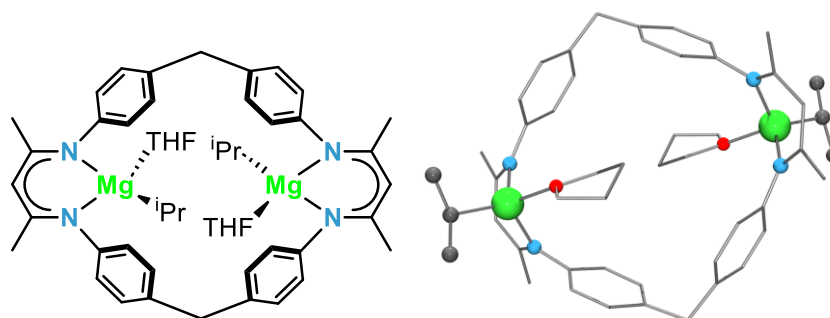


Fig. 3 Solid-state structure of an example Earth-abundant metal complex presented in this work.

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Probing the Speciation and Electronic Structure of Organozinc Reagents using X-ray Spectroscopy

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Organozinc reagents are essential for carbon-carbon bond formation in drug synthesis,¹ yet their chemistry is poorly understood. Understanding speciation and electronic structure in liquid-phase reactions is crucial. Problematically, zinc is spectroscopically quiet, mainly due to the filled 3d shell; investigating organozinc reagents is challenging using standard spectroscopies, e.g. UV-Vis, EPR, NMR. While X-ray absorption spectroscopy (XAS) is common for zinc-based compounds,² X-ray emission spectroscopy (XES) studies, particularly resonant XES (RXES), are rare.³ Additionally, X-ray spectroscopy studies of organozinc compounds are limited.

On I20, high energy resolution fluorescence detection XAS (HERFD-XAS), valence-to-core XES (VtC-XES), VtC-RXES, and time-dependent density functional theory (TDDFT) were used to study the liquid-phase speciation and valence electronic structure of various organozinc samples. This combined approach revealed the linear geometric structure of 14 organozinc compounds in non-coordinating solvents and quantified the impact of coordinating solvent ratios on diorganozinc speciation. VtC-RXES, akin to UV-Vis spectroscopy,⁴ allowed for the specific probing of Zn p-occupied to Zn p-unoccupied state transitions, helping to quantify the effects of 14 different substituents on diorganozinc species' electronic structure and reactivity (Figure 1). This study highlights the effectiveness of X-ray spectroscopic techniques in characterising the liquid-phase speciation and electronic structure of closed-shell diamagnetic complexes, including zinc.

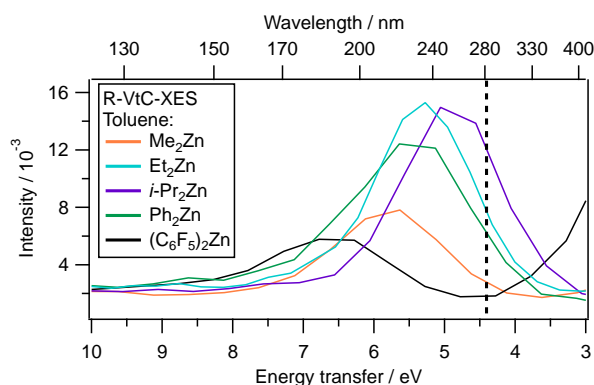


Figure 1. R-VtC-XES for Me₂Zn, Et₂Zn, *i*-Pr₂Zn, Ph₂Zn and (C₆F₅)₂Zn in non-coordinating toluene. The black dotted line represents the effective solvent cutoff for toluene using standard UV-Vis.

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Heterobimetallic d/f-block Complexes Supported by a Tripodal Ligand Framework

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In recent decades a wealth of f-block chemistry has been developed that draws on the diverse binding modes and unusual reactivity of uranium within well-defined complexes to bind and functionalize small molecules.¹ Additionally, heterobimetallic complexes have long been researched to understand the cooperativity that can emerge when two or more metal centres are held in proximity.² Our group has recently described the formation of heterobimetallic d/fblock complexes with Mn²⁺, Co²⁺, and La³⁺ by sequential metalation of the ligand (1,1,1-*tris*[(3-methoxysalicylideneamino)methyl]ethane).³ This has since been expanded to incorporate U³⁺ alongside Mn/Co within the ligand framework, and the reaction outcomes are sensitive to the reaction conditions and counter ions present. This presentation will discuss the synthesis and characterisation of both the lanthanide and actinide heterobimetallic complexes with a view to assessing their propensity to participate in small molecule activation chemistry.

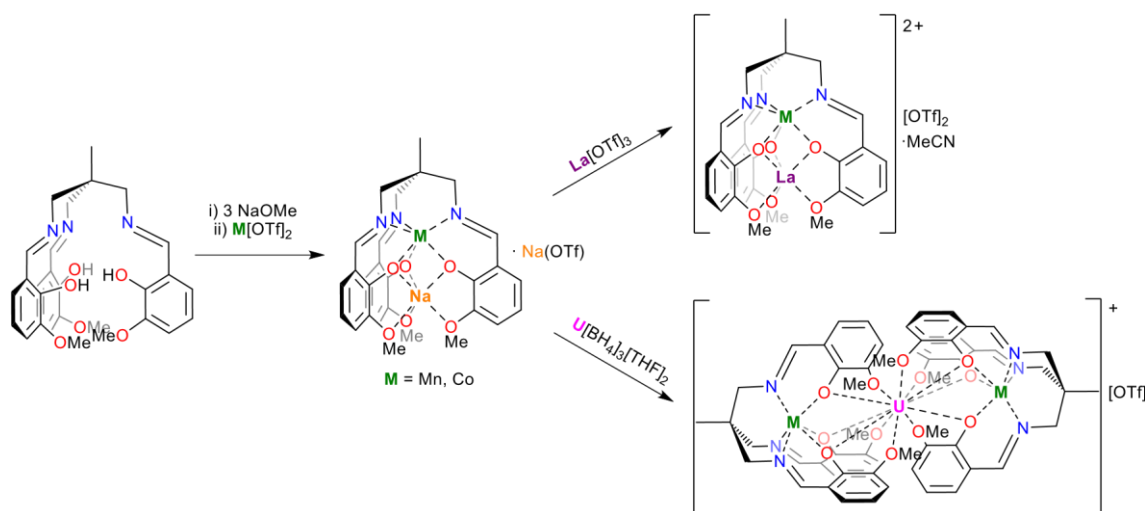


Figure 1: Synthesis of heterobimetallic complexes of (1,1,1-*tris*[(3 methoxysalicylideneamino)methyl]ethane).

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High Oxidation State *f*-Element Amide Chemistry

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Lanthanide (Ln) elements are highly electropositive and readily oxidised to Ln(III) under ambient conditions. However, except in the case of Ce(IV), oxidation to Ln(IV), or above, is energetically unfavourable under almost all conditions – save gas-phase or matrix isolation studies, or under highly oxidising conditions.¹ Nevertheless, Pr(IV) and Tb(IV) ions in solidstate materials reveal electronic structures which are intermediate between that of traditional Ln(III) ions, and that of transition metals, making their isolation in discrete molecular species an attractive target alongside an expansion of Ln(IV) chemistry to other members of the series.

Ln(IV) chemistry is limited due to large anodic potentials required for oxidation from Ln(III), and which are often incompatible with solution chemistry. For example, while Ce(IV) salts are commercially available, they are potent oxidants ($E_{1/2}$, $\text{Ce}^{\text{IV/III}} = +0.95 \text{ V vs Fc}^{+/0}$). The Tb(IV) and Pr(IV) ions are the next most accessible, though they are more oxidising than Ce(IV), with $E_{1/2}$ for $\text{M}^{\text{IV/III}} = +2.31 \text{ V}$ and $+2.41 \text{ V vs Fc}^{+/0}$, respectively. Careful ligand design can cathodically shift the onset of this $\text{M}^{\text{IV/III}}$ reduction (E_{pc}), and thus also $E_{1/2}$, to very negative potentials and generate stable Ln(IV) complexes (**Fig. 1A**). A small handful of such Tb(IV) and Pr(IV) complexes now exist (**Fig. 1B-C** for some examples).²⁻⁵ Here, we will discuss approaches towards the isolation of extremely reducing four-coordinate Ce(III) complexes, their Ce(IV) congeners, and extension of these principles to rare examples of molecular Tb(IV) and Pr(IV) complexes (**Fig. 1D**).⁶

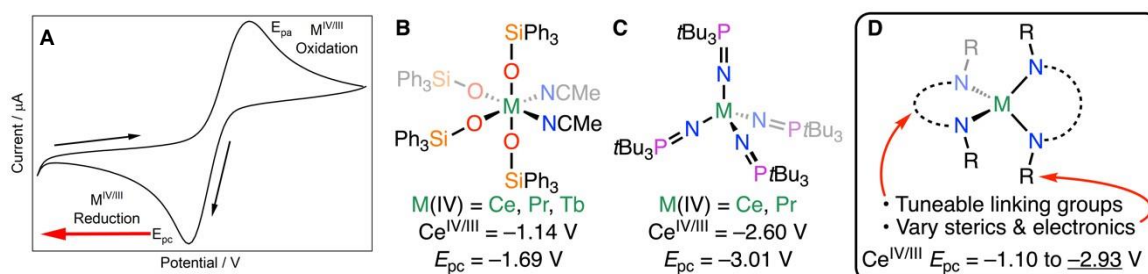


Figure 1. (A) Example cyclic voltammogram, highlighting the cathodic shift induced by appropriate ligands. (B-C) Some state-of-the-art Ln(IV) complexes. (D) Work to be discussed.

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Computational Insights into Gold-Catalysed reactions of 1,3-enynes

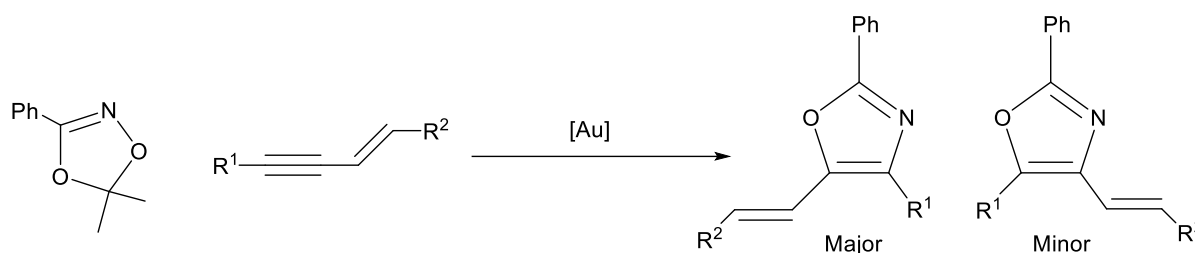
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The gold-catalyzed coupling of alkynyl thioethers with nucleophilic nitrenoids has been reported previously both synthetically^{1, 2} and computationally.³ However, the coupling of nitrenoids with 1,3-enynes could provide a synthetic route to more structurally diverse vinyl-substituted heterocycles (Scheme). Here we report a computational study which provides mechanistic insight into the gold-mediated steps on the reaction coordinate. The key states in the reaction have been mapped and the effect of selected aryl substituents (R^1 , R^2) on the overall reaction rate and isomer distribution will be discussed. The computed potential energy surface will be presented, alongside Gibbs energies calculated by optimizing structures at BP86/def2-SVP level of theory, and performing single-point energy calculations at PBE0/def2-TZVPP level of theory. Insight into the nature of the key metal-ligand interactions have also been modelled with Natural Bond Orbital analysis, which revealed information about the interaction between the 1,3-enyne and the gold catalyst.



Scheme representing the gold-catalyzed reaction of a 1,3-enyne and dioxazole

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Exploring the Ligand Properties of Azophosphines

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Bidentate ligands are frequently used in transition metal catalysis with their properties fine-tuned for the intended catalyst system. A new synthetic route for a family of bidentate P,N donor ligands called azophosphines has recently been developed, and their initial catalytic activity explored.^{1, 2} The properties of these ligands needs to be explored before they can be effectively implemented into transition metal-based catalyst systems. To do this a range of azophosphine ligands and imine analogue ligands have been modelled using density functional calculations. These ligands have been modelled in a range of different coordination environments and a variety of steric and electronic ligand descriptors have been extracted. These ligand descriptors have been added to two different ligand knowledge databases (LKB-bid and LKB-PP).^{3, 4} Principal component analysis has been used to visualize ligand space and has allowed the comparison of the new azophosphine ligands to over 400 previously calculated ligands in both databases.

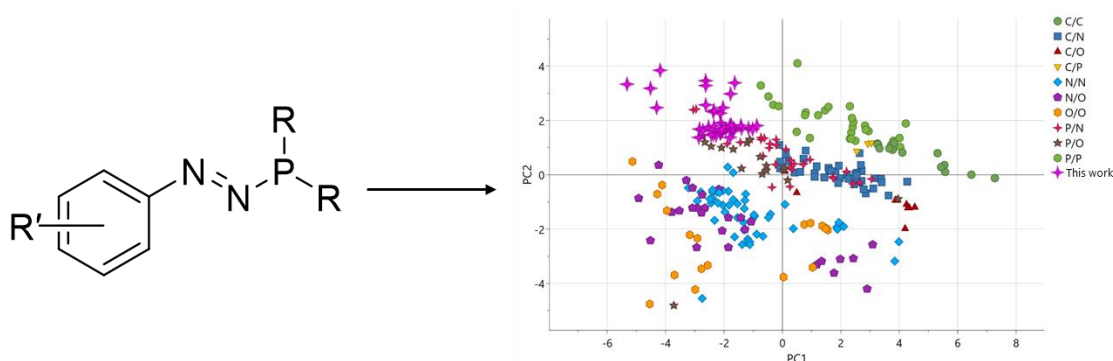


Figure 1: Azophosphine general structure (left) and PCA map of ligand space using LKB-bid database (right).

These new ligands occupy a previously unexplored region of ligand space, presenting the possibility of unique reactivity with a few ligands sitting close to ligands that have previously shown activity in transition metal-based catalysis thus giving direction for further research in this area.

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Novel Ru(II) polypyridine complexes for Upconversion: Synthesis, Spectroscopic insights and photophysical properties

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Over the years Ru(II) polypyridyl compounds have attracted a lot of attention due to their successful usage as anticancer and antimicrobial drugs.¹ Studies have shown that Ru(II)-centred MLCT states are well suited for sensitization of Ln(III)-centres leading to enhanced lanthanide luminescence. Such Ru(II)-Ln(III) assemblies have been studied for their application in optical imaging in the near infrared window² and have recently been demonstrated as the first example of a $f \rightarrow d$ molecular upconversion system.³

In this work we describe the synthesis and characterisation of novel $[\text{Ru}(\text{L})(\text{bpm})_2][\text{PF}_6]_2$ (where L = diimine), as well as discussing their photophysical properties for the potential integration into more efficient up-conversion systems with lanthanides. These complexes were synthesized from reaction of $[\text{Ru}(p\text{-cymene})(\text{L})\text{Cl}]\text{Cl}$ and 2,2'-bipyrimidine followed by anion metathesis. The compounds were characterised in solution by ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR, as well as in the solid-state by single crystal X-ray crystallography. Their photophysical properties were examined using UV-Vis absorption spectroscopy, and luminescence using steady and time-resolved spectroscopy. All were examined under aerated and degassed conditions, which, interestingly, showed a minimal quenching effect in luminescence by oxygen.

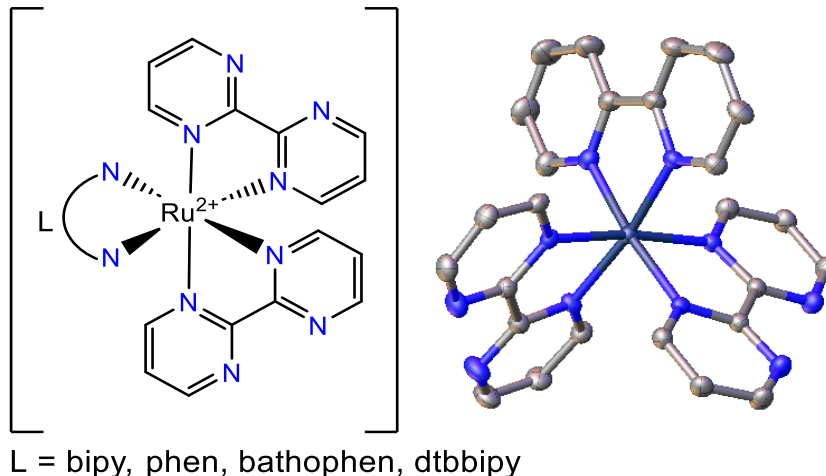


Figure 4 General Structure of $[\text{Ru}(\text{L})(\text{bpm})_2]^{2+}$ complexes omitting $[\text{PF}_6]^-$ anion and XRD structure of complex where L = bipy

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Recent Developments in Ester Hydrogenation Using Gusev™ Catalysts

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The reduction of esters to alcohols is a fundamentally important process for the manufacture of pharmaceuticals, detergents, cosmetics, flavours and fragrances. Traditionally, stoichiometric amounts of reducing agents, such as LiAlH_4 , have been used to reduce esters to alcohols thus generating significant volumes of waste. Homogeneous ester hydrogenations catalysts, such as Gusev™ catalysts, however provide a greener method and more sustainable alternative to traditional reducing agents.^{1,2}

Gusev™ catalysts provide excellent chemoselectivity for the ester functionality, exhibit turnover numbers of up to 100,000 and deliver cost-efficient methods in the production of alcohols. Distinguished applications of Gusev™ Ru-SNS catalyst include the reduction of specialty fatty alcohols under mild and solvent-free conditions. Recent developments for Ru-SNS catalysts, replacing chlorides with acetates, have demonstrated reduced activation times and improved turnover frequency.³ Gusev™ catalysts have been exclusively licensed to Johnson Matthey.

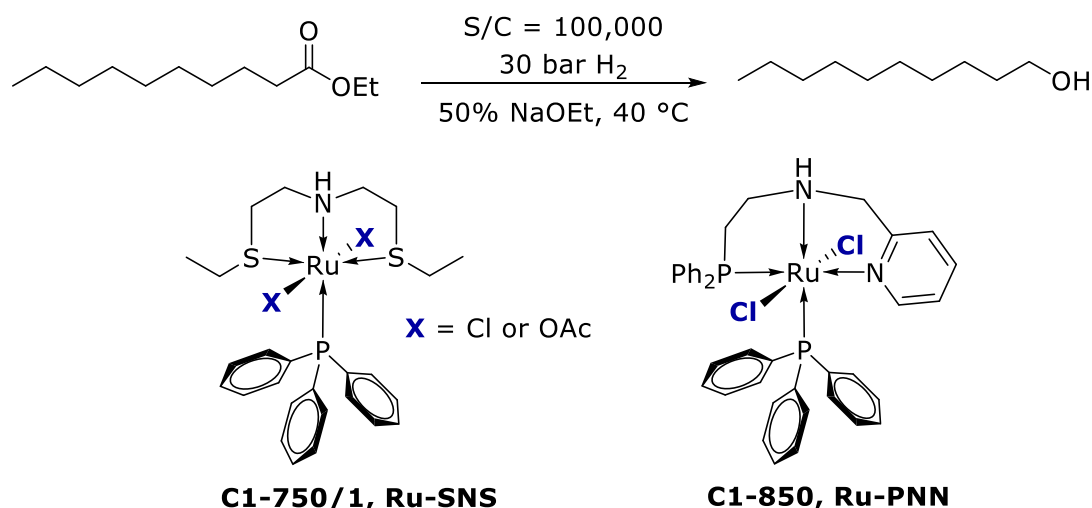


Figure 5. Hydrogenation of ethyl decanoate using Gusev™ catalysts.

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Time Resolved Spectroscopy of Group 10 Bipyridal Complexes

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This work uses time-resolved IR (TRIR) spectroscopy to detect the changes in excited state lifetime of a series of group 10 (Ni, Pd, Pt) bipyridine dichloride complexes. The IR active ring stretch modes of bipyridine ligands have been used as reporting groups in this TRIR study. The use of these modes has allowed the excited state dynamics of the complexes to be studied without altering the electronic environment by adding an additional traditional reporting group such as C=O. These complexes are related/pre-catalysts to photocatalytic species involved in reactions such as aryl C-H bond activations reported by groups such as the Mcmillans (1). This work followed from Tatsuhiko et al (2) who demonstrated that the bipyridine ligands could be used to observe the formation of a MLCT³ state in Ru(bpy)₃.

The complexes were dissolved in dichloromethane (DCM) and flowed through a Harricks cell under nitrogen. The pump wavelength was 330nm with the central wavelength of the probe sitting around 1600 wavenumbers. For all complexes two bleaches emerged at around 1620 and 1550 wavenumbers corresponding to two bipyridine ring stretch modes. The transient sits at the shoulder of the 1620 bleach at around 1610 wavenumbers. The 1620 bleach lifetimes for Ni, Pd and Pt were 20.5±3.9, 19.9±3.0 and 17.0±2.6 picoseconds respectively. These values are statistically identical which is surprising given the difference in atomic number across the complexes. This invariance in lifetime implies a different photo de-excitation scheme than proposed in the literature for a related nickel based photocatalyst (3).

Supporting DFT calculations have been run through ORCA in an effort to assign these transitions. Geometry optimisations of the ground, first excited and triplet state have been run for all complexes and for these geometries transition energies have been calculated but assignment is still pending.

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Defining the electronic structures of (hetero)metallocene anions

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Neutral and cationic derivatised transition metal metallocenes, generally $[M(C_5R_5)_2]^{0/+}$ ($R = H$, alkyl groups, silyl groups, etc.), are staples of organometallic chemistry, while anionic variants are distinctly less common.¹ As many applications of metallocenes are ultimately derived from their redox properties, accessing and thoroughly understanding these low-valent variants remains a worthwhile endeavour. The use of extreme steric bulk,² electron withdrawing silyl substituents,³ softer heteroles,⁴ or a combination of all these features,⁵ have been shown to be effective strategies for affording complexes of metals with a less favourable +1 oxidation state.

Taking inspiration from the above studies, here we target a systematic series of salts containing (hetero)metallocenes anions, seeking to determine their electronic structures by SQUID magnetometry and EPR spectroscopy. We anticipate that some of these complexes may exhibit unusual electronic configurations, e.g. non-Aufbau ground states, which we will interrogate with high-level ab initio calculations. Equally, we are interested in exploring the redox chemistry of these systems. In this contribution we present our preliminary findings on the synthesis, structure, and properties of the complexes that we have accessed to date.

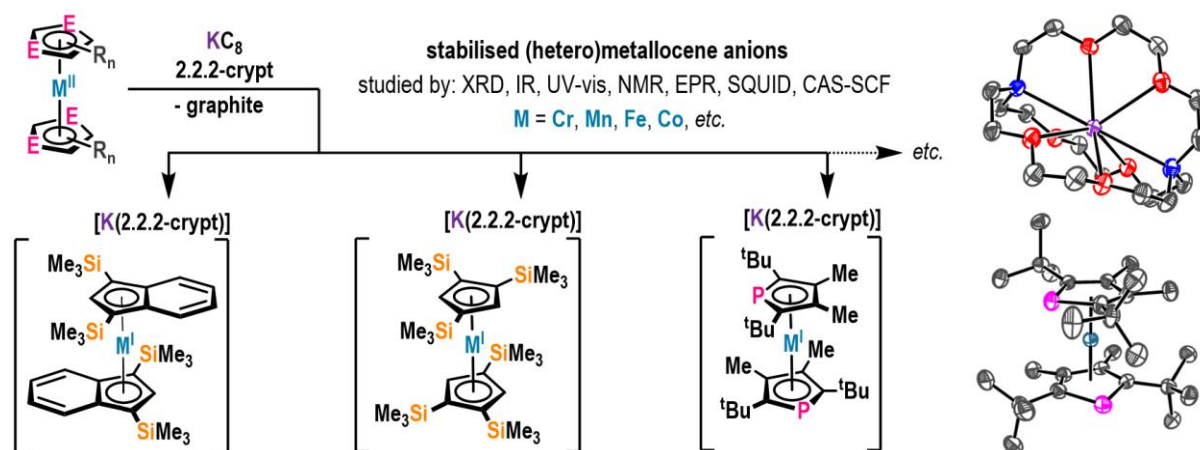


Figure: Representative derivatised (hetero)metallocene salts targeted in this study.

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Experimental actinide nano-chemistry for the future interim storage of the civil UK plutonium inventory

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During the reprocessing of spent nuclear fuel, valuable Pu and U is separated from waste fission products. This material is safely and securely stored in sealed packages under inert atmospheres as actinide oxide/dioxide nanopowder.¹ The materials are associated with a variety of challenges due to both the radiation emitted and the heat generated by radioactive decay.² It is known that these conditions could promote adventitious reactions with contaminant gases present in the storage atmospheres, such as radiolysis of water to produce H₂.³ As Pu cannot be studied within the university setting, surrogate materials (UO₂, ThO₂) have been synthesised. This poster will present initial work including the design of a reactor to perform in-situ reactivity studies using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) coupled with mass spectrometry. This will be used to interrogate the reactivity of surrogate materials with contaminant gases (Figure 1). The effects of Pu radioactivity on the surface chemistry of the surrogate materials can be simulated using the alpha beamline at the Daltan Cumbrian Facility and preliminary work to build a working reaction cell will be discussed. In addition, method development for the analysis of radioactive and highly air/moisture-sensitive samples using vibrational spectroscopy, surface area analysis and powder x-ray diffraction will be presented.

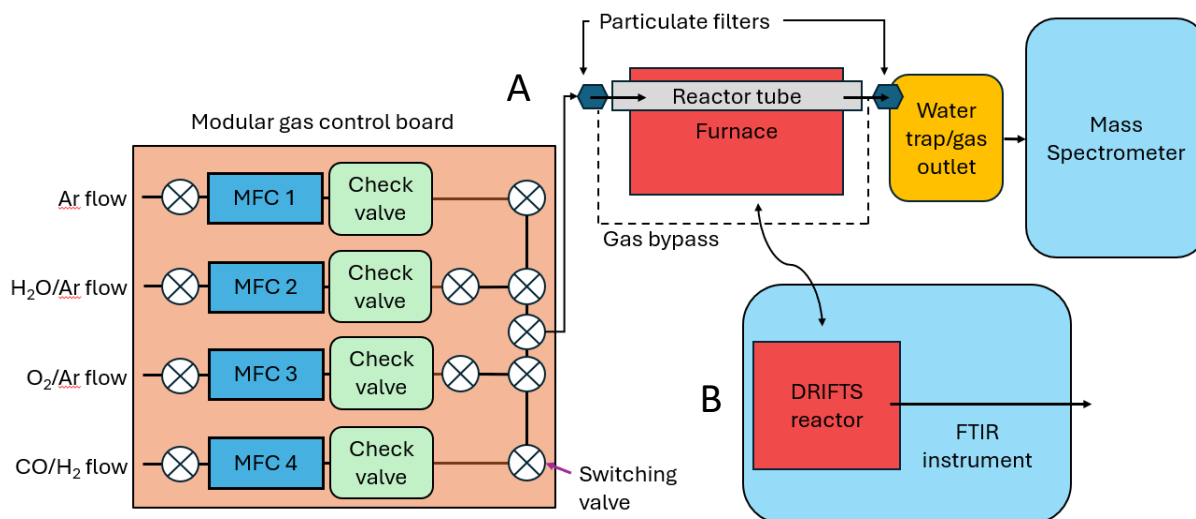


Figure 1: Flowchart demonstrating lab setup for performing analytical work on plutonium surrogate materials using in-situ FTIR (DRIFTS) and mass spectrometry. Alternative schemes for bulk reactions using a reactor tube (A) and smaller scale reactions in the DRIFTS reactor (B) are presented. MFC: Mass flow controller

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Kinetic and Thermodynamic Considerations of Transesterification in the Ring-Opening Polymerisation of Lactones

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The ring-opening polymerisation (ROP) of lactones is the method of choice to afford well-defined polyesters. Poly(lactic acid), the flagship of bioplastics, is obtained from renewable resources through industrial-scale ROP and degradable in specific conditions, such as industrial decomposition. The well-controlled and living nature of ROP can be exploited to modify polymer properties, for example via end-group functionalization or synthesis of copolymers.¹ Due to the living character of the polymerisation, sequential addition of different lactones is a common method to afford (multi-) block copolymers. However, depending on the catalytic systems and the monomer reactivity, transesterification reactions can be observed which compromise the copolymer block structure and result in scrambled polymer chains. Here, we provide further insight into the kinetic and thermodynamic parameters affecting ROP. In this work, utilising aluminium-based catechol amine ('*catam*') catalysts developed in the group,² one-pot and sequential methodologies are compared for the synthesis of copolymers using several lactones, namely lactide (LA), ϵ -caprolactone (ϵ -CL), and β -butyrolactone (β -BL). Depending on the conditions and methodologies applied, different copolymers are obtained, from well-defined to multi-block copolymers. Kinetic, mechanistic, and computational investigations are performed to identify the key factors influencing the copolymer structure and composition.

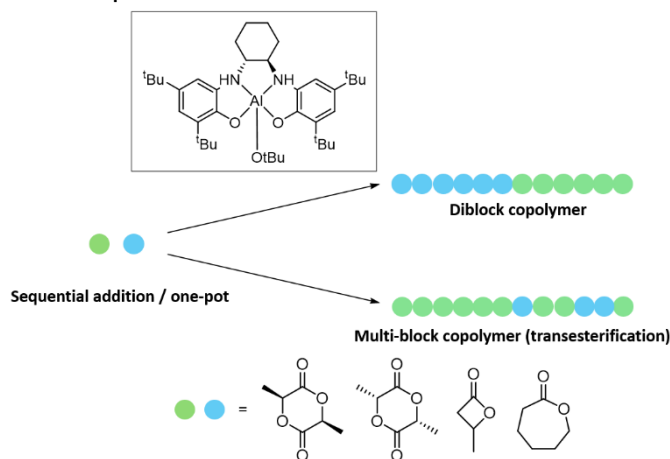


Figure 1. Formation of copolymers with different microstructures in the ROP of lactones.

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Developing Advanced Hyphenated Analytical Techniques to Quantify Iridium Speciation for Sustainable Catalysis

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Water splitting devices typically employ iridium oxide materials as anodes due to their combination of high activity and stability under the harsh acidic conditions required.¹ The scarcity of iridium is a limiting factor for the expansion of this technology to meet green hydrogen targets, hence implementation of a highly efficient closed loop recycling process is required.²

Currently, aqueous waste streams of iridium are translated to useful species such as iridium oxides via a hexahalide intermediate (Figure 1).³ Iridium speciation under aqueous conditions is notoriously complex, with, for example, iridium hexachloroiridate known to form more than seven species in acidic solution.⁴ These include the products of reduction and aquation processes which occur either spontaneously in solution, or with changing pH, temperature or concentration.⁵ An enhanced understanding of iridium speciation in aqueous solution will, therefore, be required for the optimisation of iridium recycling.

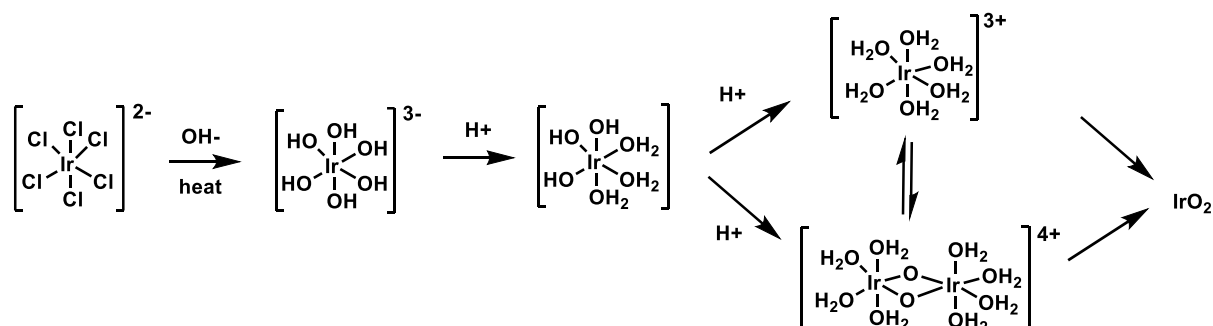


Figure 6- an example of a process by which the hexachloroiridate species is converted to an iridium oxide species. Adapted from Reference 3.

Prior attempts to identify iridium speciation using analytical techniques such as High Performance Liquid Chromatography (HPLC) and Ultra-Violet Visible (UV-Vis) spectroscopy have had limited success, with restrictions including the requirement for chelation and the inability to distinguish between species.⁴ This project therefore looks to investigate a combination of advanced hyphenated analytical techniques comprising of Cyclic Voltammetry (CV), Mass Spectrometry (MS) and UV-Vis to quantify iridium speciation in solution.

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Can Palladium Intermediates Serve as a Viable Route to Synthesise Photoluminescent Gold(III) Complexes?

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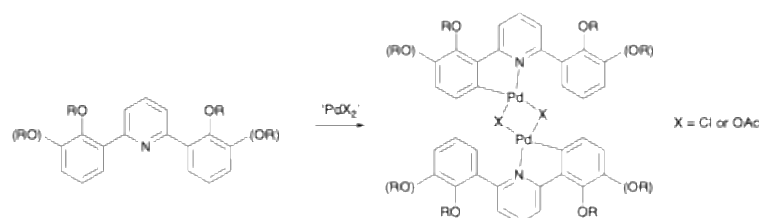
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Abstract

Doubly cyclometallated Au^{III} complexes of 2,6-diphenylpyridines have attracted attention as potential triplet emitters for electroluminescent devices¹ and we have demonstrated examples where modification of the ligands leads to emitters that are also liquid crystalline.² However, a significant inconvenience is the fact that direct auration of these ligands is extremely challenging and normally proceeds through toxic mercury(II) intermediates.³

As part of studies to try to replace mercury in these syntheses, we recently reported that dinuclear chloropalladium(II) complexes (Figure – X = Cl) can be formed of these ligands and that these complexes can successfully be transmetalated using [AuCl₄][–].⁴

Keen to explore this chemistry further, we prepared analogous dimers starting from palladium acetate (Figure – X = OAc), hoping to profit from the strongly basic nature of acetate in the subsequent C-H activation with gold. The complexes are prepared by reaction of palladium acetate with the ligand in HOAc at elevated temperature,⁵ but in contrast to their chloro analogues, are highly fluxional on the NMR timescale. In addition, the dissociation of the dimeric complex to the monomer and the existence of isomers has made the interpretation of the NMR spectra complicated. The synthesis and spectroscopic properties of these new complexes will be discussed.



Synthesis of Palladium(II) Intermediates

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Coordination Sphere Engineering in Low-Symmetry Metal Organic Cages

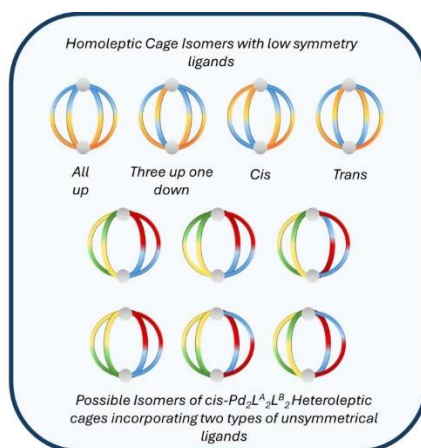
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Metal-Organic Cages (MOCs) are supramolecular structures capable of host-guest binding within their cavities, which allows them to be studied for applications such as catalysis, storage and gas sorption. Although highly symmetrical MOCs with one type of ligand have been shown to be capable of being used in multiple applications, we are interested in the exploration of lower symmetry systems to overcome limitations such as shape selective guest binding.^[1]

The challenge with creating homoleptic cages with unsymmetrical ligands is that several isomers can form in solution. Hence, directing strategies to afford orientation selective assembly need to be introduced for their controlled formation. Furthermore, the formation of heteroleptic cages is also challenging as multiple ligands need to assemble in a site-selective manner with high fidelity. I will show how the use of multiple design strategies such as geometric complementarity and coordination sphere engineering principles can provide a route for the formation of more structurally sophisticated MOC systems, as well as direct isomer selective assembly.^[2] I will discuss how interactions in the first and second coordination sphere enables isomer selectivity with both homoleptic and heteroleptic Pd (II) cage systems towards the development of structurally sophisticated, low-symmetry MOCs.^[3]



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Design and synthesis of pyridyl phosphonate-functionalised polyoxometalates

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The organofunctionalisation of polyoxometalates (POMs) offers a route towards designing organic-inorganic hybrid materials with modular structures and tunable physical properties.¹ Recent studies have shown that integrating redox-active POMs with transition metal-based coordination complexes can enhance catalytic performance through synergistic effects.² Such hybrid systems hold great promise for applications in electrocatalysis, energy conversion, and small-molecule activation.

In this work, we present the synthesis of novel pyridyl phosphonate-functionalised POMs as versatile building blocks for multi-component electrocatalytic assemblies. The pyridyl groups provide well-defined coordination sites for metal complexes, allowing precise control over the electronic and structural properties of the hybrid system. Our synthetic approach involves functionalising lacunary POM precursors with pyridyl phosphonate linkers, facilitating their integration with molecular electrocatalysts. Spectroscopic and electrochemical characterisation highlights their potential for modulating electron transfer properties and catalytic activity.

Future research will focus on conjugating molecular electrocatalysts to these pyridyl-modified POMs to construct structured multi-component systems.³ By systematically tuning the electronic interactions between the POM core and the attached catalytic units, we aim to develop efficient and selective electrocatalytic systems for sustainable energy conversion and small-molecule transformations.

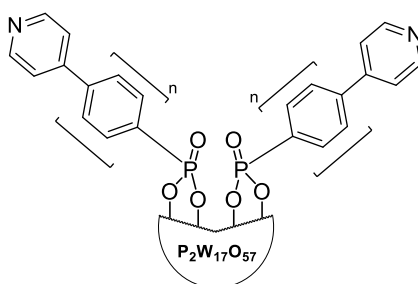


Figure 1: Proposed molecular structure of a pyridyl phosphonate-functionalised POM hybrid

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3D Printed Scaffolds for Catalytic Reactions in Flow

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Homogeneous catalysts are desirable due to the high activity and better control of selectivity compared to heterogeneous catalysts.¹ However issues such as separation of catalysts and product purification arise in homogeneous systems.¹ Heterogeneous catalysts are easier to separate and can be recycled, therefore efforts have been made to heterogenise homogeneous catalysts.¹ These include immobilization on organic and inorganic supports such as silica, metal organic frameworks and polymers.^{1,2}

Here we present our attempts at immobilizing hydrogenation catalysts on a polymer support via 3D printing. Preliminary results show the successful printing of a polymer backbone based on the work by Saccone et al.³ Functionalization of the polymer backbone has been successful with various ligands. These will be available sites for ligand exchange with transition metal complexes, such as Wilkinson's catalyst to obtain a structured heterogenized homogenous catalyst for applications in flow.

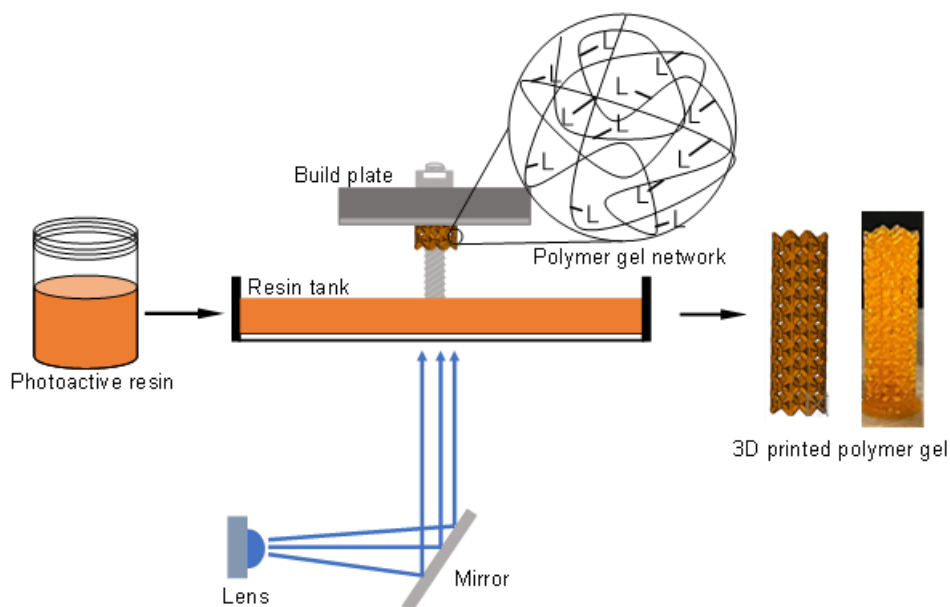


Figure 7: Schematic of process of 3D printing the photoactive resin to obtain a highly crosslinked polymer gel functionalised with a desired ligand (L).

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Rare earth small molecule activation through single-crystal to single-crystal reactions

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Rare earth small molecule activation chemistry has recently provided landmark results,¹ including the End-on nitrogen bridging and the fixation of carbon monoxide by a scandium (II) complex.^{2,3} Although the solid-state structures of starting materials and products in such transformations are typically authenticated by single crystal X-ray diffraction (XRD), the reaction mechanisms and identities of reactive intermediates are currently poorly understood. As the reactions of solid-state materials with gases are diffusion-limited, these conditions can provide more control than solution-phase chemistry. Studying small molecule activation reactions by single crystal XRD can also provide opportunities to unlock new reaction pathways, and to avoid side-reactions that give undesirable products.^{4,5}

Here we will present the use of single crystal XRD to study the encounter interactions of gases with coordinatively unsaturated rare earth complexes when reactions are initiated. This will provide new insights into f-block electronic structure and small molecule activation, which is crucial given the technological importance of these elements.

We thank the University of Manchester for funding the project.

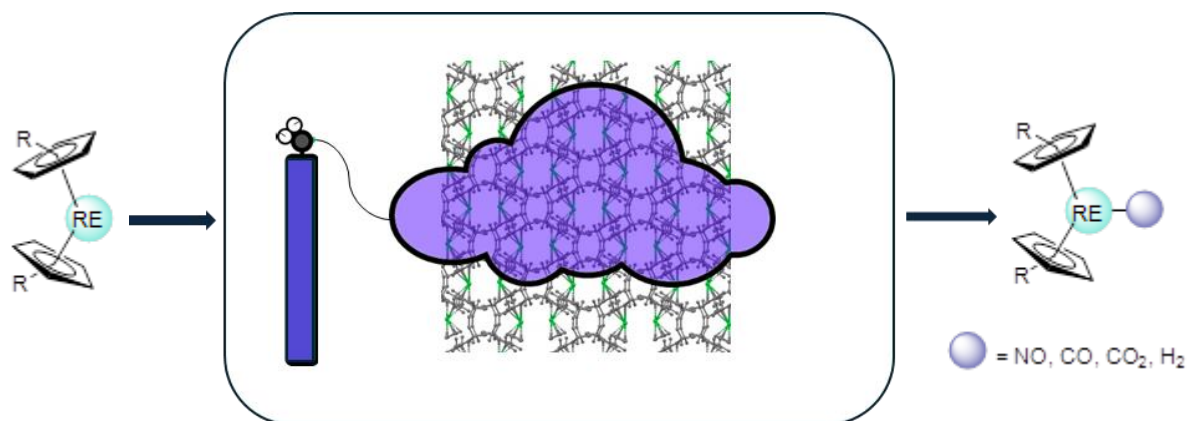


Figure 1. Schematic of solid-state/gas reaction methodology.

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Shedding Light on Low-Valent Chromium Organometallics

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Nowadays, catalytic processes still rely on the rarest transition metals on the Earth's crust (Rh, Pd, Ir, and Pt) due to their well-behaved and predictable two-electron organometallic reactivity.¹ Yet, their high cost and carbon footprint have urged chemists to explore the use of more sustainable and economical earth-abundant 3d metals as catalytic tools. In this regard, **low-valent chromium (Cr) species**, an inexpensive and abundant element, remains surprisingly underexplored in the fields of organometallic redox catalysis, albeit they are widely used in industry (e.g. Philips catalyst for ethylene polymerisation reactions) and present rich redox chemistry, as well as very low toxicity profiles.³ Nevertheless, substantial limitations must be still addressed if Cr redox catalysis is to be broadly applied, including the requirement of directing groups and the superstoichiometric use of Grignard and metallic reducing agents.⁴ Furthermore, the proposed organometallic intermediates in these transformations are ill-defined, as is the nature of the catalytically active low-valent Cr species involved.

Herein, we describe the preparation and characterisation of well-defined organometallic species based on abundant and non-toxic low-valent chromium metal (oxidation states 0 and +1),⁵ as well as the investigation of their organometallic reactivity and mechanistic insights, which is essential to (a) overcome current limitations in the field, and (b) unlock predictable and controllable two-electron catalytic manifolds.

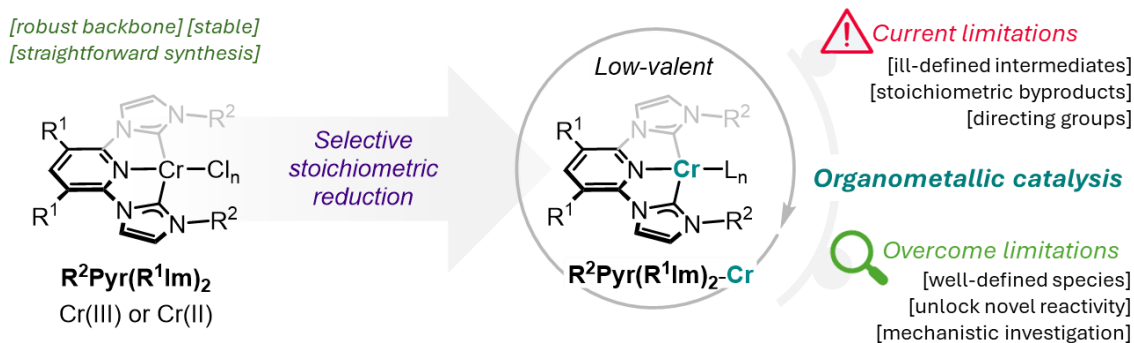


Figure 1. Well-defined organometallic Cr species described.

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Is $\text{Fe}(\text{PMe}_3)_4$ Really a Source of $\text{Fe}(0)$?

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The chemistry of iron has become increasingly important, particularly with a growing need to find new and sustainable catalysts. The $\text{Fe}(0)$ source tetrakis(trimethylphosphine)iron ($\text{Fe}(\text{PMe}_3)_4$, **A**) was originally reported in 1975 and postulated to exist in equilibrium with the cyclometallated $\text{Fe}(\text{II})$ species, **B** (Figure 1).¹ **A** has been prepared and used in numerous high-profile catalysis studies, including *ortho*-C–H activation chemistry, with **B** largely considered to be an off-cycle species.^{2,3} **A** has also been employed as a catalyst in alkylation, borylation and decarbonylation reactions, as well as being a precursor to catalysts with tridentate ligand systems such as POCOP and PSiP, which have been used to catalyse the borylation of styrenes.^{4–8} However, our preliminary studies indicate that **A** and **B** might not be in equilibrium and that, in fact, very little **A** is formed at the point of synthesis. The reversibility of the C–H activation has been analysed through the use of variable temperature NMR spectroscopy and deuterium labelling studies - these results will be presented.

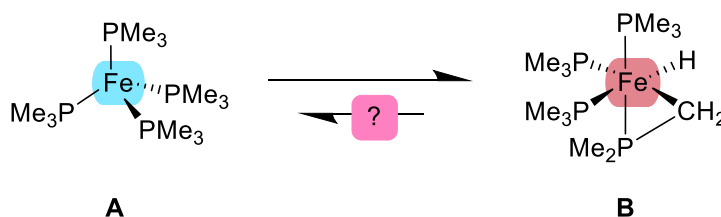


Figure 1: Tetrakis(trimethylphosphine)iron in the iron(0) and iron(II) oxidation state (complex **A** and **B** respectively), through C–H activation.

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Stabilising Tetravalent Lanthanides with Chelating Amide Ligands

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Oxidation state is fundamental property in chemistry and for the lanthanides this is typically limited to the trivalent oxidation state, M^{3+} . Almost all lanthanides have been isolated in the divalent oxidation state as M^{2+} molecular complexes¹. However, until recently only Ce had been isolated as tetravalent M^{4+} molecular complexes. This has now been expanded to Tb and Pr through the work of both the La Pierre and Mazzanti groups²⁻⁴.

Mazzanti and coworkers isolated a series of tetravalent lanthanide complexes supported by siloxide ligands with two solvent molecules of acetonitrile coordinated³. It was then shown that by replacing these acetonitrile molecules with a chelating ligand that, as expected, the electrochemical stability of the tetravalent complex could be improved⁵. In this work we take advantage of chelating amide ligands to stabilise a tetravalent Ce complex. Cyclic voltammetry reveals that the electrochemical stability of this complex is on par with the current state-of-the-art. This work will be further developed with the aim of stabilising tetravalent Tb and Pr. Expanding this chemical area will lead to new reactivity and physical phenomena.

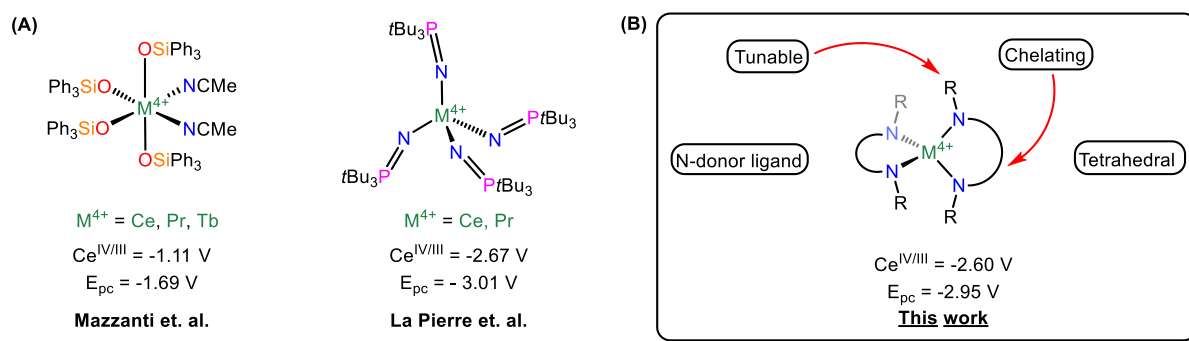


Figure 1. (A) Current state-of-the-art frameworks, Left: siloxide donors, Right: imidophosphorane donors (B) This work.

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Vanadium Complexes with Hybrid Ligands for Small Molecule Activation

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The functionalisation of abundant small molecules, such as N₂ and CO₂, into high-value chemicals is of great importance as the chemical industry strengthens their commitments to sustainability. However, the high kinetic and thermodynamic stability of these molecules typically renders them inert. Metalloenzymes enable biological systems to achieve these challenging transformations, where the transition metal-containing active site facilitates substrate binding and redox processes.¹ A synthetic approach is through activation of small molecules by a homogeneous transition metal catalyst. These catalysts often employ ligand scaffolds that offer a high degree of steric tunability, to stabilise the metal centres in low oxidation states. Anilido-aldimines ([*o*-C₆H₄(NAr¹)(CH=NAr²)][−] = AnIm) are versatile ligands, with bidentate, tridentate, and bis(bidentate) frameworks reported in the literature.² AnIm ligands with a pendant donor arm are particularly attractive, owing to their potential for multidentate chelation and further tuning of the electronic environment. Inspired by the vanadium nitrogenase FeV-cofactor, vanadium complexes have recently been employed towards N₂ activation and catalysis.^{3, 4}

This work explores the coordination chemistry of novel vanadium complexes supported by N,N,S tridentate AnIm ligands (**Figure 1**). The characterisation of these complexes, and preliminary studies of reduction reactions in the presence of N₂ and CO₂, will be presented.

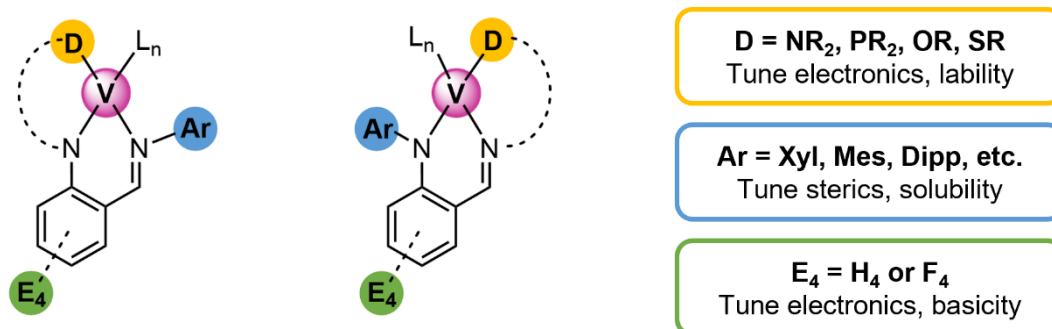


Figure 1. Proposed vanadium complexes for small molecule reactivity studies.

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Surface Functionalisation with Arylimido-Polyoxometalates for Optoelectronic Applications

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Functionalization of polyoxometalates (POMs) with arylimido groups results in the formation of hybrid materials with strong electronic communication between the organic and polyoxometalate moieties. This communication can produce charge transfer systems that display non-linear optical properties,¹⁻³ with high visible transparency and the capacity for redox switching.³ Our goal is to translate this work to surfaces in order to produce materials with bulk properties, and investigate both the electronic (charge transport) and optical properties in different redox states.

This poster will present current work synthesising arylimido-POMs with surface binding groups, and preliminary investigation of surface binding.

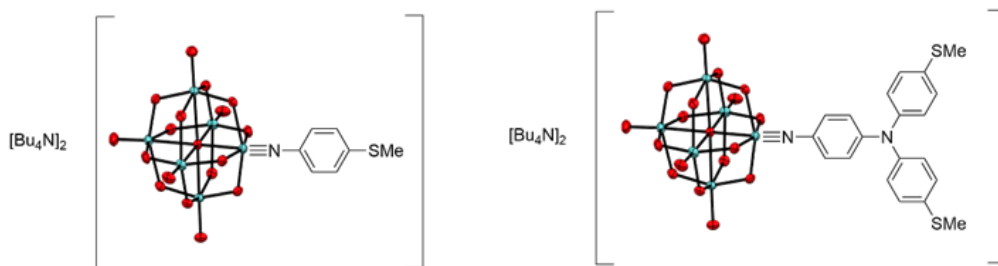


Figure 1: Arylimido-POMs derivatized with -SMe anchoring groups

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Understanding solution absorbance and photoluminescence of divalent lanthanide tris(pyrazolyl)borate complexes

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Divalent lanthanide Ln(II) materials have applications in lighting and sensing due to their tuneable absorption and photoluminescence (PL) from parity-allowed 4f-5d transitions.¹ The surrounding ligand field at Ln(II) influences the 5d energy levels and the 4f-5d energy gap, allowing tunability of absorption and PL across the visible region.² However, investigations into the effect of the ligand environment on divalent lanthanide complexes in solution are challenging due to their high reactivity, with many studies limited to the least reducing Eu(II).³ Reports of solution luminescence are progressively less common for the more reducing lanthanides Yb(II), Sm(II) and Tm(II).⁴ This research focuses a series of Ln(II) complexes (Ln = Eu, Yb, Sm) incorporating the unsubstituted hydrotris(1-pyrazolyl)borate (Tp) ligand. The Ln(Tp)₂ fragment has space in the coordination sphere for additional interaction allowing a variety of complexes to be prepared, including the monomeric [Yb(Tp)₂], dimeric [{Eu(Tp)(μ-κ¹:η⁵-Tp)}₂] and Lewis base adducts such as [Sm(Tp)₂(DME)] (Figure 1a).^{5, 6} Data are presented demonstrating the effect of Lewis base coordination on the absorbance and PL of the Ln(Tp)₂ fragment, and how this translates across the lanthanide series with changing ionic radius and electronic structure.

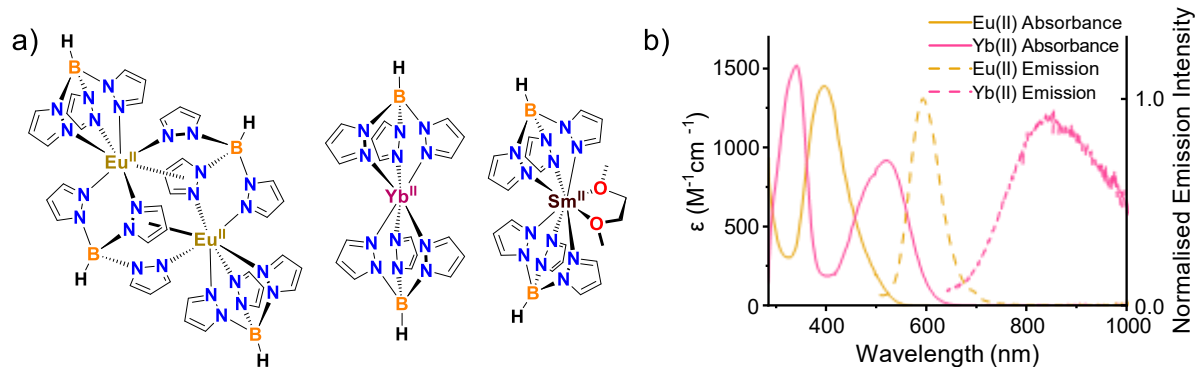


Figure 1: a) Structures of Ln(II) complexes (Ln = Eu, Yb, Sm). b) Absorbance (solid, left axis) and emission (dashed, right axis) spectra of Eu(II) (orange) and Yb(II) (pink) complexes.

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Structure, Bonding and Reactivity of a Novel Cobalt-Aluminium Complexes

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The preparation and applications of heterobimetallic complexes continue to occupy researchers in the fields of organometallic, main group, and coordination chemistry.¹ This interest stems from the promise these complexes hold as precursors to materials, reagents in synthesis and as new catalysis.

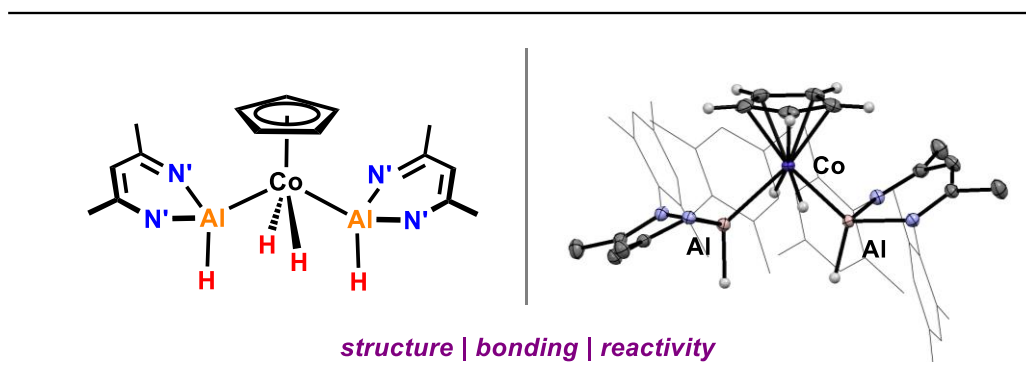


Figure 1. Single crystal structure of the heterobimetallic complex.

Here we report the synthesis and structural characterization of an unusual Cobalt/Aluminum complex (Figure 1). This species is accessible through the reaction of two β -diketiminato stabilized aluminum dihydrides with a cobalt cyclopentadienyl fragment and its structure could be determined by single X-ray diffraction. Based on crystallographic data as well as a computational analysis of the bonding situation, this species is best described as Cobalt(V) dihydroaluminum complex possessing a pseudo square pyramidal coordination geometry strongly resembling structurally related cobalt silyl complexes of the type $[\text{CpCo}(\text{H})_2(\text{SiHPh}_2)_2]$.² Moreover, we will also present the influence of different aryl substitutes on the β -diketiminato on the complex formation.

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Solvent-free Rare Earth Bis(trimethylsilyl)phosphide Complexes

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Rare Earth (RE) heavy pnictide chemistry is immature compared to that of N-donor ligands due to the preference of hard Lewis acid RE ions to bond with hard Lewis base donor atoms.^{1,2} For example, bis(trimethylsilyl)amide, {N(SiMe₃)₂}, has supported many advances in RE chemistry,³ but the chemistry of bis(trimethylsilyl)phosphide, {P(SiMe₃)₂}, is still in its infancy.² In recent years our group and collaborators have used a combination of luminescence, ³¹P NMR and EPR spectroscopy, together with DFT and *ab initio* calculations, to probe the electronic structures of solvated RE {P(SiMe₃)₂} complexes.^{4–6}

In previous work, Westerhausen reported the synthesis of the dimeric solvent-free Y(III) {P(SiMe₃)₂} complex [Y{P(SiMe₃)₂}₂{μ-P(SiMe₃)₂}]₂ (**1-Y**) by the protonolysis reaction of [Y{CH(SiMe₃)₂}₃] with 3 eq. HP(SiMe₃)₂ in toluene.⁷ We have extended this series via modified protocols to synthesise the structurally analogous complexes [RE{P(SiMe₃)₂}₂{μ-P(SiMe₃)₂}]₂ (**1-RE**) (RE = Y, Gd, Dy, Er) (Figure 1). The separate reactions of **1-RE** with 2 eq. K{P(SiMe₃)₂} gives the corresponding ‘ate’ complexes [RE{P(SiMe₃)₂}₂{μ-P(SiMe₃)₂}₂K]_∞ (**2-RE**; Y, Gd, Dy, Er). Here we report comprehensive characterisation data for **1-RE** and **2-RE**.

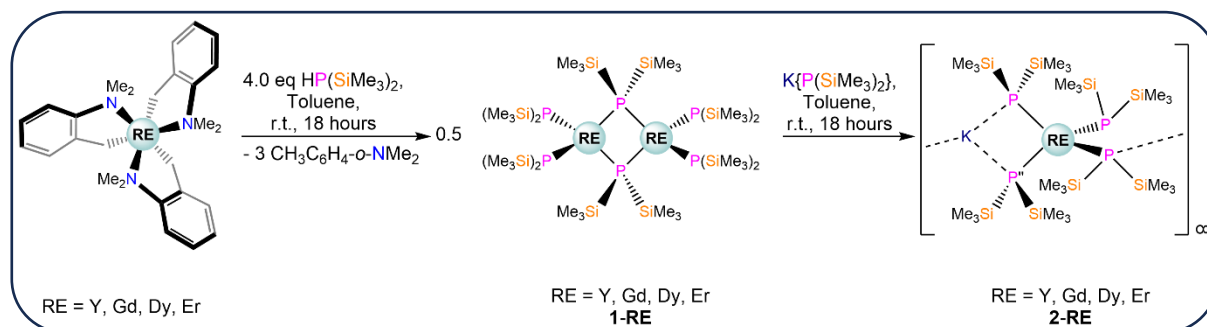


Figure 1. Synthesis of [RE{P(SiMe₃)₂}₂{μ-P(SiMe₃)₂}]₂ (RE = Y,⁷ Gd, Dy, Er; **1-RE**), and [RE{P(SiMe₃)₂}₂{μ-P(SiMe₃)₂}₂K]_∞ (RE = Y, Gd, Dy, Er; **2-RE**).

Acknowledgements: We thank the EPSRC UK National Electron Paramagnetic Resonance Service, and the University of Manchester for providing an EPSRC DTG.

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Trifluoromethanesulfonate as the Supporting Anion for Solid-State Organometallic (SMOM) Chemistry

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The use of single-crystal to single-crystal (SC-SC) reactivity using the $[\text{BAr}^{\text{F}}_4]^-$ anion ($[\text{BAr}^{\text{F}}_4]^- = [\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$) to isolate unstable or reactive organometallic species is well now established, for example for σ -alkane complexes or gold(I)-acetylene complexes.^{1,2} Other anions that can facilitate solid-state organometallic (SMOM) chemistry have been briefly investigated³, but the $-\text{CF}_3$ groups on the $[\text{BAr}^{\text{F}}_4]^-$ anion have been demonstrated to be crucial to this reactivity, by creating hydrophobic channels that can facilitate gas transport.⁴ However, the $[\text{BAr}^{\text{F}}_4]^-$ anion is expensive and alternative anions that can facilitate SC-SC reactivity are not well-explored. Here, we show that the trifluoromethanesulfonate ($[\text{OTf}]^-$) anion can act as a cheaper alternative which contains the crucial-to-SMOM-reactivity $-\text{CF}_3$ groups. It is also more coordinating than $[\text{BAr}^{\text{F}}_4]^-$ with the potential to bind κ^1 - or κ^2 - to the metal centre via one or two of the oxygen atoms and so could possibly influence reactivity, unlike $[\text{BAr}^{\text{F}}_4]^-$ which is thought to primarily have a stabilising role. *In crystallo* hydrogenation of $[(\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2)\text{Rh}(\text{NBD})][\text{OTf}]$ ($\text{NBD} = \eta^2\eta^2\text{-C}_7\text{H}_{12}$; $n = 2$ or 4) to form σ -alkane complexes has been investigated to benchmark its SMOM-reactivity. The σ -alkane complex can be formed when $n = 2$, and when left in an inert atmosphere the triflate coordinates in a κ^2 -fashion to the metal, appearing to swap places with the NBA *in crystallo*. When $n = 4$, however, the wider-bite angle phosphine makes oxidation to a Rh(III) over-hydrogenation product more favourable than the σ -alkane complex.

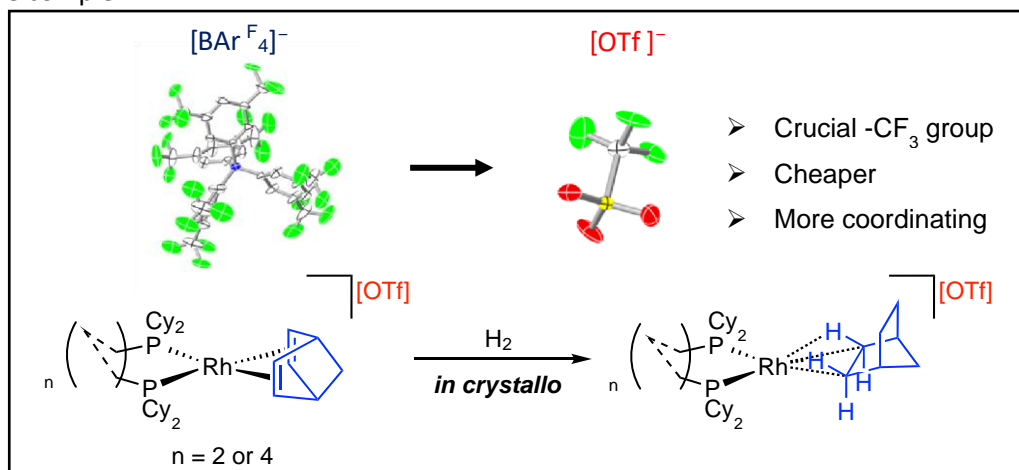


Figure 1 Molecular structure of the $[\text{BAr}^{\text{F}}_4]^-$ anion and the $[\text{OTf}]^-$ anion (top) and *in crystallo* hydrogenation of $[(\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2)\text{Rh}(\text{NBD})][\text{OTf}]$ ($n = 2$ or 4) (bottom).

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Lanthanide-containing Polyoxotitanates as Downshifting Materials for Enhanced Plant Growth

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The world's steadily growing population and global warming due to climate change are a threat to food security.¹ To meet this challenge, novel technologies are needed to increase crop production in a sustainable way. In this work, the use of luminescent down-shifting (LDS) materials based on molecular Eu³⁺-containing polyoxotitanates for plant growth enhancement is investigated.² Using a systematic, modular design strategy to optimise down-shifting properties, conversion of the ultraviolet spectral range to the photosynthetically active radiation (PAR) is achieved with quantum yields as high as 68%. The prototype Eu³⁺-compound can be incorporated into water-based acrylic varnish that can be spray-coated onto existing greenhouses. Comparing coated with uncoated greenhouses, basil plants produce 9% more leaf dry weight per plant, and a highly significant 10% increase in individual leaf dry weight. The coating reduces the amount of transmitted PAR by 8% but has advantageous effects on diffuse radiation and in reducing the internal mean temperature.³ Although there is some uncertainty as to the contribution of down-shifting, with the bulk of the increase probably being due to higher diffused light and the reduction in maximum daily temperatures, this study establishes a model for the design of LDS paints for real-world agricultural applications.⁴

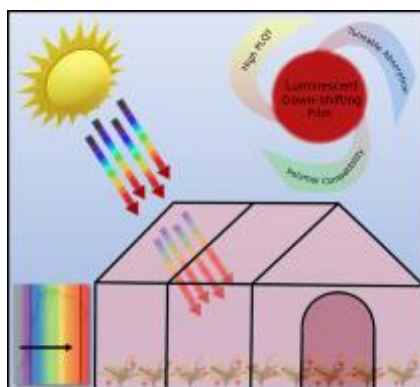


Figure 1. The concept of a downshifting coating for greenhouses investigated in this work. The incoming UV radiation is converted to PAR (mainly red light) to enhance plant growth. The coating is optimised with respect to absorption and emission (PLQY) properties as well as compatibility with commercial polymers and paints.

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Development of a Novel Presumptive Drug Testing Method on Amphetamine Type Stimulants Using Ionic Liquid Reagents

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Despite their simplicity in the face of modern developments in the analytical chemistry space, spot tests are still used frequently in forensic science.¹ In particular, the Simon's test is commonly used to differentiate between primary and secondary amines and has proven reliable in this application¹. However there has been a notable lack of innovation to improve it in terms of sustainability, robustness, preparation, stability and sensitivity. Research into ionic liquids has yielded optimistic results in terms of their versatility, flexibility and sensitivity for many fields within analytical chemistry.² This research aims to combine the mechanisms of the Simons test with the intrinsic properties of phosphonium ionic liquids to develop a new method for testing primary and secondary amines. Here, the synthesis, spot test results and chemical characterisation of four phosphonium Simon's test derived ionic liquids (P_{66614} , P_{44414} , P_{44416} & P_{4444}) are described, Figure 1. The application of these new liquids in the testing of commonly encountered amphetamine type stimulants is investigated and evaluated in comparison to its traditional Simon's test counterpart.

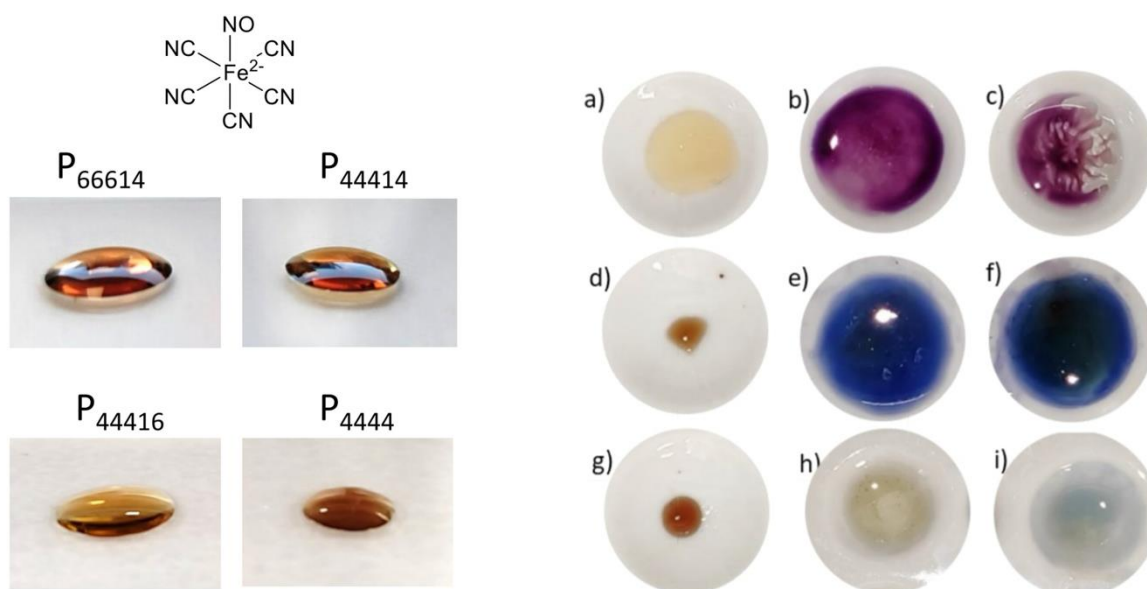


Figure 1: Active chemical structure of Simon's ionic liquid tests (left) with results of spot plate tests (right).

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Coordination Frameworks Assembled from Low-Symmetry 'Click' Cages

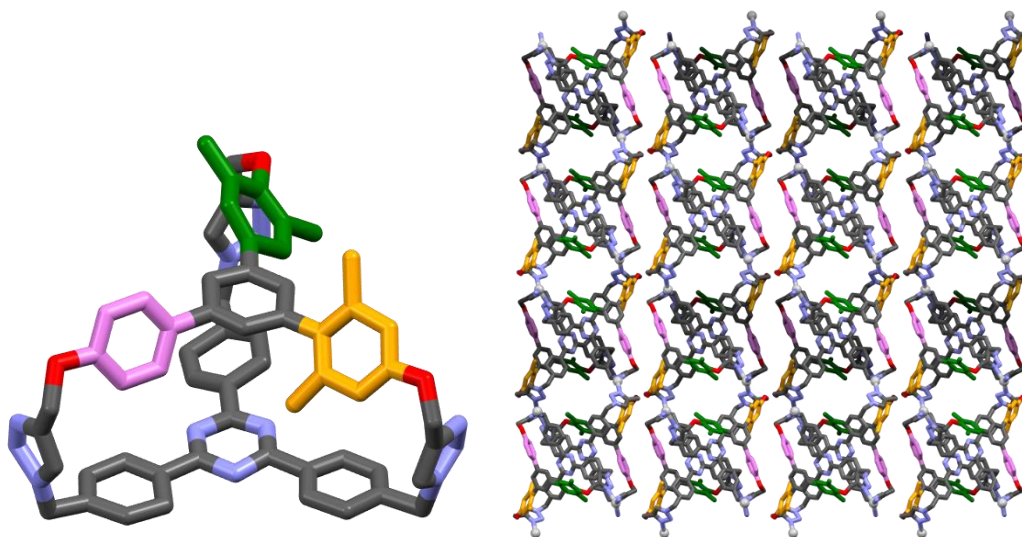
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Metal organic frameworks (MOFs) are porous crystalline materials that have had various interesting applications as transport, storage and catalytic materials.¹ MOFs has a wide range of accessible topologies from utilizing the chemistries of both organic and metal components, however, precision engineering of low-symmetry environments is a challenge. Cages are a discrete class of porous compounds that can have similar applications in solution, however their organization into the solid state while retaining their intrinsic porosity is often a limitation.² Combining these two classes of structures, implementation of discrete cages within MOFs has been shown to maintain the structural features of the cage, while utilizing the extended structure to have applications in the solid state.³

We have produced a strategy for tuning the symmetry of the cage structure under kinetic control, forming cages with C_3 , C_s and C_1 with chemically robust linkages. These can then be used as the organic component of a silver coordination framework to produce an extended material with the pore space inherited from the intrinsic porosity of the cage. This work serves as a proof of concept and shows that both the porosity of discrete materials can be implemented into an extended material and a new way that low symmetry pores can be implemented into MOF structures.



Crystal structure of chiral cage and crystal structure of Ag-chiral cage coordination framework

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Bio-orthogonal Catalysis for the Activation of Antibiotic Prodrugs

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Rising antimicrobial resistance has compromised the effectiveness of antibiotics. Resistance towards β -lactam antibiotics is of concern due to their widespread use and global reliance on them for the treatment of infections. Innovative strategies are therefore needed, with one promising approach being the localised activation of prodrugs through bio-orthogonal catalysis. This strategy ensures that the drug is only released at the site of infection, minimising off-target effects and potentially slowing resistance development.

Ruthenium-based catalysts have previously been explored for the uncaging of fluoroquinolones in Gram-negative bacteria by exploiting iron-uptake pathways, as well as for the uncaging of coumarin dyes in Gram-positive bacteria.¹⁻³ This work aims to expand the scope of this approach by investigating the activation of other antibiotic classes, including β -lactam antibiotics.

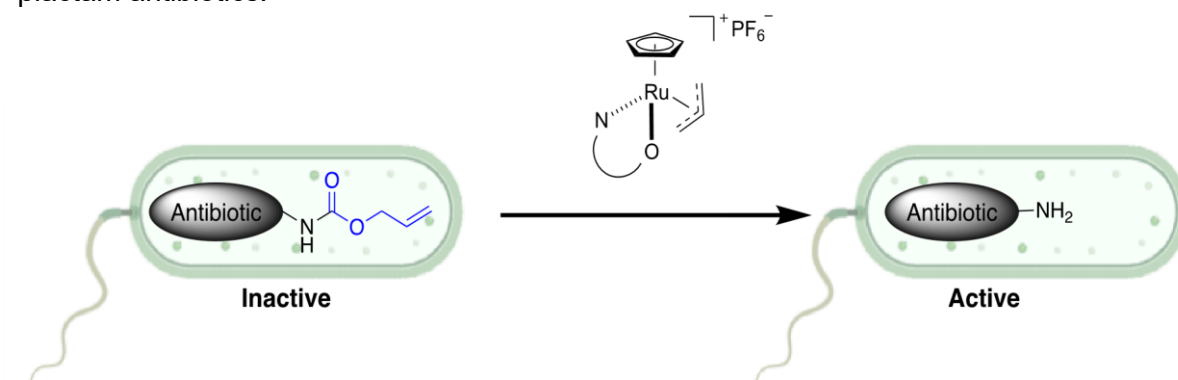


Fig. 1. Uncaging of antibiotic prodrug derivatives by a ruthenium-based catalyst.

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Cationic Metal Complex as a Promising Candidate Against Gramnegative Bacteria

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Antimicrobial resistance (AMR) has been a rising health concern with the emergence of drugresistant strains and our slow development on new antibiotics. The Gram-negative bacteria, with their complex cell membrane structure and promiscuous efflux pump, make them more resilient to antibiotics. A previous screening study showcases that metal complex has a 10times higher hit rate on antibacterial activity compared with organic compounds.¹ Meanwhile, metal complexes are not more toxic than organic compounds. Recently we discovered Re(V) dioxo complexes with promising antimicrobial activity against Gram-positive-² and Gramnegative bacteria. Herein, we present our progress in the synthesis of different Re(V) complexes and the study on their antimicrobial activities.

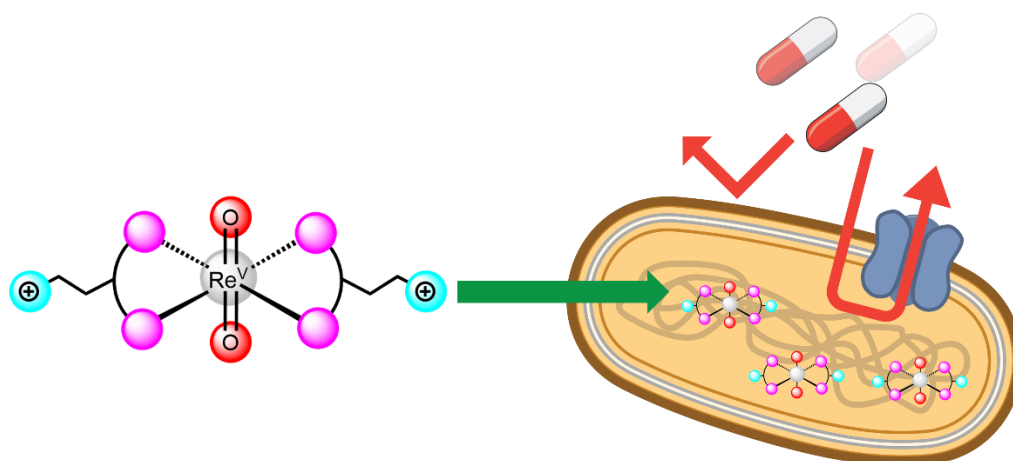


Figure 1. Schematic of cationic Re(V) metal complexes entering Gram-negative bacteria.

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Actinide Heterolide and Cyclooctatetraenide Sandwich Complexes

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The chemistry of early-mid actinide elements in low oxidation states is poorly understood compared to the transition metals¹, though redox chemistry is central to actinide separation science.² This is particularly apparent for thorium where most of the literature focuses the stable Th(IV) oxidation state, while examples of Th(III) or below are rare.³ This is due, in part, to the extremely negative Th^{IV/III} redox couple ($E^\ominus -3.3$ V vs SHE), though this can be tuned by coordination chemistry.³⁻⁵

All Th^{III} complexes to date feature 1st-row p-block donors to stabilise the metal centre, and almost exclusively substituted cyclopentadienide (Cp^R, {C₅R₅}), or cyclooctatetraenide, {C₈R₈}, ligands (**Fig. 1A**).³ Cyclic {EC₄R₄} (E = P, As, Sb, Bi) heterolides are isolobal to Cp^R ligands, but are weaker π -donors and better π -acceptors.^{6,7} As such, they may provide greater stability to electron-rich, low oxidation state metal centres and provide spin-active spectroscopic handles for examining the electronic structure of open-shell complexes.^{6,7}

Thus, heteroleptic heterolide cyclooctatetraenide sandwich complexes could be promising ligand systems for stabilising Th(III) metal centres. However, while the synthesis of these complexes on trivalent rare-earth complexes is facile (**Fig. 1B**) extension of this motif to the actinide elements is challenging.^{8,9} In this work we discuss the synthesis, electronic structure, and reactivity of low oxidation state *f*-element complexes towards this goal.

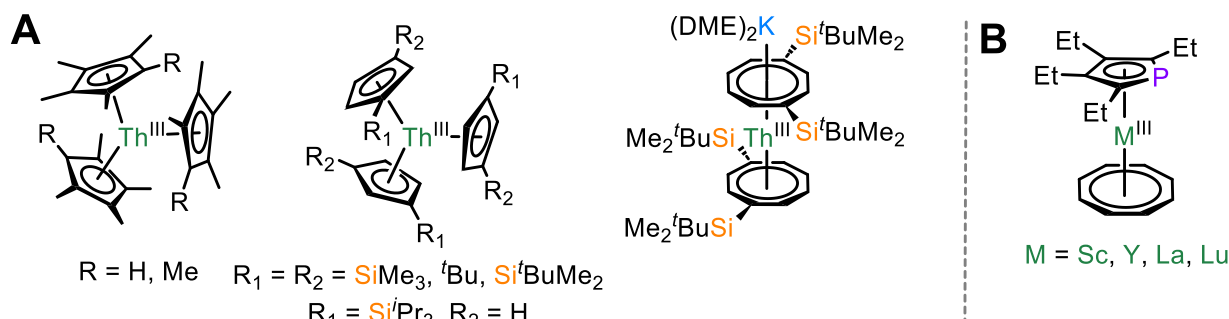


Figure 1. Previous Th(III) complexes and examples of heteroleptic rare-earth phospholide complexes.¹

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Synthesis and characterisation of polypyridyl pincer complexes of first-row transition metals

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Current electrocatalysts for the hydrogen evolution reaction (HER) typically rely on platinum-group metals and there is a need to move towards more sustainable alternatives. Recent studies have shown that pincer complexes of the first-row transition metals can act as catalysts for a variety of C-H activation processes.¹ Preliminary studies have also shown that pincer complexes may provide a route to new HER electrocatalysts.² More work is needed to understand the potential of the systems.

Here, we set out to prepare a range of sterically restricted polypyridyl complexes that allow us to study the interplay between molecular structure, complex (ligand and metal ion-based) redox properties and electrocatalytic performance in the electrochemical HER, ideally under aqueous and aerobic conditions. We show that disubstituted polypyridyl-based ligands can be used to support a new range of mononuclear complexes and that the properties of the complexes can be tuned through modification of ligand substituents.

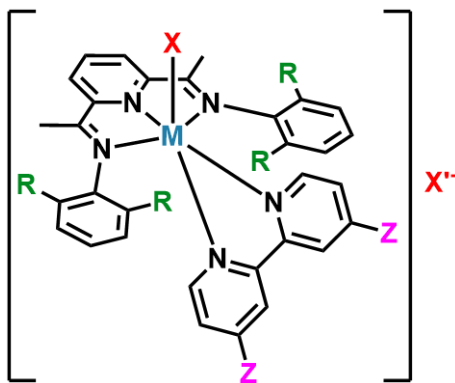


Figure 8. General structure of the polypyridyl complexes reported in this work (M = Co; R = Me, ⁱPr; Z = H, COOH; X = Cl⁻; X' = PF₆⁻, BF₄⁻)

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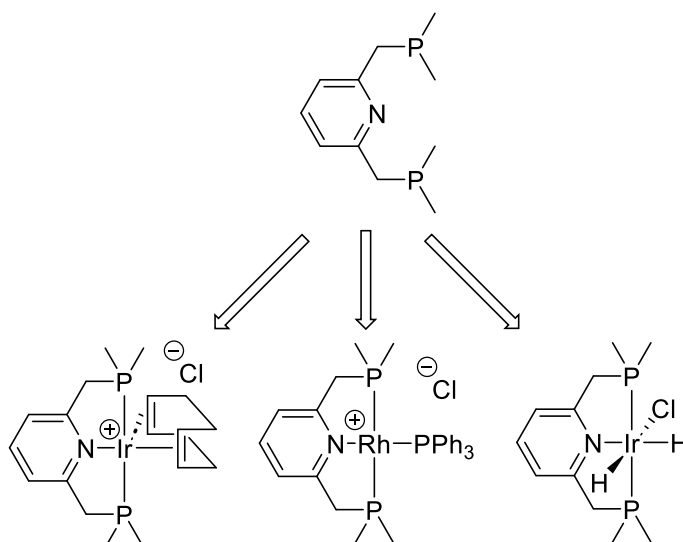
New Pincer Complexes for C-H and CO₂ Activation

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Pincers are strongly binding tridentate ligands that are typically rigid and occupy a meridional geometry. Transition metal pincer complexes have found applications in many challenging reactions, such as C-H bond activation and catalytic CO₂ reduction. PNP pincer ligands (named for the phosphorus-nitrogen-phosphorus arrangement of coordinating atoms) are a particularly prominent class. While PNP ligands with large steric bulk on the phosphine atoms have been extensively studied,¹⁻⁷ complexes with minimally substituted PNP ligands remain relatively unexplored.



Development of tetramethyl-PNP pincer complexes.

This work focuses on the development of the tetramethyl-PNP (MePNP) ligand and the synthesis and reactivity of iridium and rhodium MePNP complexes in C-H activation and CO₂ reduction.

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Structural Diversity of Alkali-Metal Amidomanganate(II) Complexes

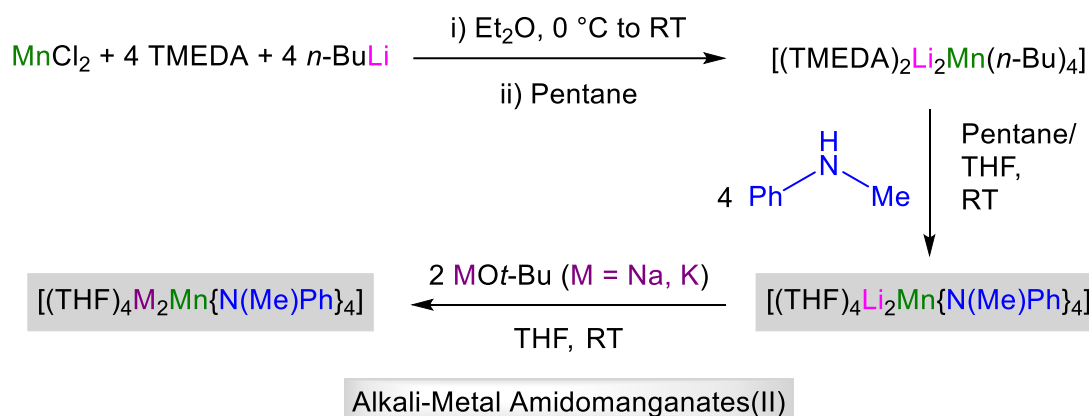
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Seeking to overcome the restraints of s-block organometallics, bimetallic reagents have become more prevalent in recent years, imparting enhanced reactivity which cannot be achieved by the corresponding parent single metal systems.¹ In particular, we have illustrated the atom economical synthesis of symmetrical bis(aryls) and conjugated 1,3-diynes using alkali-metal tetra(alkyl) manganates [(TMEDA)₂M₂Mn(CH₂SiMe₃)₄],^{2, 3} capable of affecting direct Mn-I exchange (M = Li) of aryl iodides² and Mn-H exchange of terminal alkynes (M = Li, Na, K)³ with subsequent tetraaryl and tetraalkynyl manganate intermediates initiating C-C homocoupling under one pot methodology.^{2, 3}

Breaking new ground in this developing area, this poster demonstrates the preparation and characterisation of a new family of homoleptic lithium amidomanganates(II) incorporating a diverse selection of amide ligands which dictate the stoichiometry, constitution and structure of the resulting complex.⁴ Obtained lithium amidomanganates(II) can undergo direct alkali-metal exchange with heavier alkali-metal alkoxides MO^t-Bu (M = Na, K) (Scheme 1). Applicability of prepared alkali-metal amidomanganates(II) as bases towards enolizable ketones has also been assessed.



Scheme 1. Direct deprotonation of *N*-methylaniline by tetra(butyl) manganate [(TMEDA)₂Li₂Mn(*n*-Bu)₄] followed by the addition of alkali-metal alkoxide to form heavier alkali-metal amidomanganates(II).

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The coordination chemistry of a novel pentadentate carbazole ligand framework for heterobimetallic complexes

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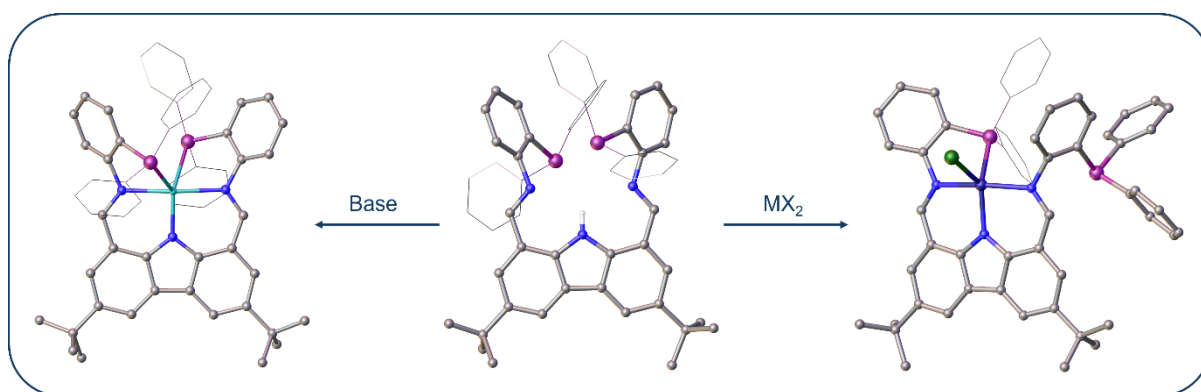
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The synthesis of novel heterobimetallic complexes is incredibly important to further our knowledge of metal-metal bonding, cooperativity, and reactivity. Such compounds also have a range of applications, including as gas phase sensors, molecular magnets, and catalysts.^{1,2}

The rational design of ligand frameworks is essential to stabilise these complexes. In recent years there has been an increase in popularity of multidentate carbazole-based pincer ligands, likely owing to their robust synthesis from cheap and readily available precursors, and their easily tuneable steric and electronic properties.³ Tridentate carbazole pincer ligands are well reported and have been used to synthesise both homoleptic and heteroleptic transition metal complexes, whilst ligands with more than three binding sites are less well researched.

Herein we present the synthesis of a novel carbazole based pentadentate (PNNNP) preligand designed to support the synthesis of bimetallic complexes. The preligand features both hard amine and soft phosphine donors, providing a five-coordinate binding site through which multiple metals can coordinate.

Initial results have shown the coordination of a single metal centre in the central binding pocket of the ligand, both with and without bases, with results confirmed by single crystal X-ray diffraction and NMR spectroscopy, affording ideal candidates for the coordination of a second metal.



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Acceptorless alcohol dehydrogenation using a sulfur-based manganese catalyst

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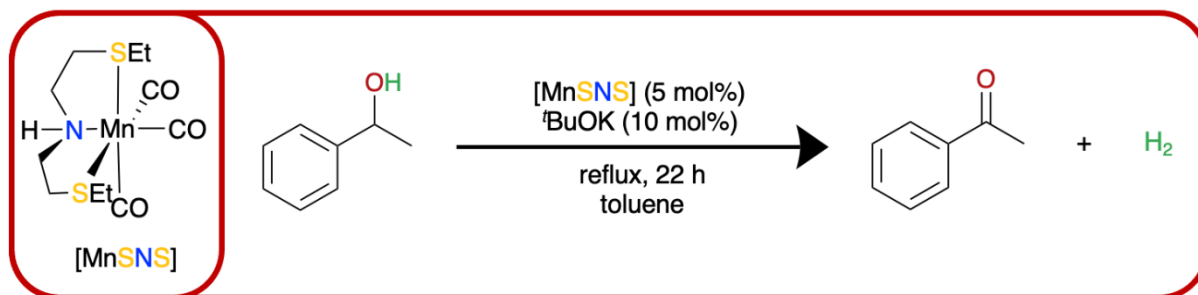
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Reversible carbonyl formation from alcohols via Acceptorless alcohol dehydrogenation (AAD) have shown promise as a hydrogen storage medium for use as an energy vector.¹ This chemistry has long been dominated by noble metals, particularly ruthenium, osmium and iridium,¹ which raises questions over these catalysts sustainability. Whilst advances have been made with base metal AAD catalysts, notably iron, manganese and cobalt,² these advancements often utilize phosphorus-based ligand systems which can be synthetically difficult to work due their air sensitive nature.

As such sulfur-based ligand systems are a rational alternative due to their air stability and their relative ease of use. Building on work by Schörghamer *et. al.* with ruthenium-sulfur AAD catalysts³ and manganese-sulfur hydrogenation catalysts by Grover *et. al.*,⁴ herein we present a manganese-sulfur catalyst capable of performing AAD reactions.

From our initial results, the effect of ligand lability has on AAD reactions as well as any impact of complex geometry and electronics can be explored.



Reaction scheme for manganese-catalysed AAD reaction using a sulfur-based ligand system.

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Design and Application of Polyethylene-based Block Co-polymers

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Polyethylene (PE) is among the most widely used synthetic nonpolar polymers, owing to its unique and tunable properties, low production cost, and ease of manufacturing. However, its inert nonpolar nature presents challenges for broader application, necessitating the development of nonpolar-polar PE-based block copolymers to expand its utility across various fields. Here, we present the synthesis and characterization of end-functionalized polyethylene (PE) via catalyzed chain-growth polymerization, employing an iron(II)-based catalyst to facilitate the development of PE-based block copolymers using ring-opening polymerization (ROP). The initial stage focused on synthesizing the iron(II)-based paramagnetic catalyst, which, in conjunction with an activating co-catalyst and a chain transfer agent (CTA), was used to polymerize ethylene. The resulting linear PE chains were then end-functionalized with hydroxyl (-OH) terminal groups, which served as macroinitiators for the ring-opening polymerization of cyclic monomers, such as lactones. This study demonstrates the feasibility of utilizing these hydroxyl functionalities to synthesize PE-b-lactone block copolymers. Comprehensive structural and thermal characterization of the resulting copolymers validating successful synthesis will be presented.

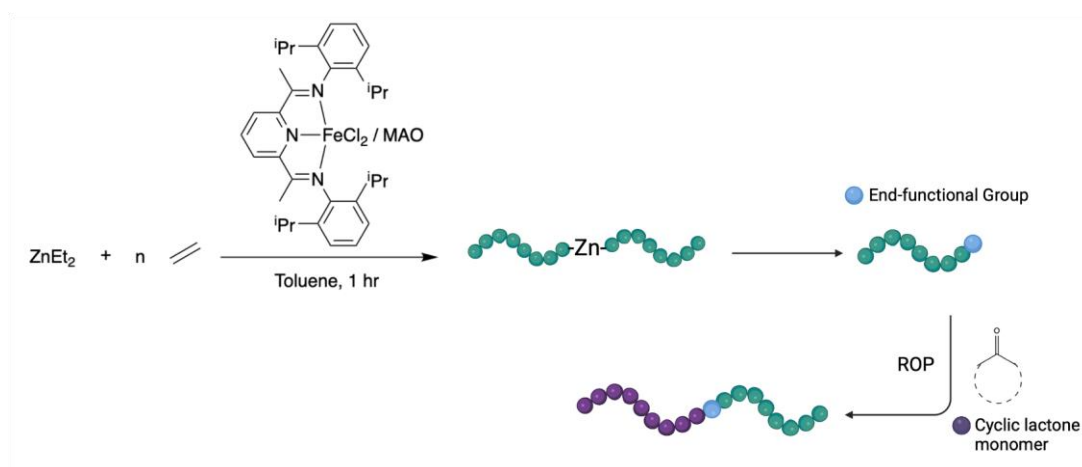


Figure.1: General Scheme for the ROP of PE-based block copolymers

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Electro-fixation of Carbon Dioxide into Polymers with Polyimine Nickel Homogeneous Catalysts

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Anthropogenic CO₂ emissions have significantly contributed to global warming, making it a critical environmental concern. Although CO₂ capture technologies have progressed considerably, methods for utilizing captured CO₂ remain under exploration. Due to the thermodynamic stability and kinetic inertness of CO₂, more effective energy sources and catalysts are necessary to overcome these challenges. This study presents the electrocatalytic fixation of CO₂ into diene to synthesize a key intermediate - adipic acid in polymer industry. Nickel complexes were selected as homogeneous catalysts for the electrocarboxylation reaction, with its electrochemical properties characterized using a state-of-the-art technique — rotating disk electrode (RDE) cyclic voltammetry (CV). Application of electrons from current in the presence of the catalysts enabled the targeted compound's synthesis, as opposed to reactions without the catalytic system. Despite a successful catalytical case, yields were limited by catalyst deactivation due to competing reactions. This work provides insights into catalyst design for CO₂ conversion in electrochemical systems, with potential for further exploration of various Ni-based complexes.

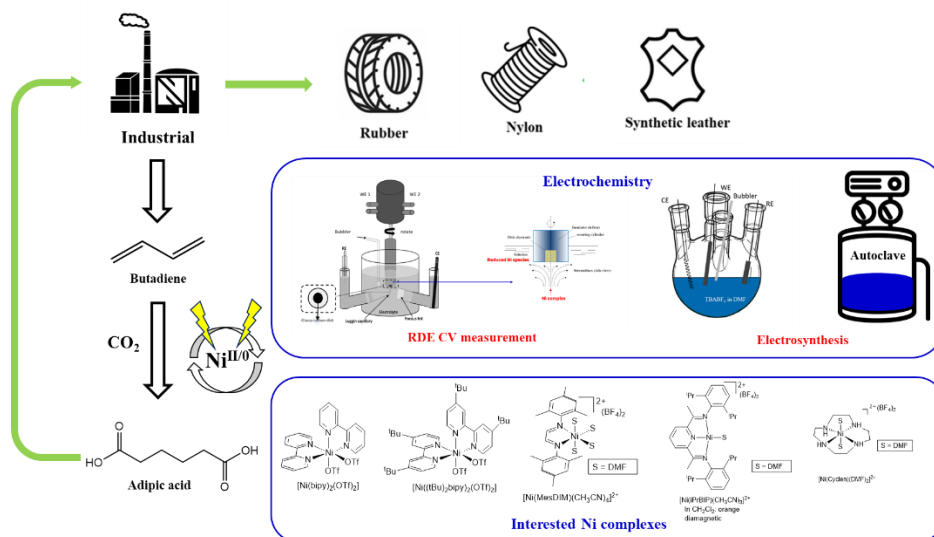


Figure 9: Electrochemical and Electrosynthesis Approaches for Industrial Waste Valorisation: Different Nickel Complexes in Sustainable catalysis process

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Complexes of Divalent Scandium Bearing Heterocyclic Ligands: Synthesis, Reactivity and Electronic Structure

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Whilst the trivalent oxidation state is favoured for all rare earth (RE) ions, molecular examples of formally divalent complexes have been reported for all save radioactive Pm.¹ With larger RE ions, anionic *tris*-(substituted)cyclopentadienide (Cp^{R}) complexes of the form $[\text{cation}][\text{RE}(\text{Cp}^{\text{R}})_3]^-$ have proven accessible and are amenable to reactivity and electronic structure studies.¹ This motif has not been extended to the lightest RE element, Sc, owing to its small size. However, analogous $[\text{Sc}(\text{L})_3]^-$ *pseudo-D*_{3h} species with monodentate amide or aryloxy ligands have been reported (**Fig. 1-A**). These formal Sc(II) complexes share electronic structure features with the $[\text{RE}(\text{Cp}^{\text{R}})_3]^-$ anions, most pertinent being that the SOMO of all is a non-bonding $\{n+1s(nd_{z^2})\}$ hybrid orbital of predominantly metal-parentage.^{2,3}

More recently, neutral Sc(II) complexes have been reported based on the $\{\text{NHA}r^{\text{Pr6}}\}$ ($\text{Ar}^{\text{Pr6}} = \text{C}_6\text{H}_3\text{-2,6-}\{\text{C}_6\text{H}_2\text{-2,4,6-}i\text{Pr}_2\}$) (**Fig. 1-B**) and $\{\text{Cp}^{\text{ttt}}\}$ ($\text{Cp}^{\text{ttt}} = \text{C}_5\text{H}_2\text{-1,2,4-}t\text{Bu}$) (**Fig. 1-C**) ligand frameworks.^{4,5} The electronic structures of both diverge from the $[\text{Sc}(\text{L})_3]^-$ anionic complexes above, and $[\text{Sc}(\text{Cp}^{\text{ttt}})_2]$ closely resembles a typical transition metal metallocene.⁵ These differences facilitate remarkable reactivity that contrasts other divalent rare earth complexes, such as allowing access to the first rare earth carbonyl complex (**Fig. 1-C**).⁶

Our group is interested in influencing and probing the electronic structure of rare earth complexes by including ligands bearing heteroatom centres. To this end, we have recently reported a series of heteroleptic trivalent metallocenes featuring phospholide ligands.⁷ Motivated by the stabilizing influence these ligands are known to confer to low-valent metal complexes,⁸ here we report our efforts to expand this work, and we will discuss the synthesis and preliminary reactivity of low-valent hetero-metallocene species (**Fig. 1-This work**).

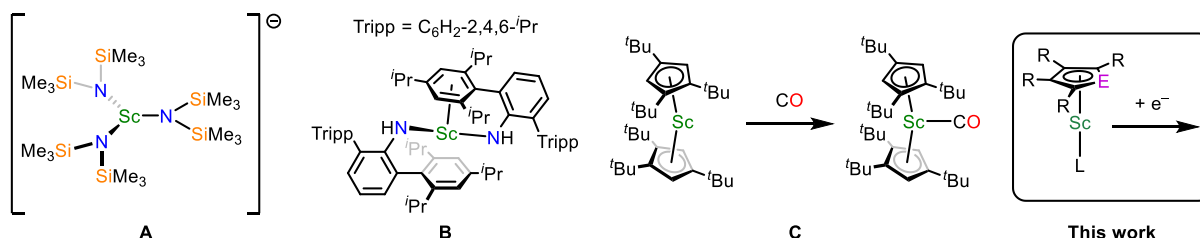


Figure 1. (A) The $[\text{Sc}\{\text{N}(\text{SiMe}_3)_2\}_3]^-$ anion; (B) $[\text{Sc}(\text{NHAr}^{\text{Pr6}})_2]$; (C) $[\text{Sc}(\text{Cp}^{\text{ttt}})_2]$ and its carbonyl complex; (**This work**) Reduction chemistry of scandium sandwich complexes bearing heterolide ligands.

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Mapping the Trajectory for C–H Activation in Solid-State σ -Alkane Complexes

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C–H activation of alkanes is a key step in the functionalization of inert hydrocarbons in which σ -alkane complexes are central intermediates.¹ Highly unstable in solution, many σ -alkane complexes have now been synthesized and characterized crystallographically via Solid-state Molecular OrganoMetallic (SMOM) chemistry. These studies have revealed how alkane coordination to metal centres occurs via diverse $M\cdots H-C$ interactions, ranging from monodentate (η^1) through bidentate (η^2) to bifurcated ($\eta^2;\eta^2$) coordination modes.² These binding modes have previously been characterised qualitatively using non-covalent interaction (NCI) plots; however, the quantitative aspects of these interactions are less well explored.³

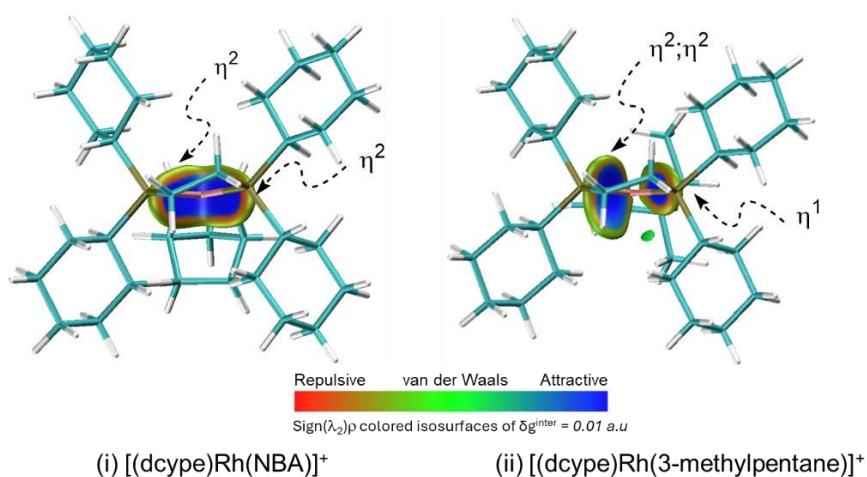


Figure 1: IGMH isosurfaces showing different $M\cdots H-C$ interactions in two Rh σ -alkane complexes of (i) norbornane (NBA) and (ii) 3-methylpentane; dcype = $Cy_2PCH_2CH_2PCy_2$. Geometries are viewed in the Rh coordination plane from behind the centre of the dcype backbone.

In this work, we have characterized $Rh\cdots H-C$ interactions in Rh σ -alkane complexes using density functional theory (DFT) calculations combined with the independent gradient model based on Hirshfeld partitioning (IGMH), focussing on quantitative aspects of different interaction types.⁴ Additionally, we have examined the reaction profiles for the subsequent C–H activation in $[(dcype)Rh(NBA)]^+$ and $[(dcype)Rh(cyclohexane)]^+$. Our results highlight parallels to Crabtree's seminal work on the reaction trajectory of C–H oxidative addition.⁵

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i-Motif DNA-Based Asymmetric Catalysis with Au Carbenes

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Au(I) has been used widely in asymmetric synthesis.¹ However, chirality transfer is difficult due to geometric constraints with Au(I) complexes. Using Au(III) can overcome this, but introduces complex instability.² This project will explore the selective interaction of β -N-stabilised Au(III) carbenes with i-motif DNA to induce asymmetry in chemical transformations through an original supramolecular chiral pool approach (Figure 1). A library of Au(I) and Au(III) carbene complexes will be synthesised from a collection of novel allenes, containing an array of N-heterocycles, for biophysical analysis with i-motif DNA.

Interactions with DNA can also be indicative of biomedical applications, with β -pyridine-stabilised Au(I) and (III) carbenes having also shown promising anticancer, antimicrobial and antifungal properties, which will be explored further in the group.^{3, 4}

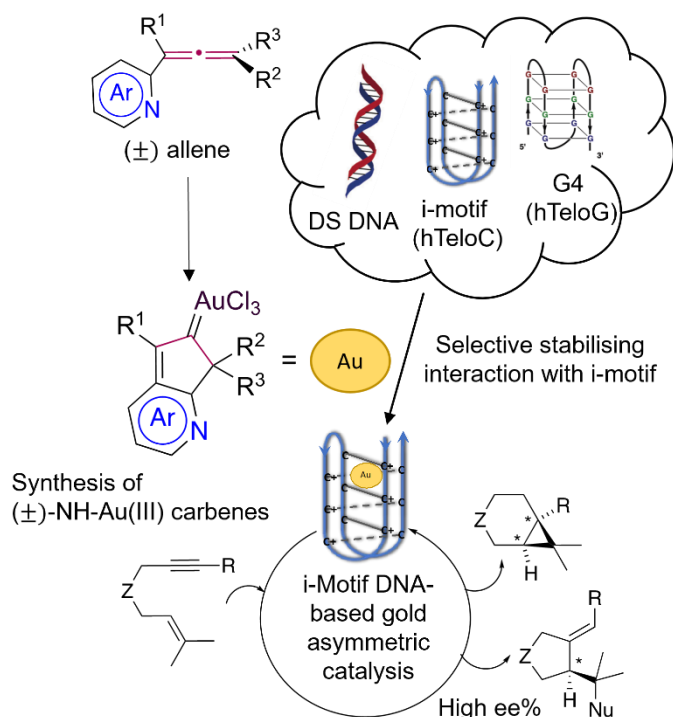


Figure 1 Graphical summary of the project.

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Catalytic Investigation of Oxidation Reactions Promoted by Self-Assembled Cubic Co(II)-Cages in Aqueous Media

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Water-soluble coordination cages with hydrophobic interior cavities are of considerable interest as enzyme-like catalysts across a variety of applications. We have previously reported on the oxidation of xanthene based dye molecules facilitated by a cuboctahedral Co(II) coordination cage (**Co**₁₂) under very mild aqueous conditions.¹ This accelerated oxidation was caused by the colocalization of the substrate dye molecule (enclosed within the cage) and the primary oxidising agent, SO₄^{•-} (surrounding the cage) which generated through the redox reaction of peroxymonosulphate ions with Co(II). Herein, we report the catalytic oxidation of xanthene based dyes also occurs in the presence of a cubic Co(II) coordination cage (**Co**₈). The catalytic studies using UV-Vis spectroscopy also display the enhanced activity of **Co**₈ when compared to other Co(II) coordination cages, including **Co**₁₂, and other M(II)₈ cubic coordination cages with redox active metal (Fe(II) and Ni(II)). These findings contribute to the understanding of how the local environment of coordination cages effect their catalytic behaviour.

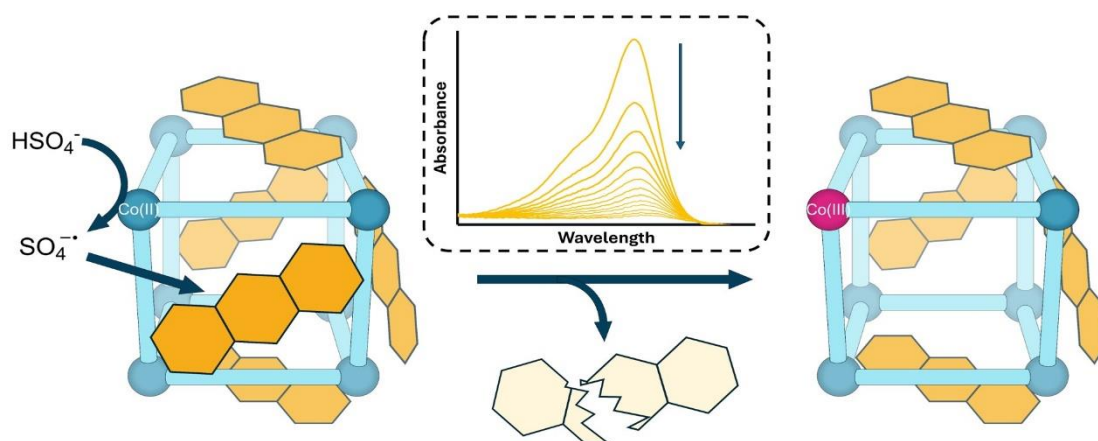


Figure 1 – Catalytic degradation of xanthene based dyes using cubic Co(II) coordination cages.

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On the Hunt for Copper(II) Bis-Silyl Amide: How Automation Solves Decade-Long Challenges

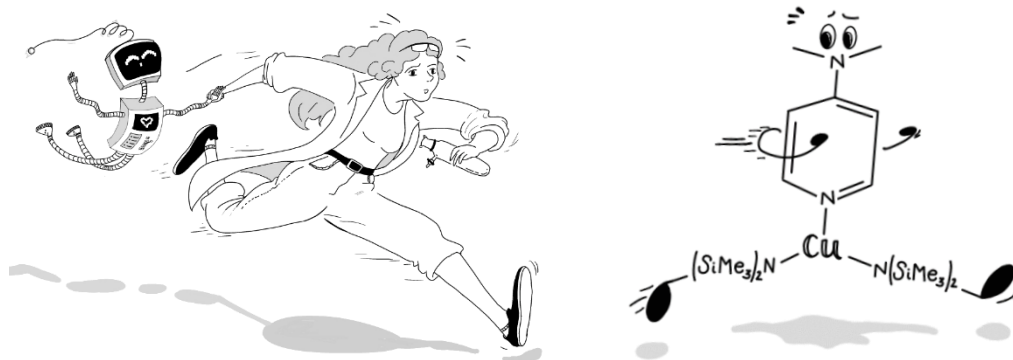
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Copper is an attractive, naturally abundant catalyst which can be exploited in cross-coupling reactions yielding amines, amides, imides and other key covalent linkages.^[1] However, although copper can access a myriad of reactions in a more economic and sustainable way compared to its better-known palladium alternatives, it fails as an industrial catalyst. It notoriously suffers from homogeneity issues, low turnover rates and high catalyst loadings, leaving it out of favour with commercial giants. To take advantage of copper's behaviour, soluble analogues of catalytic intermediates such as copper amides are of interest. In this case, transition metal silyl amides have proved effective precursors but the Cu(II) example has continued evading synthetic chemists.^[2-4]

Herein, we report a synthetic methodology for the preparation and isolation of $[\text{LCu}\{\text{N}(\text{SiMe}_3)_2\}_2]$ which is made possible through the application of state-of-the-art automation technologies.^[5] We also explore the synthesis and reactivity of a ligand-free Cu(II) bis-silyl amide as a catalytic precursor and a potential intermediate to accessing Cu(III) species.



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Aluminylene-Base-Metal complexes towards sustainable catalysis

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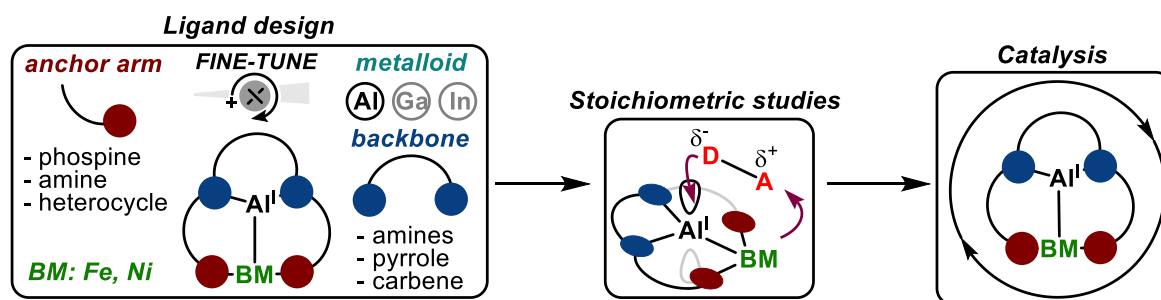
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Noble metals (NM) are highly valued for their ability to efficiently modify organic molecules through predictable two-electron organometallic pathways. However, their scarcity, fluctuating costs, and substantial carbon footprint present significant challenges for sustainable synthetic processes. As an alternative, catalysts derived from abundant, cost-effective, and environmentally friendly base metals (BM) have shown great promise. However, their predominant one-electron redox reactivity often complicates control over catalytic function.¹ Thus, a key challenge in modern catalysis is to combine the advantages of both NM and BM to develop sustainable, selective, and predictable catalytic systems.

Fe and Ni stand out as promising BM candidates, yet their effective utilization requires carefully designed ligands to direct selectivity and regulate specific redox states.² In this context, chemical metal-ligand cooperation—where ligands actively participate in bond-forming and bond-breaking processes—offers an appealing strategy to enable controlled two-electron redox events in BM catalysts.³ Notably, low-oxidation-state Al ligands emerge as particularly intriguing due to their strong σ -donor capability and π -acidity.⁴ Additionally, Al is abundant, cost-effective, and environmentally benign, making it a highly attractive component for sustainable catalysis. While Al ligands have been extensively studied in NM catalysis,⁵ their integration with BM systems like Fe and Ni remains largely underexplored.⁶

This project seeks to navigate this uncharted frontier by synthesizing Al-BM heterobimetallic complexes and investigating their catalytic applications, particularly in small molecule activation. To achieve this, we have designed and synthesized pincer scaffolds engineered to preserve intermetallic bond integrity while effectively accommodating both metal centres.



Scheme 1. Project design towards cooperative Aluminylene-Base-Metal catalysis.

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Computational Study of Methane Activation at an Iridium Cyclometallated PONOP Complex in the Solid State

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Metal complexes with supporting pincer ligands have been used extensively in the study of hydrocarbon C-H bond activation in solution.¹ In 2009 the first example of a σ -methane complex in solution was characterised spectroscopically at a neutral Rh-PONOP complex.² An alternative approach to study σ -alkane complexes is through Solid-state Molecular OrganoMetallic (SMOM) Chemistry.³ A recent example involves methane activation at the cyclometallated iridium PONOP complex, **1**⁺ that has been characterised directly in the solid state (Figure 1).⁴

This poster describes the results of periodic density functional theory investigating this methane activation process. **Pathway A** involves rate-limiting C-H reductive coupling via **TS(1⁺-2_a⁺)** to form 14e⁻ [Ir(PONOP)]⁺ (**2_a⁺**), followed by methane activation to obtain [Ir(PONOP)(H)Me]⁺ (**3⁺**). Alternative mechanisms all involve initial CH₄ addition followed by C-H bond formation at the cyclometallated arm. The most accessible (**Pathway B**) involves an Ir(V) intermediate (**2_b⁺**). **Pathway A** is computed to be the most stable with an overall barrier of 31.1 kcal/mol. This work will compare these different reaction mechanisms in both the solid-state and in the gas-phase.

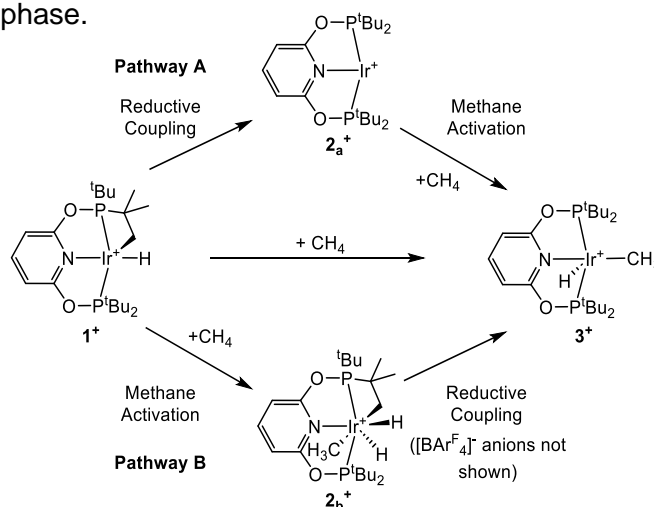


Figure 1: Possible pathways for the addition of methane to cyclometallated iridium PONOP complex **1**⁺.⁴

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Novel Janus Ditopic *N*-Heterocyclic Carbene-Based Bimetallics for Tandem Catalytic Applications

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Aryl imines are key precursors to most drug syntheses. Although these intermediates are readily produced *via* an acid catalysed reaction between anilines and aldehydes/ketones, manufacturing the aniline-based starting materials can be problematic.¹ To mitigate this, heterobimetallic iridium/palladium tandem catalytic systems coupling nitroaryls and primary alcohols into aryl imines, i.e. that developed by Peris and coworkers using Janus ditopic *N*-heterocyclic carbenes (Di-NHCs), are of increasing interest (**Figure 1A**).² As a one-pot process using a single heterobimetallic catalyst, these systems offer reduced solvent waste, lower energy demands, and improved catalytic efficiency from increased metal-metal cooperativity.³ However, the metal-metal communication in the existing catalysts is not optimised, and the electronic and distance influence on the metal-metal synergy in these systems is unknown, which limits further applicability.⁴ Herein we report our current progress in synthesising two different Janus Di-NHC-based iridium and palladium homo-/hetero-bimetallics (**Figure 1B**) to investigate the effects of inter-metal distance and ligand conjugation on metal-metal synergy. Increased conjugation in the aromatic-linked Di-NHC compared to the system used by Peris and coworkers potentially offers improved metal-metal cooperativity.

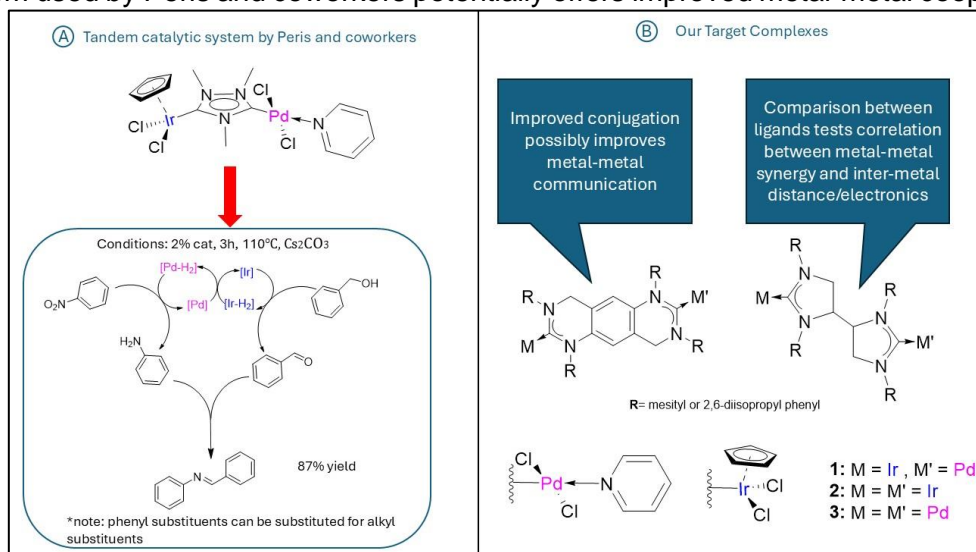


Fig 1. A) Iridium/palladium heterobimetallic complex, by Peris and coworkers, coupling nitroaryls and primary alcohols into aryl imines. **B)** Our target homo/hetero-bimetallic iridium and palladium systems.

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Hydrogen bonding in metastable metallocenium dimers

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Noncovalent interactions between equally charged systems have garnered some attention in the past decade, particularly after the controversial coining of the “anti-electrostatic” terminology to describe their bonding.¹ In these dimers noncovalent interactions, such as hydrogen bonds, can be strong enough to overcome the coulombic repulsion and allow dimer formation even in the gas phase, yielding metastable species.

We recently systematically characterized a series of hydrogen bonded dimers of metallocene carboxylic acid and amide derivatives, considering species isoelectronic with ferrocene, which included metastable cation-cation and anion-anion systems (Fig. 1a).² In addition to the structural and energetic characterization, and comparison with X-Ray structures from the CSD database, this work also revealed possible reactivity in the metastable state, showing how proton transfer between the monomers has a lower barrier than their dissociation.

The electronic structure of metallocenes is well-known to be strongly affected by the substituents on the Cp ring, so we have now extended our studies to probe substituent effects on such metastable species (Fig 1b). Perhaps as expected, we find that electron-donating (-withdrawing) groups (de)stabilize inter-cationic dimers, and the reverse takes place for inter-anionic dimers. Even though the (de)stabilizing effect is larger on the binding energies than on the dissociation barriers, we have found, surprisingly, that substituent effects can be strong enough to allow the formation of dication-dication dimers.

Finally, the effect of conformational changes that allow secondary interactions between the substituents is currently under study (Fig 1c). In particular, we have found that some of these dimers can be substantially more stable although they have yet to be seen experimentally. Nonetheless, we believe they can be found, when paired with the right counterions.

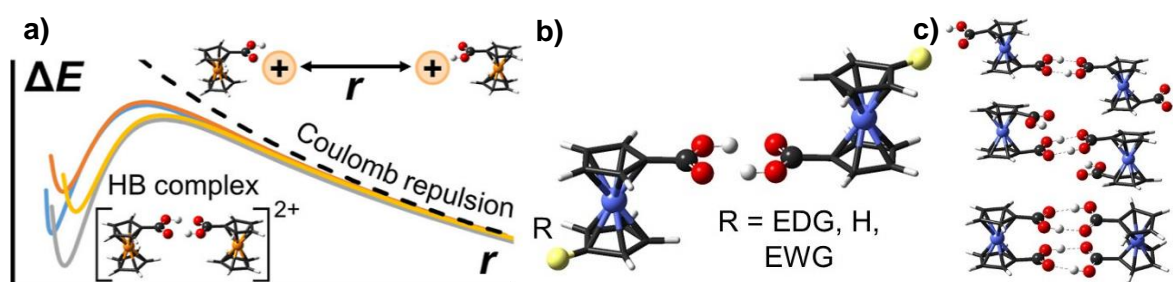


Figure 1. Summary of the work to be presented. a) Previous work on the general features of metastable hydrogen bonded metallocene dimers b) New work on the substituent effects c) An example of how the substituents can interact with each other, yielding more stable dimers not yet found experimentally.

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A Hexagonal Bipyramidal Uranyl(V) Single-Ion Magnet Showing Finger-Type Photoluminescence

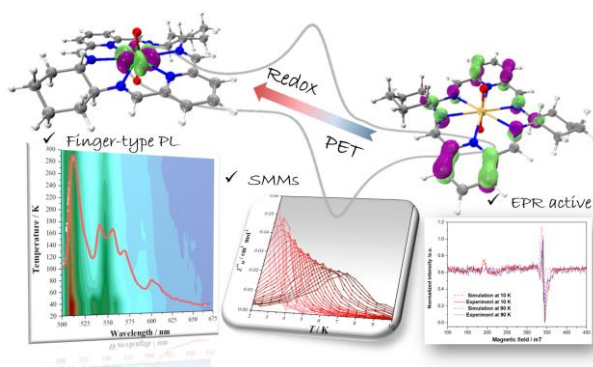
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The occurrence of uranyl(V) compounds in nuclear fuel cycles and radioactive waste necessitates a deep understanding of the electronic structure of this $5f^1$ species. Characteristic properties of pentavalent uranium can include single-molecule magnet (SMM) behavior and characteristic finger-like luminescence. However, both properties have not previously been observed in the same uranyl(V) complex. Herein, we show that one-electron reduction of the hexagonal bipyramidal uranyl(VI) compound $[\text{UO}_2(\text{L}^{\text{N}6})][\text{BPh}_4]_2$ (**1-U**) gives the uranyl(V) congener $[\text{UO}_2(\text{L}^{\text{N}6})][\text{BPh}_4]$ (**2-U**) ($\text{L}^{\text{N}6}$ is a hexadentate N-donor with two connected bis(imino)pyridine groups). In addition to field-induced slow magnetic relaxation, **2-U** displays photoluminescence upon excitation at 440 nm, the first time that both phenomena are observed in one uranyl(V) complex. The emission from **2-U** is characterized by five well-resolved bands in the region 510–586 nm, in contrast to the broad emission observed for **1-U** centered on 650 nm. The relationship between the electronic structure of **1-U** and **2-U** is emphasized by the photochromic behavior of **1-U** which, upon irradiation at 365 nm, adopts a stable photoexcited state **1-U*** following a ligand-to-metal electron transfer, with the magnetic and spectroscopic properties of **1-U*** being similar to those of **2-U**. A computational study of **1-U** and **2-U** explains their contrasting emission profiles in terms of the uranyl oxo ligands participating in the key transitions for **2-U** but not for **1-U**.



An EPR-active uranyl(V) complex with hexagonal bipyramidal symmetry demonstrates finger-type photoluminescence and field-induced slow magnetic relaxation.

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Exploring the Electronic Structure of Acetyl Coenzyme A Synthase: Heterobimetallic Mimics of the A-cluster

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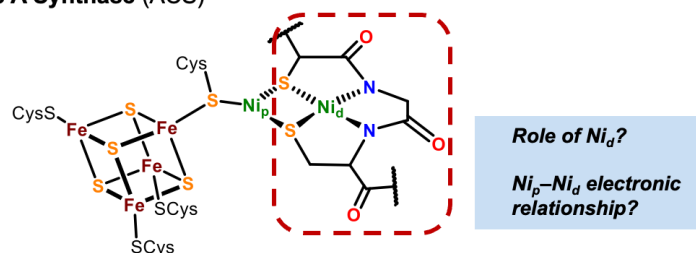
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The bifunctional activity of acetyl coenzyme A synthase (ACS) plays a key role in the Wood-Ljungdahl pathway of autotrophic carbon fixation, synthesizing acetyl coenzyme A (acetyl-CoA) – an important metabolic intermediate for energy storage and cellular regulation.^{1,2} This synthesis is the highly efficient biochemical equivalent of the industrial Monsanto process,³ which produces acetic acid using a toxic and expensive rhodium complex.

The ACS active site, known as the A-cluster, features two nickel ions distinguished by their relative position to a [4Fe-4S] cubane cluster: a proximal (Ni_p) and a distal (Ni_d) nickel ion. The Ni_p is the proposed site of all organometallic transformations throughout the entire catalytic cycle.^{2,4} Numerous experimental and theoretical studies have probed this mechanism,⁵ but understanding is limited, with two competing proposed pathways with the Ni_p in different oxidation states.²

A). Acetyl Coenzyme A Synthase (ACS)



B). ACS Heterobimetallic Synthetic Plan

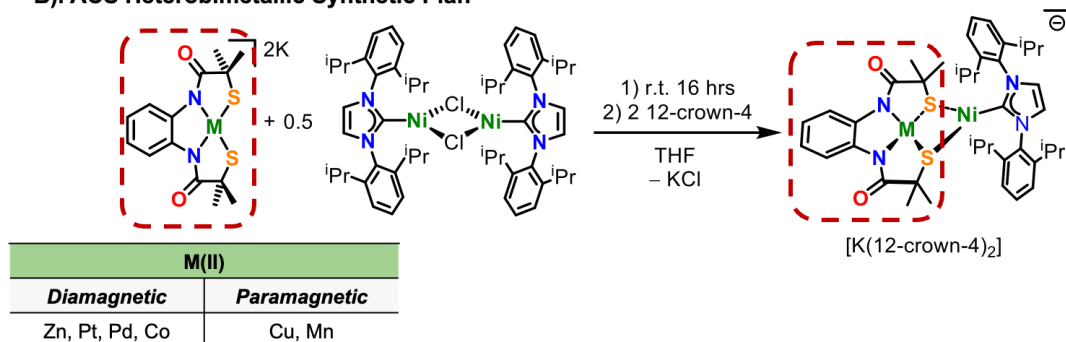


Figure 1: **A).** synthetic model of A-cluster and key questions addressed in this work **B).** heterobimetallic synthetic plan of this work

To gain insights into the structure-function relationship of ACS, we have synthesized heterobimetallic complexes mimicking A-cluster, where the distal metal (M_d) is systematically replaced (Figure 1). Using various spectroscopic (i.e. UV-vis, EPR, etc.) and DFT computational methods, evaluation of each heterobimetallic complex relative to the homometallic analogue will allow for detailed evaluation of the electronic structure and its metal-dependency.

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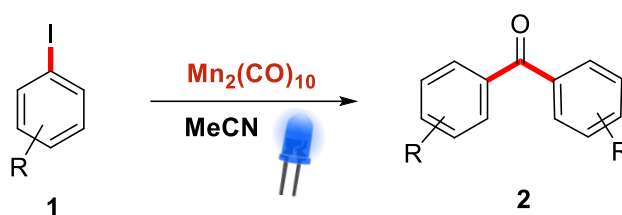
Light-driven manganese-assisted carbonylation of aryl iodides.

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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 $\text{Mn}_2(\text{CO})_{10}$ under visible light, has been uncovered. Photolysis of aryl iodides, **1**, in the presence of $\text{Mn}_2(\text{CO})_{10}$ affords excellent yields of benzophenone derivatives **2** (Scheme 1).



Scheme 1: Carbonylation of iodoarenes **1**.

Detailed mechanistic studies indicate that $\text{Mn}_2(\text{CO})_{10}$ serves as a CO source as in operando rapid scan infra-red spectroscopy data demonstrate that it is readily converted to $[\text{Mn}(\text{NCMe})]_6[\text{Mn}(\text{CO})_5]_2$. The reaction is promoted by electron-rich solvents (e.g. acetonitrile, pyridine, benzonitrile, and benzyl cyanide) which is consistent with undergoing ligand exchange with the photochemically generated $\text{Mn}(\text{CO})_5$ radical, resulting in the *in-situ* release of CO and disproportionation of $[\text{Mn}_2(\text{CO})_{10}]$.

A comprehensive substrate scope will be reported as well as other applications of using $[\text{Mn}_2(\text{CO})_{10}]$ as a convenient light-activated source of CO.

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From the preparation of highly reactive mid-valent group 5 and 6 synthons to their application for Mo(III) vapor-phase precursor synthesis

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Transition metal halides are ubiquitous synthons for the preparation of organometallic complexes. Ideally, it is preferred to use metal halides of the same oxidation state as the complex of interest, in order to avoid the use of external reductants and the generation of unnecessary waste. Thus, it is critical to employ stable, but reactive halide salts of desired oxidation states for the preparation of organometallic complexes. While group 5 and 6 halides are commercially available, the mid-valent halides are often significantly more expensive and less reactive than their low- and high-valent counterparts. This is due to their high crystallinity and polymeric nature of the salts. Utilizing PhMe_2SiH as an organoreductant, the synthesis of highly reactive, uncoordinated MCl_4 ($\text{M} = \text{Nb, Ta, Mo, W}$) salts can be obtained in high yields.¹ These amorphous salts can also be further derivatized to produce synthons with neutral donors, such as thf, dme, and PEt_3 .

This methodology can also be expanded to produce Mo(III) synthons, which are desirable compounds for the synthesis of pseudo-octahedral homoleptic M(III)L_3 ($\text{L} =$ bidentate monoanionic ligand). Such species are attractive as vapor phase precursors for chemical vapor deposition (CVD) and atomic layer deposition (ALD) of thin films.^{2,3} In particular, there is significant interest in a variety of Mo-based thin films, such as molybdenum oxides, dichalcogenides, nitrides, oxynitrides, carbides, or elemental thin films, with broad ranging applications in electronics, solar, sensing, and catalysis.⁴ While this M(III)L_3 is a common motif amongst a majority of known precursor molecules across metals with a stable +3 oxidation state, it is largely lacking for Mo; indeed, homoleptic Mo(III) species remain exceedingly rare in the literature.⁴ Leveraging our Mo(III) synthons, the synthesis of tris($\text{N,N'$ -di-isopropylacetamidinate)molybdenum(III), Mo-(iPr-AMD)_3 (**1**), was successfully achieved; the first example of a homoleptic Mo(III) amidinate.⁵ Expanding on this work, we have recently prepared tris($\text{N,N'$ -di-isopropyl-2-dimethylamido-guanidinate)molybdenum(III), Mo(iPr-GND) (**2**); to the best of our knowledge the first example of a homoleptic Mo(III) guanidinate.⁸ Both materials showed thermogravimetric behavior commensurate with successful vapor phase delivery, and indeed, in the case of (**1**), successful ALD growth of molybdenum oxynitride films was demonstrated. Both (**1**) and (**2**) were additionally successfully applied to aerosol-assisted CVD growth of Mo-based materials.

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Small Molecule Activation with Porous Salts

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Despite the extensive development of metal-organic frameworks (MOFs), systems capable of engaging in metal-to-ligand π -backbonding interactions remain relatively underexplored. Expanding this chemistry is particularly promising for tunable small molecule activation, with implications for selective adsorption and catalysis. To complement existing MOF strategies, we have focused on porous coordination cages (PCCs) as modular building blocks for porous material design. In this work, we explore the incorporation of coordinatively unsaturated, π -basic transition metal centers into porous salts—materials assembled from oppositely charged PCCs—to create highly tunable porous phases. Specifically, we demonstrate the incorporation of π -basic ruthenium sites within a charged porous cage and examine its role in carbon monoxide chemisorption and activation. Additionally, we show that a non-porous molecular ruthenium complex can serve as a charge-balancing counterion, yielding porous salts with similar selectivity for CO binding. These findings establish design principles for leveraging porous salts as tunable platforms for small molecule activation and beyond.

Synthesis of Gold (I) Complexes with Bioactive Ligands as Dual-action Anti-cancer Agents

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Cancer is a leading cause of death globally. Current chemotherapeutics have resistance, low bioavailability, low uptake and unpleasant side effects¹⁻². Since the introduction of Auranofin as a chemotherapy agent, interest has risen in gold-based chemotherapeutics, their synthesis and antitumour effects. Their unique mechanism of action allows for a new approach by targeting enzymes responsible for the REDOX system, resulting in a lethal rise in Reactive Oxygen Species (ROS), triggering cell death. This produces a more selective drug, limiting off-target effects and reducing side effects³⁻⁴. However, challenges remain with resistant cancer strains. Incorporating a bioactive molecule offers a new dual-action approach. Specifically, Plant-based hydroxy-cinnamic/benzoic acids are the primary focus of this research, as many polyphenols have exhibited anti-cancer activity⁵⁻⁶. We aim to show how these complexes behave when introduced to cells (i.e., uptake, distribution, localisation), their effectiveness in 2D monolayer and 3D in-vitro tumour spheroids, and their effects on cellular processes.

To do this, a novel synthetic route prepares gold(I) complexes with bioactive polyphenol ligands by preparing an acetylacetonate precursor complex before being substituted with the carboxyl group of the chosen ligand. This rapid, room-temperature, one-pot approach has synthesised 15 complexes, each of which will be characterised and biological activity studied via numerous methods, including cytotoxicity screens, fluorescence imaging, activity assays, 2D and 3D cell cultures and ICP-MS/ICP-MS Imaging techniques. This work provides new insights into the effects of small-molecule polyphenols on these complexes' efficacy while simultaneously validating and optimising our novel synthetic approach. Our work has found that our new approach to synthesis is both practical and efficient in producing these complexes. Further, our studies will show how these complexes behave in cell cultures and their extra- and intracellular behaviours, uptake, distribution, and cytotoxic effects on different cancers and healthy control cells.

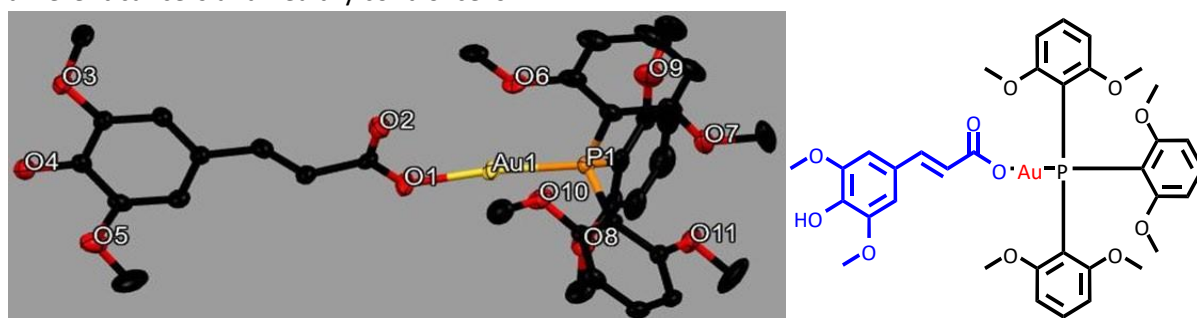


Figure 1: Molecular structure of Au (Ferulic Acid) (Tris(2,6-dimethoxyphenyl) phosphine). Selected bond distances (Å) and angles (°): Au(1)-P(1) 2.223(1), Au(1)-O(1) 2.052(3), and O(1)-Au(1)-P(1) 173.26(9).

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Group 13 Metal Complexes of Tripodal Schiff Base Ligands

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The development of heterobimetallic complexes in recent decades has been fuelled by the unique reactivity that is often inaccessible in homobimetallic and monometallic systems.¹ Though early/late transition metal heterobimetallic systems have asserted their dominance within the literature, interesting chemistry has been demonstrated in heterobimetallic systems composed of d and f-block metal pairings, such as the cleavage of dinitrogen across a U–Rh bond.²

Our group has recently shown that tripodal Schiff base ligands are effective frameworks for the support of 3d-4f heterobimetallic systems.³ The abundance and cheap cost of main group metals as d-block metal alternatives provides a unique chemical avenue within which to explore heterobimetallic complexes. The synthesis and characterisation of a monometallic aluminium complex supported by a tripodal Schiff base ligand will be presented, with aims to further metalate with 4f and 5f metals.

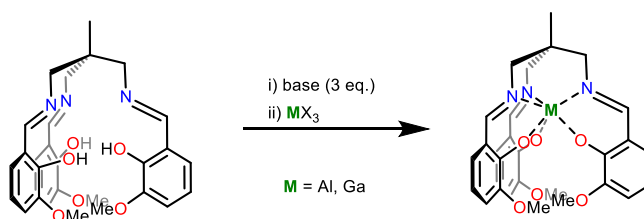


Figure 1: Synthesis of group 13 metal complexes of (1,1,1-*tris*[(3 methoxysalicylideneamino) methyl]ethane).

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Synthesis of dinuclear Pd complexes with a dinucleating pyrazolate scaffold

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Homo- or hetero-dinuclear (bimetallic) complexes offer unique possibilities for catalytic transformations and small molecule activation through intermetallic cooperativity.¹ Such complexes may be constructed with a dinucleating bridging ligand that hold two metals in close proximity, allowing for cooperative or tandem reactivity between the metal centres.^{2–6}

Previously we synthesised a family of dinuclear cobalt μ -peroxo complexes for oxygen reduction catalysis, based on the oxidatively robust bispyridyl-pyrazolate *cis*-dinucleating ligand scaffold, **bpp**. Here we have expanded our investigations into mono-, di- and multi-nuclear Pd complexes, using a derivatised **bpp** scaffold designed for forming *cis*-dipalladium complexes. The complexes have an intermetallic binding pocket with the metals in close proximity (Pd-Pd 4.9 Å). A tetra-Pd bis-‘clam-shell’ (‘taco’) complex was also synthesised, exhibiting two axial Pd-Pd closed-shell interactions (Pd-Pd 3.8 Å), giving rise to interesting oxidative behaviour in cyclic voltammetry experiments. We are investigating the properties and reactivity of these complexes, with a focus on their bimetallic nature and the potential for metal-metal cooperativity.

Now that the suitability of the derivatised **bpp** scaffold with palladium has been established, we are also investigating the ligand as a platform for Pd-M hetero-bimetallic complexes, and the synthesis of dinuclear Rh and Ir complexes, with an interest in investigating dinuclear hydrogenations and carbonylations.

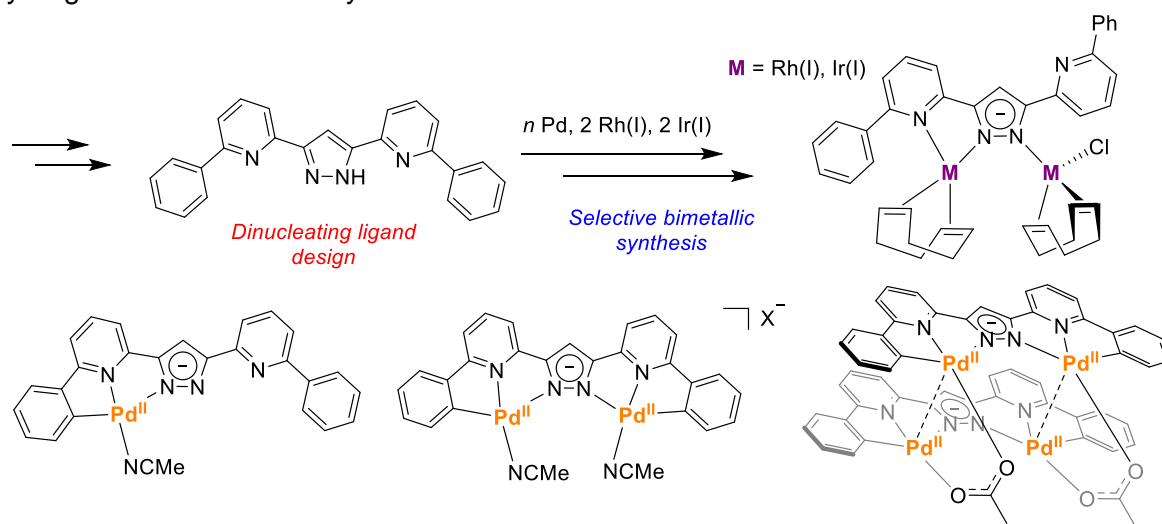


Figure: Synthesis of multinuclear Pd, Rh and Ir complexes with a dinucleating ligand scaffold

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Synthesis of Froehde reagent using ionic liquids

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Presumptive reagents are used to identify unknown analytes such as illicit substances. Many presumptive test reagents were first created in the late 19th century to mid 20th, since then, very little research has been completed. The purpose of using ionic liquids to synthesise these reagents is to identify methods which may be more time efficient and safer to produce. Research has been completed on various test reagents. Each reagent was produced by mixing the active compound of the respective reagent with various ionic liquids. Each of these were then analysed and compared with the use of various techniques. This was completed to determine how each ionic liquid functioned for the presumptive testing of unknown analytes. The Froehde test is one reagent that has been synthesised using 10 different ionic liquids and compared to the traditional synthesis. The Froehde reagent tests for a variety of substances such as: Heroin, MDMA, LSD, Paracetamol etc. The reagent was synthesised by combining sodium molybdate and the respective ionic liquids in a 1:2mmol respectively. When reacting with Paracetamol, the Froehde test should turn from clear to blue. When initially added, no visible change could be seen with any ionic liquid reagents. However, when 20µl of H₂SO₄ was added to the matrix, a visible reaction was seen in 4 of the reagents, with P666-14 & P444-16 both producing a deeper blue than that traditional synthesis method of the reagent (Figure 1). In conclusion, it was found that ionic liquids can be used for the synthesis of presumptive test reagents, observing the same colour changes. However, we now have all of the promising material properties of ionic liquids.

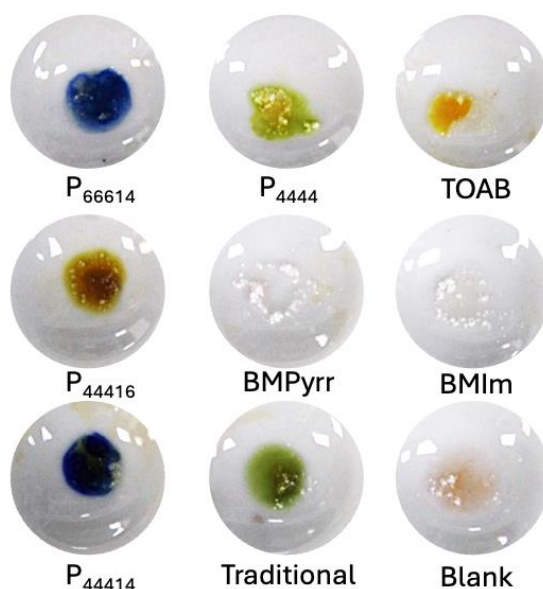


Figure 10- Spotting Plate showing reaction between Froehde Reagent and Paracetamol.

The National Electron Diffraction Facility – Offering 3DED analysis for air-sensitive samples

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Single-crystal X-ray diffraction has been the main-stay of structure determination for over a century. Advancements in hardware and software have pushed the technique to the absolute limit of the probe itself, yet many samples remain challenging or impossible to study. A key limitation is the need for sufficiently large crystals. Powder XRD, while an alternative, has significant limitations for routine structure determination.

3D electron diffraction (3DED) provides a single-crystal diffraction technique applicable to crystals orders of magnitude smaller than those used for X-ray methods, due to the comparatively stronger interaction of electrons with matter. The use of electrons for diffraction mandates several considerations distinct from those of XRD, e.g. the use of a high vacuum environment. Despite these challenges, 3DED is an invaluable addition to the structure characterisation arsenal. Besides expanding analysis to sub-micron crystals, it also allows distinction of multiple crystalline phases in a mixed sample, the detection and impurity identification, and (with appropriate equipment) *in-situ* elemental analysis.



Figure 1. Electron diffraction as a structure solution technique

The recently established National Electron Diffraction Facility (NEDF) secured two fully operational instruments, housed at the Universities of Southampton and Warwick, providing 3DED capability and expertise to researchers across the UK as part of the National Crystallography Service. This presentation introduces 3DED, shares experiences, and showcases the capabilities of the new equipment, including upcoming capability for highly air-sensitive samples. We will highlight key differences between ED and XRD that impact experimental design and data interpretation and flag access routes, increasing the visibility and accessibility of this brand-new technique.

Palladium Imidoyl fragments for the entrapment of Carbon Dioxide and its mimics

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In the shift to a more sustainable future, the utilization of CO₂ as a cheap, abundant feedstock is an attractive prospect. As a C1 building block, CO₂ can be used to synthesise key industrial reagents such as methanol, formic acid, urea and dialkyl carbonates as well as a host of polymers. However, the inert nature of CO₂ is a key challenge to its utilisation in these synthesise, thus fuelling significant research into new avenues for activating this molecule.

Metal imidoyl complexes have previously demonstrated interesting reactivity, with the imidoyl group acting as a pendent nucleophile to facilitate cycloaddition reactions with a variety of heteroallenes.¹⁻⁴ This reactivity has yet to be studied with CO₂, however. Hence, in this work we will describe the preparation of a series of novel palladium-imidoyl complexes and present their preliminary reactivity studies.

The reactivity of these complexes was initially investigated using isocyanates (RNCO) and isothiocyanates (RNCS) as suitable CO₂ mimics. The complexes trap out these heteroallenes to form five-membered palladacycles with the imidoyl nitrogen attacking the central, electrophilic carbon whilst a vacant site generated on the palladium centre coordinates one of the heteroatoms. Characterisation of the palladacycles reveals the selectivity of heteroatom-palladium coordination is controlled by the hard-soft characteristics of the donor as well as steric effects. The activity of the palladium-imidoyl complexes in the presence of CO₂ is then detailed.

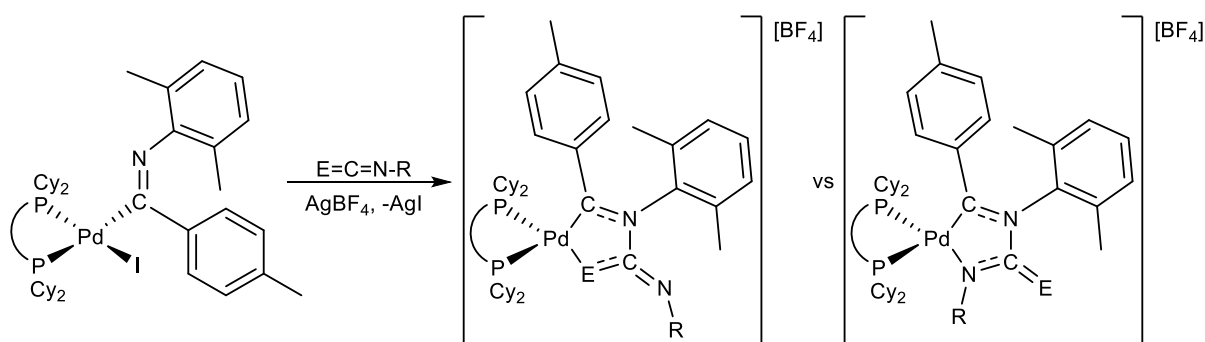


Figure – Cycloaddition of isocyanate (E = O) or isothiocyanate (E = S) by palladium-imidoyl complexes

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Novel chelators for scandium (radio)isotopes for theranostic applications

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Scandium isotopes have attracted significant attention for their potential use in oncology. Preclinical studies emphasized the applicability of Sc-47 in targeted β^- -therapy with similar success compared to the clinical standard ^{177}Lu .¹ The main advantage of ^{47}Sc is the availability of the diagnostic counterparts ^{44}Sc , clinically proved for positron emission tomography (PET), or ^{18}F , the most frequently used PET isotope worldwide and forming stable bonds with scandium.² When labelled to a molecular target of therapeutic interest, the $^{44/47}\text{Sc}$ or $^{47}\text{Sc}/^{18}\text{F}$ pairs have great potential for sequentially imaging and treating the diseased tissue.³ This requires a bifunctional chelator forming highly inert complexes with scandium. Currently, DOTA is considered the gold standard scandium chelator due to the high robustness of the corresponding complex. However, radiolabelling is unspecific and requires acidic conditions, long reaction times, and increased temperature incompatible with sensitive targeting moieties of clinical interest. Further, straightforward radiolabelling under mild conditions is essential for developing a synthetic workflow suitable for kit formulation.^{4,5} Thus, this study focuses on the development of chelators with improved labelling kinetics whilst maintaining high *in vivo* stability. This can be achieved by combining acyclic chelators and donors with steric restrictions, a chelator offering these requirements is $\text{Bn}_2\text{DT3A}$ (Figure 1) previously used to label Ga-68 under physiological conditions.⁶ During our work focusing on scandium, $\text{Bn}_2\text{DT3A}$

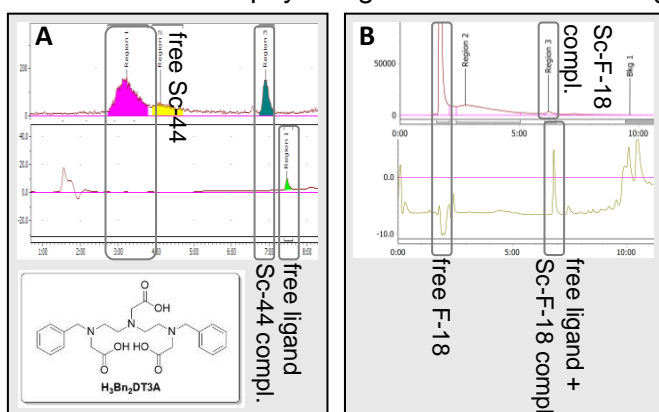


Figure 1: Preliminary radiolabelling experiment of $\text{Bn}_2\text{DT3A}$ with A) ^{44}Sc (pH = 4, [L] = 100 mM, 45 min) and B) $[^{18}\text{F}][\text{ScF}]^{2+}$ (pH = 4, [L] = 100 mM, 15 min) proved incorporation of the radionuclides by radio-HPLC (Radio (top) and UV chromatogram (bottom)).

showed complexation of Sc-45 (natural scandium) proved by pH-dependent ^1H -NMR and UV-Vis spectroscopy. Further, treatment of the scandium complex with a fluorine source resulted in the formation of a Sc-F bond confirmed by ^{19}F -NMR spectroscopy. The findings with non-radioactive isotopes were confirmed in labelling experiments proving the incorporation of ^{44}Sc and $[^{18}\text{F}][\text{ScF}]^{2+}$ (Figure 1) into the chelator. These findings suggest that $\text{Bn}_2\text{DT3A}$ provides an ideal basis for a chelator for scandium isotopes in imaging and therapy.

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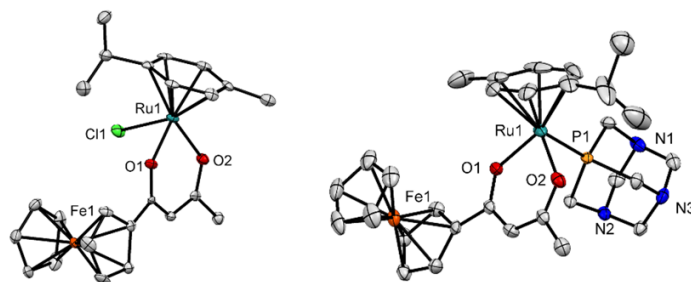
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Ferrocenyl β -Diketonate Ruthenium(II)-Arene Complexes as Potential Anticancer Agents

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Ruthenium compounds have emerged as promising alternatives to platinum-based chemotherapeutics, and this is in part, due to the success of Ru(III) coordination compounds, e.g., NAMI-A ([RuCl₄(DMSO)(Im)]ImH] where Im = imidazole). These compounds are prodrugs, and their main mode of action is suggested to be an intracellular reduction to an active Ru(II) species.¹ Since this discovery, Ru(II) compounds, especially those based on "piano stool" arene compounds, have sparked significant interest. Unlike the Ru(III) coordination compounds, the Ru(II) organometallics are easier to synthesis, can be stable in aqueous media, often have lower cytotoxicity against normal cell lines and increased cancer cell selectivity.



Molecular structures of [(*p*-cym)Ru(Fc-acac)X], where X = chloro (left) and X = PTA (right). Hydrogen atoms and counterions are omitted for clarity, and displacement ellipsoids are placed at the 50% probability level.

It is well documented that modifications to the organic ligands surrounding the Ru(II) metal centre and the overall charge of the complex, can effect the compounds biological activities. Our group have focused Ru(II) compounds with O,O chelating ligands, such as ferrocenyl β -diketonates,^{2,3} as ferrocene is known to increase reactive oxygen species (ROS) in cells and cause cell death. Alongside others, we have designed Ru(II)-arene compounds of the type [(*p*-cym)Ru(Fc-acac)(Cl)] (Figure, left) which incorporate functionalised ferrocenyl β -diketonates (Fc-acac), and reported their anticancer activities were dependent on the functionality of the ligand.^{4,5} Herein, we report new Ru(II)-arene complexes of the type [(*p*-cym)Ru(Fc-acac)(PTA)](PF₆) (Figure, right, PTA = 1,3,5-Triaza-7-phosphaadamantane), and report an improvement in solubilities and cancer cell selectivity against ovarian carcinoma, and on changing from neutral to cationic compounds.

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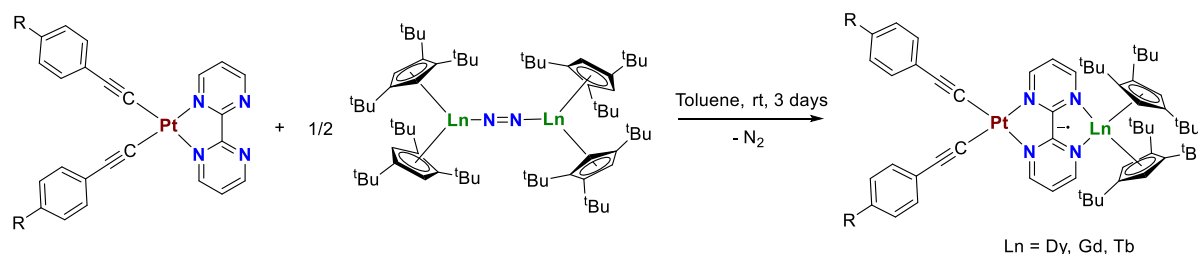
5d-4f heterobimetallic radical complexes with potential luminescent properties

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Heterobimetallic d-f complexes often demonstrate unique and highly efficient luminescence.¹ This owes to the synergistic properties of the metals, whereby d-block metals typically absorb UV or visible light, which can transfer this energy to nearby highly luminescent f-block metals.^{1,2} However, d-f block complexes containing radical bridged ligands are more sparse, but could allow for further tuning of the electronic properties, due to alterations in transitional energy levels. In this work, mononuclear complexes [Pt(bpym)(CC-C₆H₄R)] (R = H, CF₃) (bpym = 2,2'-bipyrimidine) have been used to prepare heterobimetallic 5d-4f complexes; [(CC-C₆H₄RPt(bpym))(LnCp^{ttt}₂)] (Cp^{ttt} = 1,2,4-C₅^tBu₃H₂), via reaction with a highly reducing dinitrogen-bridged lanthanide metallocene; [(Cp^{ttt}₂Ln)₂(μ-1,2-N₂)].³ Bpym acts as an ideal bridging ligand for this work, as it has two binding sites, is easily reduced to its radical anionic state, and forces the metal centres into close proximity, allowing for efficient d → f energy transfer.⁴ Structural characterisation suggests that the bpym ligand has been reduced to its radical anionic state after the reaction, evidenced by the decrease in the C-C bond distance connecting the two rings from 1.49 Å to 1.41 Å. Future EPR, SQUID and luminescence measurements are planned to explore the magnetic, electronic and luminescent properties complexes.



Scheme 1: Synthesis of [(CC-C₆H₄RPt(bpym))(LnCp^{ttt}₂)] (R = H, CF₃)

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