

***RSC Southern Dalton Regional Meeting
2024
Programme & Abstracts***

Programme

10.00-10.40 Registration (with tea/coffee/biscuits)

10.40-10.45 Welcome and Introduction

10.45-11.30 **Ruth Webster**

“Mechanistic Investigations into Iron(salen) Catalysed Reduction Reactions”

11.30-11.50 Arpan Mondal

“Masked Divalent Chemistry of Isocarbonyl-bridged Trivalent Lanthanide Metallocenes”

11.50-12.10 Laura English

“Synthesis, Reactivity and Computational Studies of the [NCCCCO]⁻ Cyanoketenate Anion”

12.10-12.30 Daniel Wilson

“Inserting Three-Coordinate Nickel into [4Fe-4S] clusters”

12.30-13.45 Lunch and Poster Session

13.45-14.30 **Richard Layfield**

“The Pursuit of Exotic Oxidation States in Molecular f-Element Chemistry”

14.30-14.50 Gaby Audsley

“B-Cl vs B-H Oxidative Addition at Ni(IMes)₂ for the Formation of Unsupported Ni-Boryls”

14.50-15.10 Joseph Zurakowski

“Metal-Ligand Bond Activation in a Tucked-In Iron Diphosphine Complex”

15.10-15.30 Andreas Phanopoulos

“Epimerisation at Main Group Centres”

15.30-16.00 Break for coffee / tea / biscuits

16.00-16.45 **Thibault Cantat**

“En route to more energy efficient silicon and boron hydrides using molecular catalysis”

16.45-17.30 **Eva Hevia**

“Harnessing Cooperative and Coordination Effects to Tame Organosodium reagents”

17.30-19.00 Wine Reception and Poster Session

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Invited Speakers

Professor Richard Layfield
University of Sussex, United Kingdom



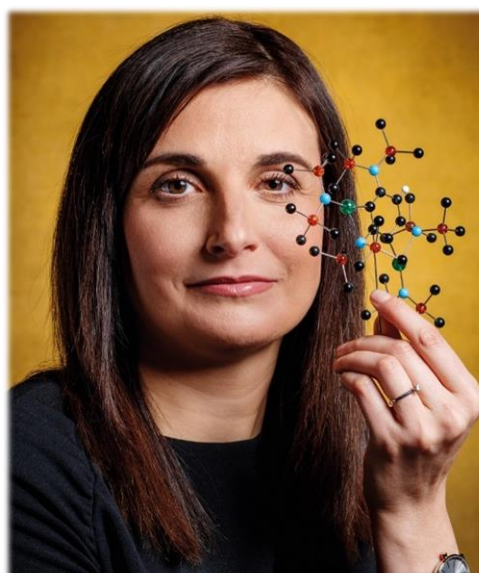
Dr Ruth Webster
University of Cambridge, United Kingdom



Dr Thibault Cantat
CEA Saclay, France



Professor Eva Hevia
Universität Bern, Switzerland



Contributed Talks

Masked Divalent Chemistry of Isocarbonyl-bridged Trivalent Lanthanide Metallocenes – O

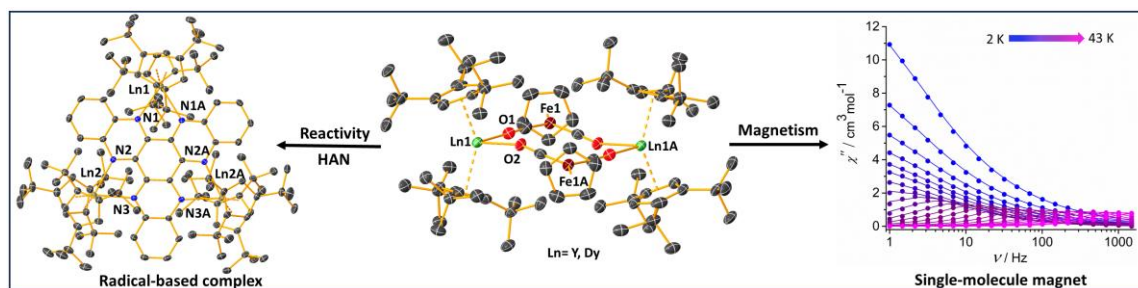
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Recently, divalent lanthanide metallocenes have attracted significant attention due to their small molecule activation chemistry and single-molecule magnet (SMM) behaviour.^{1,2} Metallocenes of the ‘non-classical’ divalent lanthanides (Dy, Tb, Ho, Nd, Er) are of great interest here as they can form radical-bridged complexes in reactions with N-heterocycles, leading to SMMs with strong magnetic hysteresis with coercivity, and high blocking temperatures (T_B).^{3,4} However, isolation of non-classical divalent lanthanide metallocenes is challenging as they are highly reactive and often only stable at low temperatures.

To circumvent this problem, we have considered that the cyclopentadienyliron dicarbonyl anion (Fp^-) can behave as a reducing agent, readily losing an electron to form Fp_2 . We reasoned that the Fp -bridged lanthanide metallocene $[(Cp^{ttt})_2Ln-\{m-(OC)_2FeCp\}]_2$ ($Ln = Dy^{III}$, Y^{III} , and $Cp^{ttt} = 1,2,4$ -tri-tert-butylcyclopentadienyl) would also behave as reducing agents and, therefore, could be surrogates for divalent lanthanides. The target compounds were synthesized according to Scheme 1.



Scheme 1. Magnetism and reactivity of Fp anion bridged lanthanide metallocenes.

The magnetic study reveals the presence of slow relaxation of magnetization under zero field for the Fp -bridged dysprosium complex, which is also confirmed by ab initio investigations. Further, it has been observed that these complexes can easily eliminate Fp_2 dimer and reduce N-heterocyclic compounds, to give radical bridged trimetallic SMMs (Scheme 1).

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Synthesis, Reactivity and Computational Studies of the [NCCCO]⁻ Cyanoketenate Anion - O

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Cyanoketene is a fundamental molecule that is actively being searched for in the interstellar medium.¹ Its deprotonated form (cyanoketenate) is a heterocumulene that is isoelectronic to carbon suboxide whose structure has been the subject of debate. However, the investigation of cyanoketene and its derivatives has been hampered by the lack of practical synthetic routes to these compounds until recently.² We report the synthesis of the cyanoketenate anion in [K(18-crown-6)][NCCCO] (**1**) as a stable molecule on a multigram scale in excellent yields (>90%).³ The structure of this molecule is probed crystallographically and computationally.

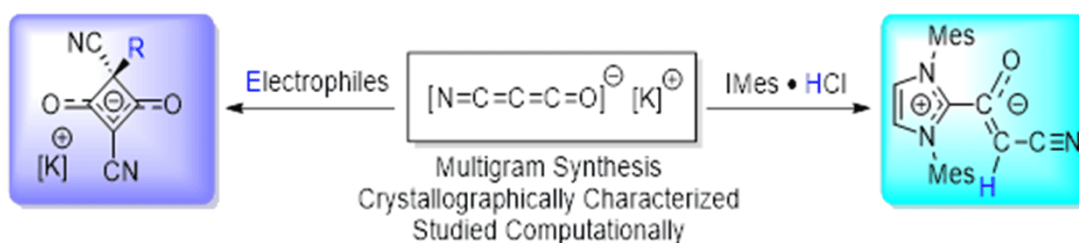


Figure 1: Explored reactivity of [K(18-crown-6)][NCCCO].

We also explore the protonation of **1**, and its reaction with triphenylsilylchloride and carbon dioxide. In all cases, anionic dimers are formed. The cyanoketene could be synthesized and crystallographically characterized when stabilized by a N-heterocyclic carbene. The cyanoketenate is a very useful unsaturated building block containing N, C and O atoms that can now be explored with relative ease and will undoubtedly unlock more interesting reactivity.

References

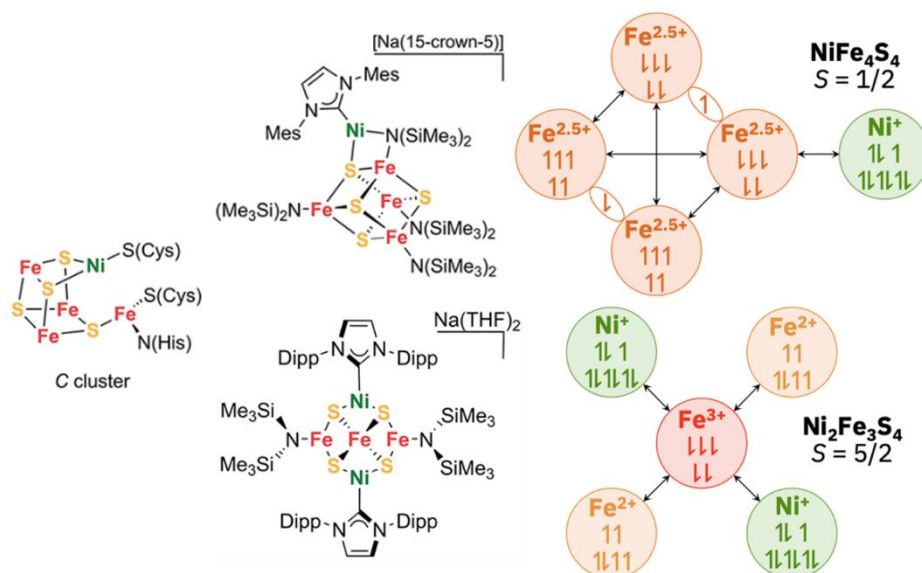
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Inserting Three-Coordinate Nickel into [4Fe-4S] clusters

Daniel W. N. Wilson,[†] Majed S. Fataftah,[†] Zachary Mathe,[†] Theodore J. Gerard, Brandon Q. Mercado,

Serena DeBeer, and Patrick L. Holland. [†]Authors contributed equally.

Metalloenzymes can efficiently achieve the multielectron interconversion of carbon dioxide and carbon monoxide under mild conditions, and use heterometallic clusters for these bond activations. Anaerobic carbon monoxide dehydrogenase (CODH) performs these reactions at the *C* cluster, a unique nickel-iron-sulfide cluster that features an apparent three-coordinate nickel site. How nature assembles the [NiFe₃S₄]-Fe_a cluster is not well understood. In this study, we use synthetic clusters to demonstrate that electron transfer can drive insertion of a Ni⁰ precursor into an [Fe₄S₄]³⁺ cluster to assemble higher nuclearity nickel-iron-sulfide clusters with the same complement of metal ions as the *C* cluster. Notably, initial electron transfer results in a [1Ni-4Fe-4S] cluster in which a Ni¹⁺ ion sits outside of the cluster and solid-state characterization indicates weakening of cubane Fe-S bonds. Modifying the Ni⁰ precursor results in the insertion of two nickel atoms into the cluster, concomitant with ejection of an iron to yield an unprecedented [2Ni-3Fe-4S] cluster which features four three-coordinate metal sites. Both clusters are characterized using magnetometry, electron paramagnetic resonance (EPR), Mössbauer, and X-ray absorption spectroscopy, and supported by DFT computations that are consistent with nickel in the +1 oxidation state. The characterization and relevance of cluster rearrangement to the assembly of CODH will be discussed.



B-Cl vs B-H Oxidative Addition at Ni(IMes)₂ for the Formation of Unsupported Ni-Boryls - O

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Transition-metal boryls (M-BX₂) play a pivotal role in the borylation of unsaturated organic substrates and catalytic C-H activation processes.^{1,2} Although the field of transition metal-catalysed borylation reactions is dominated by the use of precious metals, economic and environmental incentives have led to a particular focus on the incorporation of first-row transition metals as promising alternatives.³ Despite reports of Ni-catalysed borylation reactions proposing Ni-boryls as key intermediates,⁴ examples of isolated and structurally characterised Ni-boryls remain scarce.

Rare unsupported Ni-boryls *trans*-[Ni(IMes)₂(BX₂)Cl] (BX₂ = Bcat, Bdan) have been prepared *via* the oxidative addition of chloroboranes ClBcat and ClBdan at Ni(IMes)₂.⁵ Interestingly, the oxidative addition of the analogous hydridoboranes HBcat and HBdan is not observed and products isolated from these reactions show competing reaction pathways. Computational studies investigating the mechanism of B-Cl and B-H oxidative addition at Ni(IMes)₂ showed that B-Cl activation proceeds readily *via* nucleophilic displacement of Cl⁻, whereas concerted B-H activation is kinetically inaccessible. In addition to this, reactivity studies of Ni(IMes)₂(Bdan)Cl towards nucleophiles MeLi and Na[Et₃BH] led to substitution of the chloride ligand and the formation and characterisation of the new Ni-boryl complexes *trans*-[Ni(IMes)₂(Bdan)Me] and *trans*-[Ni(IMes)₂(Bdan)H].

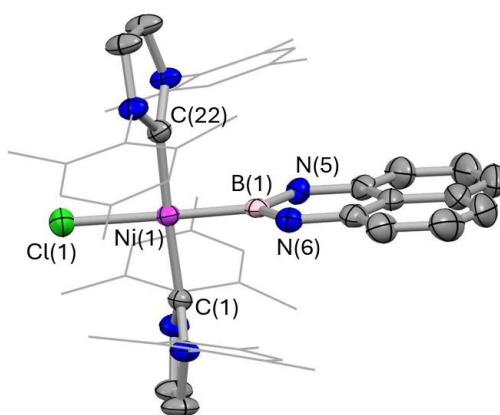


Figure 1: New nickel-boryl complex *trans*-[Ni(IMes)₂(Bdan)Cl] as determined by single crystal X-ray diffraction.

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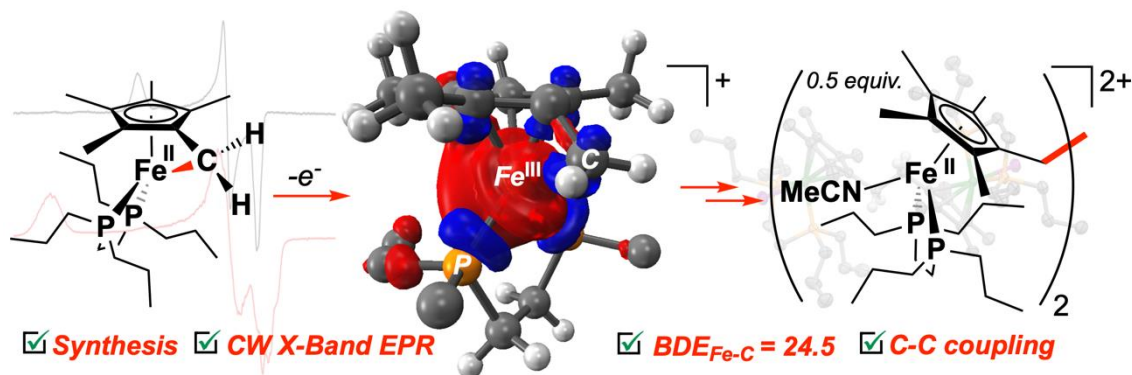
Metal-Ligand Bond Activation in a Tucked-In Iron Diphosphine Complex – O

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Pentamethylcyclopentadienide (Cp^* ; C_5Me_5^-) plays a central role as a supporting ligand in organometallic chemistry. In recent years, the modification of Cp^* groups has become an area of focus in an effort to form reactive transition metal complexes.^{1,2} Herein, we show that deprotonation of a $\text{Cp}^*-(\text{CH}_3)$ group with $n\text{-BuLi}$ on $[\text{Cp}^*\text{Fe}(\text{dnppe})(\text{N}_2)]^+$ (dnppe = 1,2-bis(di- n -propylphosphino)ethane) gives the first example of a tucked-in iron diphosphine complex, $[(\eta^6\text{-C}_5\text{Me}_4=\text{CH}_2)\text{Fe}(\text{dnppe})]$ (**1**).³ This molecule showed rich metal-ligand cooperativity in the activation of a variety of electrophiles such as CO_2 , PhCHO , HBCy_2 , $\text{Br-Au}^{\text{I}}\text{-PPh}_3$, and $\text{B}(\text{C}_6\text{F}_5)_3$. We also examined the one-electron oxidation of **1** with $[\text{Cp}_2\text{Fe}]^+$ ($\text{Cp} = \text{C}_5\text{H}_5^-$). Upon oxidation, $[\text{Fe}]\text{-C}$ bond homolysis results in a reactive terminal $\{\cdot\text{CH}_2\}$ radical moiety, ultimately leading to $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bond formation through C-C coupling.⁴ Freeze-quenched CW X-band EPR spectroscopy identified the $[(\eta^6\text{-C}_5\text{Me}_4=\text{CH}_2)\text{Fe}(\text{dnppe})]^+$ intermediate, and a radical trapping experiment with TEMPO resulted in the $\{\text{CH}_2\text{-TEMPO}\}$ coupled product. Computations revealed a low $[\text{Fe}]\text{-C}$ bond dissociation energy ($\text{BDE}_{[\text{Fe}]\text{-C}} = 24.5 \text{ kcal/mol}$) with respect to an analogous, unstrained complex $[\text{Cp}^*\text{Fe}(\text{dnppe})(\text{CH}_3)]^+$ ($\text{BDE}_{[\text{Fe}]\text{-C}} = 47.8 \text{ kcal/mol}$). Facile bond homolysis thus occurs due to the ring-strain inherent to **1**, resulting in the observed dimerization and $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bond formation. This work paves the way for future opportunities in metal-ligand cooperativity using $\{\text{Cp}^*\text{Fe}\}$, where uniquely decorated Cp^* -rings and thermodynamic insights into $\{\text{Fe-C}\}$ bond strength holds promise for further reaction development with respect to small molecules and catalysis.

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Epimerisation at Main Group Centres – O

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Despite Grignard reagents ubiquity in organic synthesis,^[1] the configurational instability of magnesium–alkyl compounds has significantly hindered their direct use for the installation of chiral centres (Figure 1a).^[2] The stability of Grignard reagents themselves has not been directly studied since the 1960's. This was primarily accomplished by monitoring the exchange kinetics of diastereotopic protons adjacent to the magnesium centre (Figure 1b).^[3,4] More broadly, the epimerisation kinetics and mechanisms for pro-chiral main group complexes in general remain almost completely unexplored.

We have synthesised a series of racemic magnesium– and zinc–alkyl complexes that also contain diastereotopic protons, giving characteristic resonances allowing exchange to be probed (Figure 1c). Exchange rates were investigated by variable temperature NMR to probe epimerisation kinetics across the series. Solvation significantly effects exchange rates, with strongly binding solvents dramatically slowing the epimerisation. Experiments and computation (density functional theory) were used to probe various mechanisms, with a transient dimeric species likely critical. This knowledge could be leveraged to produce enantiomerically enriched chiral main group complexes from achiral organic fragments.

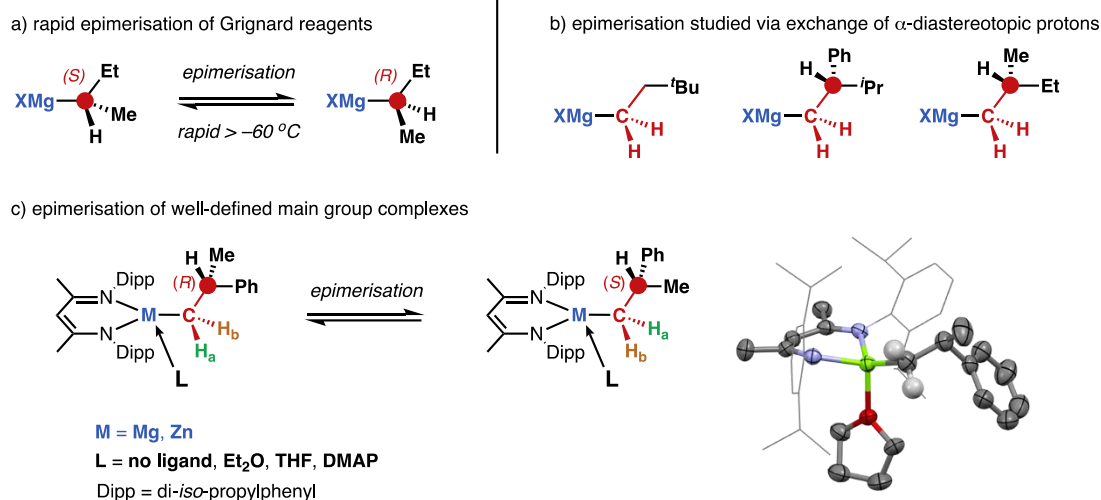


Figure 1. Overview of epimerisation at main group complexes

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Posters

Expedition into Room-temperature-Stable Electrides (RoSEs) – P

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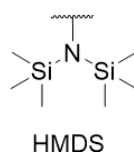
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Electrides represent a distinct category of compounds that deviate from the conventional structures of covalent, ionic, or metallic compounds¹. In this kind of material, electrons disassociate entirely from their parent atoms, occupying interstitial spaces amidst cation, thus assuming an ionic role². In this case, it has great potential application to various technologies³ especially as a strong reducing reagent in both organic synthesis and inorganic synthesis. However, up to now, only a few room-temperature stable electrides⁴ are reported and their further application has been hampered by poor stability, accessibility, and scalability. Also, their isolated discoveries make it difficult to get a comprehensive insight of electrides formation and make electrides formation controllable. In 2023, a heterobimetallic group-1 metal Room-temperature stable electrides $K^+(LiHMDS)e^-$, was successfully synthesized using readily available and cost-effective starting materials (K metal, and LiHMDS), by us, via rapid and scalable mechanochemistry ball milling method⁵. Building upon this synthesis approach, we expanded the repertoire of group-1 heterometallic electrides family, denoted as $M[M'HMDS]e^-$ (M and M' are group-1 metals Li, Na, and K; color of products is shown in the table). Analysis of all these electrides (1-9) by EPR, magnetometry, solid-state NMR, powder-XRD and electroconductivity measurements will further unveil a comprehensive understanding of the mechanisms underlying electrides formation and the influence of metals on their properties.

Table. Reactions between Group1 metals and metal amides

	LiHMDS	NaHMDS	KHMDS
Li	3	6	9
Na	2	5	8
K	1	4	7



The colours provide a visual guidance to the products' actual colour. Obviously, 3 pairs of products have same colour (2&6, 1&9, 4&8). Further investigation of their diagonal relationship is ongoing.

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Repurposing of Fluorinated Gases using Reactive Organolithium Reagents. P

Hodan Ruada Warsame, Sarah Patrick and Mark R. Crimmin*

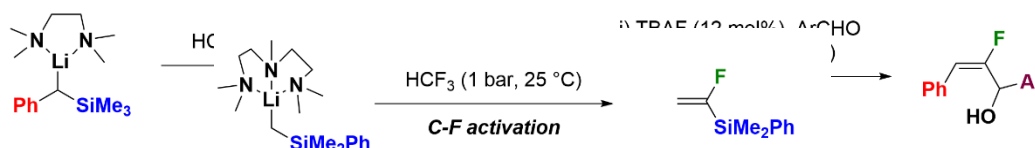
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Fluorinated gases (F-gases) are volatile molecules, with low boiling points featuring a least one fluorine atom. Examples include trifluoromethane (HFC-23), 1,1,1,2-tetrafluoroethane (HFC-134a), and pentafluoroethane (HFC-125).¹ HFC-23 is a greenhouse gas with a 100-year global warming potential (GWP₁₀₀) 14,800 times greater than of CO₂.² It is produced as a by-product of the manufacture of poly(tetrafluoroethylene) (PTFE) on a multikilo tonne scale annually.³ There are very few examples for the repurposing of HFC-23 in the literature, and currently no efficient processes exist of the direct formation of alkenes from HFC-23.^{4,5,6}

In this work, we report the room temperature defluoroalkylation of HFC-23 using two different organolithium reagents forming fluorinated vinylsilane products in moderate yields. The two organolithium reagents were successfully isolated and fully characterised by X-ray crystallography, and NMR (¹H, ¹³C, ⁷Li, ²⁹Si, DOSY). Density functional theory (DFT) analysis of the mechanism suggests that the reaction proceeds through defluorination followed by a silyl migration step.

The fluorinated vinylsilanes obtained can be used as reagents for the onwards synthesis of fluorinated products, including the TBAF-promoted synthesis of α -hydroxy-vinylfluorides.



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Photoelectrochemical Water-Splitting with BiVO₄/BiFeO₃ heterojunctions as effective photoanodes - P

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The intermittency of renewable energies poses great challenges in the energy transition, and a method for long-term energy storage that meets the shortfalls of battery technologies must be established. Hydrogen as a solar fuel is poised to play a crucial role in this transition by serving as a versatile energy carrier, with superior energy density, and the ability to be produced solely from water. Photoelectrochemical (PEC) water splitting holds significant potential by enabling the direct conversion of solar energy into hydrogen fuel, offering a clean and efficient way to store renewable energy. In order to make this technique commercially viable, a photoanode must be developed that not only meets performance requirements, but is scalable, cost effective, and consisting of earth abundant materials.

Bismuth Vanadate (BiVO₄) and Bismuth ferrite (BiFeO₃) are two standout photoanode materials due to their desirable band gaps of 2.4 eV and 2.1 eV, allowing high PEC efficiencies with the absorbance of a large proportion of visible light. One of the main issues these materials face is their low charge transport resulting from fast recombination of electrons and holes after formation. Layering of these materials has shown to greatly improve recombination rates by forming complimentary p-n heterojunctions¹.

Aerosol-assisted chemical vapour deposition (AACVD) is a technique whereby precursors are dissolved into a solvent which is aerosolised and passed over a heated substrate. AACVD is a highly scalable and cheap deposition method that can be applied to produce a wide range of thin film semiconductors and heterojunctions.

This poster presents a novel AACVD-based approach using tailor-made precursors to fabricate complimentary BiVO₄/BiFeO₃ thin film heterojunctions as photoanodes. Films were characterised via Raman spectroscopy, X-ray diffraction, and scanning electron microscopy. Linear sweep voltammetry under simulated sunlight was used to measure water splitting performance of a given photoanode material. BiVO₄ films with no modifications yielded a photocurrent density of 1.45 mA.cm⁻² at 1.23 V vs RHE. With the addition of a BiFeO₃ layer to establish a BiVO₄/BiFeO₃ heterojunction, an improved photocurrent density was measured of 2.18 mA.cm⁻² at 1.23 V vs RHE. To the authors knowledge, this is the highest photocurrent density of any CVD-grown BiVO₄ or BiFeO₃ film to date.

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Fluorescent phosphines for metal sensing: synthesis and characterisation of pyrazolyl-phosphine oxides - P

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In recent years, phosphorus-appended heterocycles have transitioned from simple laboratory curiosities into valued compounds in a range of fields.¹ One route into such species is through the cycloaddition reactions of azophosphines; which are underreported compounds containing an N=N-P functionality with phosphorus in the neutral, trivalent state, recently reported by Cummins et al.² and concurrently developed in the Jupp group.³

Here, we report the synthesis of novel pyrazolyl-phosphine oxides *via* the cycloaddition reactions of azophosphines. We have used a combination of density functional theory and experimental evidence to elucidate the mechanism of this unusual transformation. The applications of these species as a sensor for metal cations has then been explored,⁴ showing that pyrazolyl-phosphine oxides can act as selective phosphorus-based fluorescent sensors for certain metals.

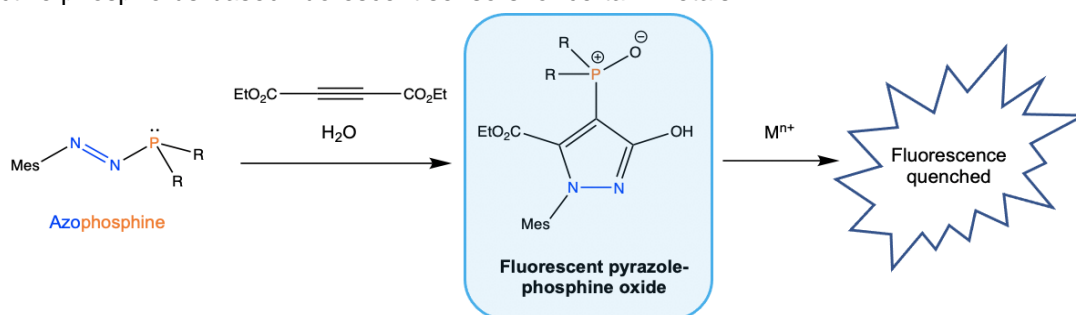


Figure 1: Synthesis of pyrazolyl-phosphine oxides *via* azophosphines.

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Field Effect Aerosol Assisted Chemical Vapour Deposition (FE-AACVD) of Thin Film Materials (P)

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Thin film inorganic materials as seen in metal oxide semiconductors can perform wide-ranging electronic and energy storage applications are of great interest to both industry and society. Metal oxide materials generated by Aerosol Assisted Chemical Vapour Deposition (AACVD) via chemical precursor decomposition on a heated substrate have been shown to possess highly crystalline morphologies suitable for performing photoelectrochemical water splitting as a means of energy storage. [1][2] AACVD processes have no requirement for precursor volatility, enabling the use of bulky and single source molecules which undergo clean and stoichiometric decompositions to target thin films at moderate temperatures. [3]. This work will introduce electric and magnetic fields during the deposition process to access novel morphological synergies from a range of dipolar and frequently paramagnetic precursors being synthesised [4]. Titanium (III) / titanium (IV), tantalum (V) and cerium (III) / cerium (IV) oxide thin films are being targeted for photoelectrochemical water splitting. This technique aims to produce green hydrogen as an energy source from water and sunlight – by overcoming the energy barrier of an oxygen evolution reaction [5]. Tuning of the morphological properties of these films will lead to increase their efficacy and stability whilst reducing their band gaps for increased light absorption. Further applications with similar materials will be considered for e.g., spintronics uses in the future.

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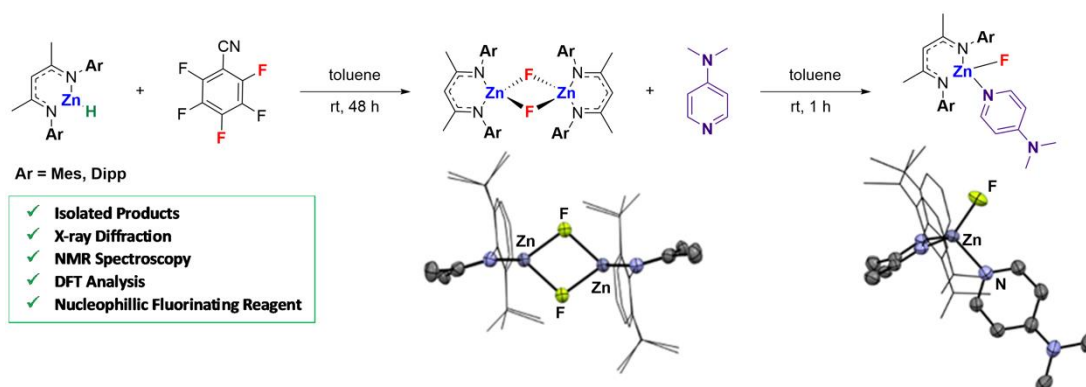
Synthesis and Reactivity of Zinc-Fluoride Coordination Complexes – P

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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.

The synthesis of a series of zinc fluoride complexes was achieved using pentafluorobenzonitrile as a fluorine source (Figure). While dimeric in the solid-state, these resulting complexes react quantitatively with N,N-dimethylaminopyridine (DMAP) at room temperature to form monomeric zinc-fluoride complexes featuring a terminal fluoride ligand. Four compounds were successfully isolated and their structure and bonding 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 – this is likely due to the relatively weak nature of Zn–F bonds.



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Elucidation of the Molecular Effect of Isoquinoline on Iron-Speciation and Mechanism in Iron-Catalysed Aryl-Heteroaryl Cross-Coupling – P

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Iron-catalysed cross-coupling reactions have attracted significant interest in organic synthesis as sustainable and low-cost alternatives to the precious metals catalysts commonly used in these transformations. Whereas there has been significant progress in Fe-catalysed coupling reactions between C(sp²) and C(sp³) centres, the formation of C(sp²)-C(sp²) bonds remains problematic because of homocoupling side reactions.¹ Knochel and co-workers reported an iron catalysed C(sp²)-C(sp²) cross-coupling reaction between N-heterocyclic halides and various aryl magnesium reagents, using simple iron salts and isoquinoline to enhance yields and reaction rates.² While this transformation represents the state of the art in aryl-heteroaryl iron-based coupling, the role that isoquinoline has in achieving effective cross-coupling remains largely undefined. Here, we expand the current molecular level understanding of this additive effect on iron speciation and mechanism utilizing a physical-inorganic approach, using *in situ* spectroscopic methods combined with single crystal X-ray diffraction (SC-XRD).

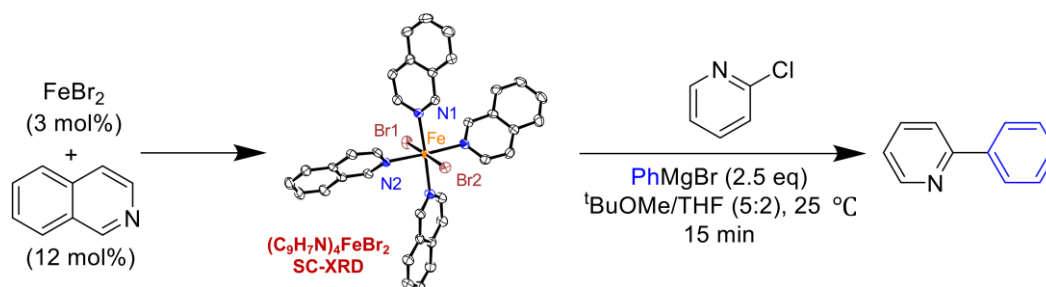


Figure 1. Aryl-heteroaryl cross-coupling enabled through the formation of isoquinoline-iron complexes.

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A Generalised Pathway Towards Novel Low-Valent Alkene-Stabilised Fe(0) Complexes - P

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Abstract

Iron (0) catalysts are central to numerous organic transformations including C-H activation and alkene functionalisation. Development of new Fe(0) species are important to addressing current challenges in the field, as well as expanding the utilisation of such complexes by clearly defining their roles within catalysis. Recent studies revealed a new pathway to these species by first reacting a simple FeCl₂ salt with N,N,N',N'-Tetramethylethylenediamine (TMEDA), followed by addition of a β -hydride alkyl Grignard to form an alkene-stabilized Fe(0) complex.¹ This reaction pathway enables access to highly active Fe(0) complexes for hydromagnesiation of styrene derivatives as well as Fe(0)-NHC complexes effective for C-H activation.^{2,3} Furthermore, this synthetic procedure to generate a reactive Fe(0) species provides a generalisable pathway that allows for not only extended usage, but also further insights into the reactivity of such complexes. This presentation describes these results and further extensions to new types of Fe(0)-alkene complexes.

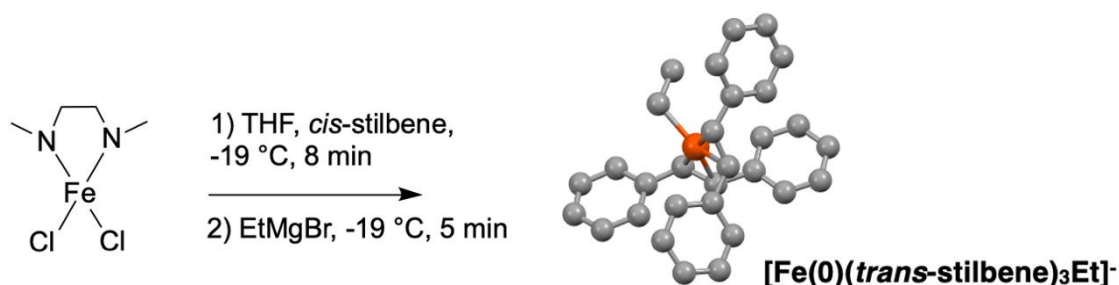


Figure 1. Formation of an Fe(0) *trans*-stilbene complex.

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Lifting The Lid On Iron-Catalysed Reductive Alkyl-Alkyl Cross-Couplings (P)

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Transition metal catalysed alkyl-alkyl bond formation, *via* cross-coupling, plays an important role in the organic synthesis toolkit. Despite considerable progress in recent years, iron's utility in this area has remained stunted due to a reliance on organometallic substrates, such as Grignard reagents, which bring with them functional group incompatibilities.¹ The emerging field of iron-catalysed reductive cross-couplings aims to circumvent this issue *via* the use of "mild" reducing agents to generate reactive iron intermediates.^{2,3} Examples of iron-catalysed reductive cross-couplings remain limited due to a poor mechanistic understanding of existing systems. Molecular level insights into such reactions will permit design principles to be established for efficient alkyl-alkyl bond formation, in turn, advancing method development.

Towards this goal, we are carrying out the first detailed mechanistic investigation into an iron-catalysed reductive cross-coupling between alkyl halides and olefins reported in 2023 by G. C. Fu and co-workers (Figure 1).² Using freeze-trapped 80 K Mössbauer spectroscopy and single-crystal X-ray crystallography, we have been able to identify speciation during catalysis, allowing for a working model of the catalytic cycle to be established.

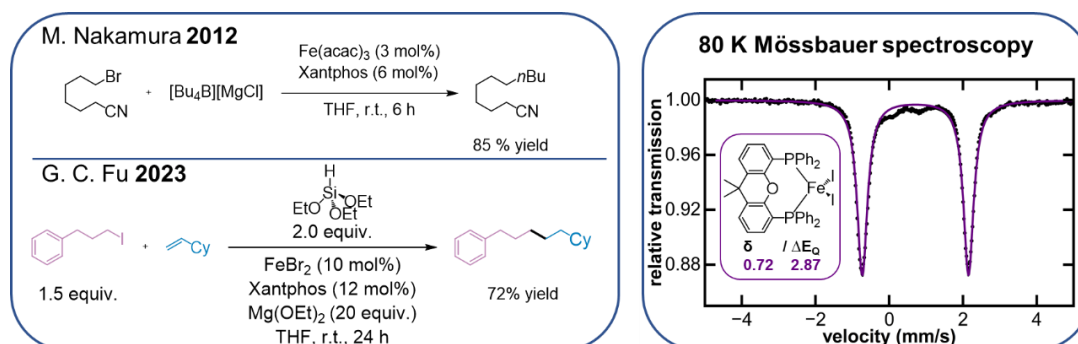


Figure 1. Iron catalysed C(sp³)-C(sp³) cross-coupling reactions and a 80 K Mössbauer spectroscopy as a tool for investigating speciation .^{1,2}

References

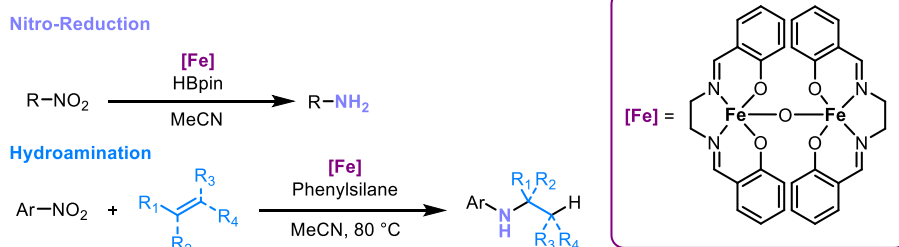
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Facile Reductions of Nitro-Organics Mediated by an Fe(salen) Complex - P

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Iron catalysis offers an attractive alternative to the more commonly-used precious metals due to its high abundance and low cost, along with the additional benefits of being a non-toxic and environmentally-benign metal.^[1] A large number of transition metal salen complexes have been reported and are capable of mediating lots of organic transformations.^[2] While iron catalysis is becoming prevalent in a range of organic transformations the iron-catalysed reduction of nitro-groups is relatively underdeveloped. With current methods often requiring longer reaction times and high catalyst loadings and temperatures.^{[1],[3]} The reduction of nitro-compounds has been a transformation of great synthetic interest throughout the years due to the wide variety of resulting products that can be accessed.^{[1],[3],[4]} In particular, the complete reduction of the nitro moiety to the corresponding amine is of great importance owing to the fact amines are known to be versatile organic building blocks.^[3]



The limitations associated with these methods mean that the reduction of nitro-compounds offers an alternative and convenient method for accessing functionalised amines. In light of this, herein we report the use of the Fe-salen catalyst alongside a reducing agent for the selective one-step reduction of various nitro-compounds to yield synthetically important products under very mild reaction conditions in short reaction times. Based on our understanding of how the mechanism for pre-activation of the catalyst proceeds and comparison to current literature, we successfully extended the reactivity to one-pot hydroaminations giving rise to a wide variety of highly functionalised secondary amines in excellent to moderate yields.^[4] During our investigation into the one-pot hydroaminations a trend in reactivity was observed which was found to be unique compared to current literature examples.^[4] In light of this, the trend has been explored further by both synthetic and computational analysis.

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The Active Encounter Complex in Frustrated Lewis Pair Chemistry – P

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Formed of sterically hindered Lewis acids and bases, frustrated Lewis pairs (FLPs) are able to activate small molecules, and show excellent catalytic activity.^{1, 2} Through the pre-association of the bulky acid and base in such reactions, we utilise an encounter complex to rationalise the termolecular reactivity of these systems; understanding the formation of this encounter complex is vital to rationalising FLP reactivity.^{3, 4} Our research seeks to build upon existing literature to probe and quantify the interactions that hold these compounds together as an encounter complex.⁵⁻⁷ By using UV-vis spectroscopy we exploit the charge-transfer band to calculate the association constant (K_a) using supramolecular chemistry techniques. Through our research, we aim to develop our understanding of this encounter complex; expanding the catalytic scope of these systems where fine tuning the Lewis acid and base substituents can allow us to maximise and control their reactivity.

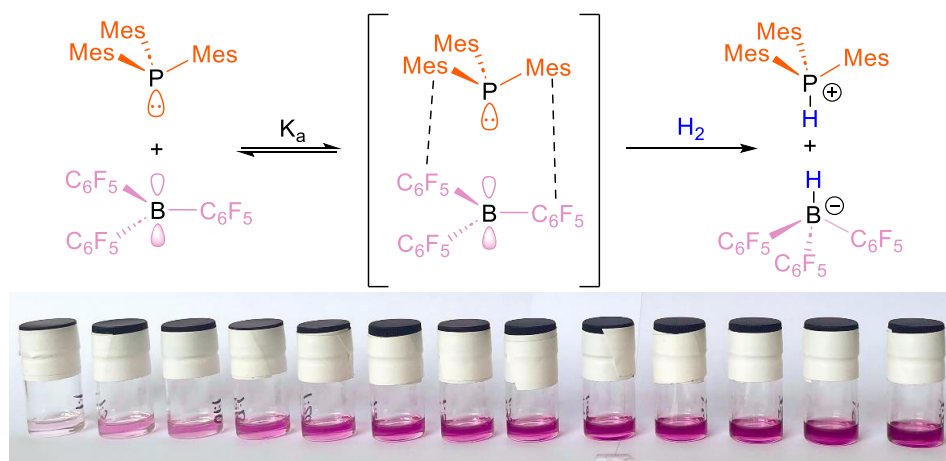


Figure 1: Top; The encounter complex formed by a B/P based FLP for facilitating small molecule activation, such as H_2 for hydrogenation of organic molecules. Bottom; increasing concentrations of our Lewis base component leading to an increase in λ_{max} permitting a novel analytical handle for these systems.

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Photo(redox)-promoted reductive elimination at p-block element centres – P

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Precious metal catalysis is vastly important in building molecular complexity. It relies on a metal's ability to cycle through different oxidation states easily to carry out important bond forming reactions (C-C, C-O, C-H) using oxidative addition, transmetallation and reductive elimination steps. Many of the elements involved are scarce and expensive. Attempts have therefore been made to emulate this reactivity using more earth-abundant elements, shifting attention towards the main group. Whilst many systems are now able to react via oxidative addition stoichiometrically, closing full catalytic cycles remains largely elusive. This work explores the capability of main group centres such as β -diketiminato supported gallium and T-shaped phosphine systems to achieve catalytic turnover, with focus on the final reductive elimination step. We use photoredox catalysts – a novel technique to inorganic catalysis - to transiently oxidise these complexes to induce reductive elimination of the substrate. Chemical oxidation methods and cyclic voltammetry have been used to investigate the redox reactivity of these species and isolate intermediates with an aim towards developing transition metal-like catalytic cycles in the future.

Mixed valence $\{\text{Ni}^{2+}\text{Ni}^{1+}\}$ clusters as models of Acetyl Coenzyme A Synthase Intermediates

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Bacterial enzymes are known to utilize the Wood-Ljungdahl Pathway (WLP), which outlines the conversion of carbon dioxide into acetyl coenzyme A (acetyl-CoA), a key biological metabolite.^{1,2} Central to the WLP is acetyl-CoA synthase (ACS), one of the few nickel-containing enzymes, which catalyzes the synthesis of acetyl-CoA from CO. The active site of ACS is known as the A-cluster, which consists of a $\{\text{NiNi}\}$ cluster bridged to a $[\text{Fe}_4\text{S}_4]^{n+}$ cluster (Figure 1a).

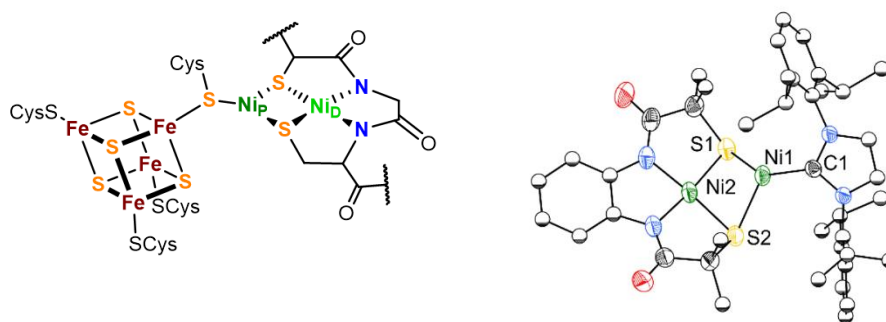


Figure 1: (left) The A-cluster of the ACS cofactor, highlighting the coordination environments of the two nickel centers, namely Ni_P (proximal) and Ni_D (distal); (right) Solid-state structure of the isolated mixed valent bimetallic anion, $[\mathbf{1}]^-$

Many mechanisms for probing the activity of ACS have been proposed and debated amongst the bioinorganic community, with arguments for divergent diamagnetic (nickel (0/II)) and paramagnetic (nickel (I/III)) mechanisms, with extensive research conducted to understand, isolate, and quantify intermediates along both proposed pathways.^{2,3} In an effort to probe the role of the two nickel centers (with varying oxidation states) of significance to the A-cluster, we report the first bimetallic models of two hypothesized intermediates on the paramagnetic pathway of ACS function, namely an anionic $\{\text{Ni}^{2+}\text{Ni}^{1+}\}$ cluster $[\mathbf{1}]^-$ featuring a three-coordinate Ni-center with similarity to the A cluster, which reacts with carbon monoxide to yield a $\{\text{Ni}^{2+}\text{Ni}^{1+}\text{-CO}\}$ cluster $[\mathbf{2}]$ analogous to the enzymatic CO-bound A cluster. Synthesis of these bimetallic complexes, along with characterization via X-ray diffraction, and NMR, UV-Vis, and electron paramagnetic resonance spectroscopies, will be discussed.⁴

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Synthesis, characterisation and small molecule activation prospects of macrocyclic diazacryptands as supramolecular hosts for dicopper(I) - P

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Transition metal complexes of macrobicyclic diazacryptands have seen a wealth of applications over the last 30 years since the facile ligand synthesis *via* Schiff base condensation was developed and reported by J. M. Lehn in the 1980s.¹ Such applications include, but are no means limited to, catalysis,² anion recognition,³ small molecule activation⁴ and chemosensing.⁵ Most notably, reports of diazacryptates have seen a recent resurgence in the literature arising from the pioneering work of J. Nelson and her team's development of 'cascade chemistry' for ensuing coordination of anionic species into the central cavity of the cryptate.⁶ This has resulted in numerous publications on the 'hot topic' of CO₂ reduction using diazacryptate complexes in recent years.^{7,8} Diazacryptands clearly have remarkable structural modifiability and offer the potential to synthesise a diverse range of heterobimetallic complexes; there is evidently still unexplored possibilities for such an adaptable ligand framework. Our research has focussed on coordination of Cu(I) ions into 'octaaminocryptands', N(CH₂CH₂NHCH₂RCH₂NHCH₂CH₂)₃N (where R = *p*-xylyl (**L1**), *m*-xylyl (**L2**)), featuring TREN capping groups and xylyl bridging spacers. Cu(I) ions provide an excellent opportunity to study different properties of the resultant complexes, without interfering solvent molecules binding to additional coordination sites, as the copper(I) ions are coordinatively saturated in the pseudo-tetrahedral binding pockets. Initially, it was observed that the dicopper(I) cryptates for both cage ligands exhibited limited solubility when the chosen counter-anions were tetrafluoroborates. Using different Cu(I) salts allowed us to alter the observed solubilities tested in numerous common organic solvents; it was shown that the incorporation of the highly lipophilic BARF (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) anions offered superior solubility in a much wider range of organic solvents, following the order [Cu₂(**L**)]([OTf])₂ < [Cu₂(**L**)]([BF₄])₂ < [Cu₂(**L**)]([PF₆])₂ << [Cu₂(**L**)]([BARF])₂. XRD studies revealed the expected greater intermetallic Cu - Cu distance for the *p*-xylyl derivative complexes relative to those with *m*-xylyl spacers. Intriguingly, the non-coordinating anions also marginally affect the Cu - Cu distance, which follows the order BF₄ > PF₆ > OTf based on the XRD structures obtained thus far. These preliminary results suggest that, in addition to directly modifying the structure of the macrobicyclic cage, varying the anion is another method for subtly tuning the intermetallic distance. Growing suitable single crystals of the dicopper(I) cryptates with BARF anions are still on-going.

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Mechanistic and Structural Insights into Effective Alkyl-Alkyl Cross-Coupling with Iron-Xantphos (P)

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Alkyl-alkyl bond formation is a cornerstone of chemical synthesis, yet C(sp³)-C(sp³) cross-couplings with iron remain significantly underdeveloped despite the attractiveness of iron methods for sustainable catalysis. Early studies by Nakamura demonstrated the effectiveness of an iron-Xantphos catalyst in Suzuki-Miyaura cross-coupling of simple alkyl substrates,¹ while more recent studies have expanded these reactions to include the formation of quaternary centers.² While highly promising, these reactions suffer from limited product yields that must be overcome to be competitive for practical synthetic use. To overcome these challenges, developing molecular-level insight into the key iron intermediates and mechanistic pathways that enable effective alkyl-alkyl cross-coupling with iron is essential. Towards this goal, we have pursued detailed mechanistic studies of iron-Xantphos catalyzed alkyl-alkyl coupling reported by Nakamura, including the nature of the in-situ formed iron-Xantphos intermediates, their reactivity and plausible mechanism are identified by a combination of ⁵⁷Fe Mössbauer spectroscopy, SC-XRD (single-crystal X-ray diffraction) and reactivity studies. This work demonstrates the prevalence of alkylated iron(II)-Xantphos intermediates as key reactive species. Furthermore, evaluation of the ligand and its structural effects on the iron intermediates allowed the identification of the necessary conditions for successful reactivity, providing a platform for bespoke ligand design and iron-catalyzed alkyl-alkyl cross-coupling method development.

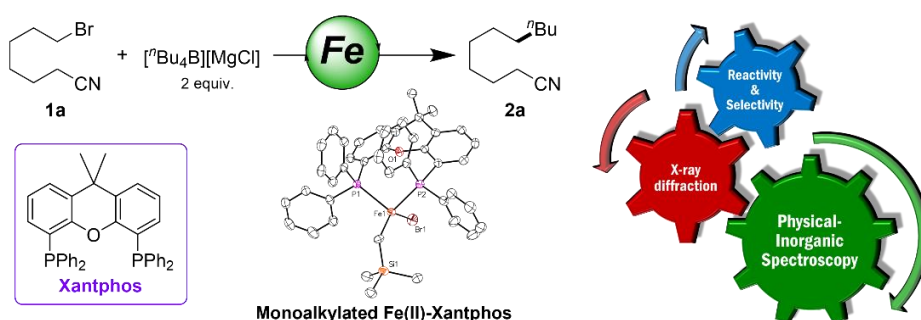


Figure 1. Insight into key iron-Xantphos intermediates and mechanistic pathways.

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Using Twin Screw Extrusion as a Route to Biodegradable Medicines, including Metallodrugs

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There is a pressing need for new approaches to chemical manufacturing that are more sustainable than conventional solvent-based methods. Twin-Screw Extrusion (TSE), in which reagents are mixed and conveyed along a confined, temperature-controlled barrel by two intermeshing, co-rotating screws,¹ is emerging as a viable mechanochemical technique in which continuous, solvent-free synthesis, favourable to industrial implementation, can be achieved. Specifically, it has been shown capable of the continuous, kg h^{-1} synthesis of cocrystals,² Metal Organic Frameworks (MOFs)³ and active pharmaceutical ingredients (APIs)⁴ with Life Cycle Assessments (LCA) highlighting that TSE offers cost, sustainability, and operational advantages over conventional, solvent-batch processes.⁵ Herein, we will demonstrate the use of TSE for sustainable synthesis of biodegradable APIs. This will not only result in sustainable, solvent-free manufacture, which is beneficial to the environment, but will also reduce the bioaccumulation of these medicines in our rivers and ecosystems. We demonstrate a range of syntheses extending from organic compounds to metallodrugs.



Figure: Twin-screw extruder employed in the continuous, solvent-free synthesis of organic and coordination compounds.

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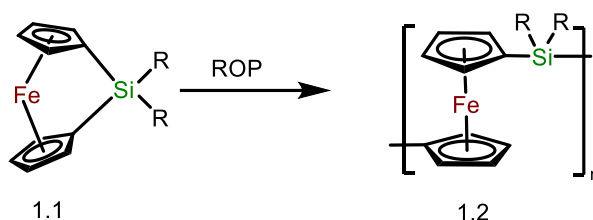
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Water-Soluble Poly(cobaltoceniumsilane) - P

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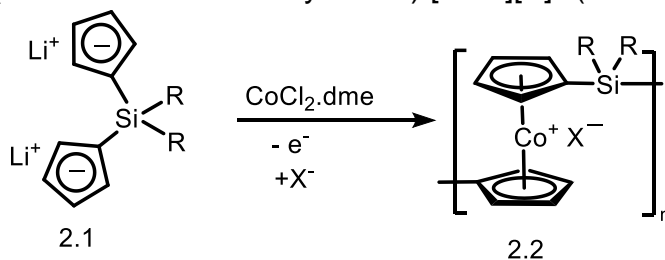
Metallopolymers are a class of hybrid material that blend the versatile processing capabilities of polymers with the unique functionalities of metal centres, with applications ranging from catalysis to advanced electronics.¹

One well-known method for synthesizing main-chain metallopolymers involves the ring-opening polymerization (ROP) of strained metallocene-based cyclic monomers with linked cyclopentadienide ligands, commonly known as *ansa*-metallocenes or metallocenophanes.² The ROP of dialkylsila[1]ferrocenophanes (1.1) to yield high molar mass poly(ferrocenyldialkylsilanes) (Scheme 1.1), in particular, is well-reported in literature.³



Scheme 1: ROP of dialkylsila[1]ferrocenophane, 1.1

However, the development of polymetallocenes based on cobalt has shown gradual progress due to challenges in both monomer and polymer synthesis and there are limited examples of main-chain poly(cobaltocene) materials to date.⁴ Results will be presented on the synthesis and characterisation of a novel cobaltocenium-containing polyelectrolyte, poly(cobaltoceniumdimethylsilane) [PCS][X]_n (X = PF₆⁻, Cl⁻).



R = alkyl, X = Cl⁻, PF₆⁻

Scheme 2: Polymerisation of dialkylsila[1]cobaltocene, 2.1

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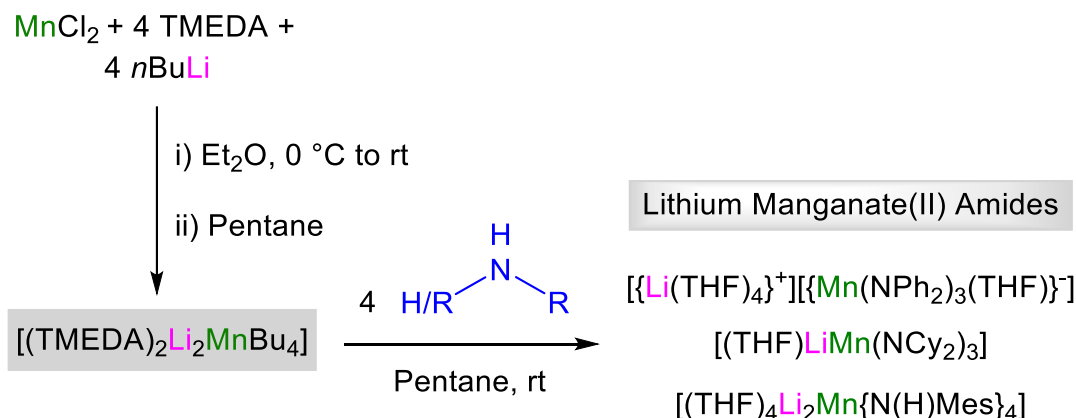
Synthesis and Structural Diversity of Lithium Manganate(II) Amides - P

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Amongst the catalogue of organomanganese(II) reagents, alkali-metal manganates have emerged as a new family of compounds which can deliver unique chemistry which cannot be replicated by conventional alkali-metal or manganese reagents on their own.¹ Recently, we have demonstrated the ability of alkali-metal manganates [(TMEDA)₂M₂Mn(CH₂SiMe₃)₄] to affect a direct Mn-I exchange (M = Li) of aryl iodides,² and Mn-H exchange of terminal alkynes (M = Li, Na, K).³ Newly obtained tetraaryl and tetraalkynyl manganate intermediates can undergo C-C homocoupling affording a range of valuable bis(arenes) and conjugated 1,3-diynes with excellent atom economy under one pot methodology.

Breaking new ground in this evolving area, this poster presents the synthesis and characterisation of a new family of lithium manganates incorporating a variety of amide ligands. Moving away from established synthetic routes, such as salt metathesis and co-complexation, we investigate direct deprotonation of parent amine by tetraalkyl lithium manganate [(TMEDA)₂Li₂MnBu₄] which can be prepared from commercially available reagents. This synthetic approach solves the issue of limited accessibility of suitable precursors and poor solubility of Mn(II) salts. The effects that steric and electronic variations of the amide ligand have on stoichiometry, constitution, and structural motif of these heterobimetallic compounds have also been assessed (Scheme 1).



Scheme 1. Direct deprotonation of primary and secondary amines by *in situ* formed tetrabutyl lithium manganate [(TMEDA)₂Li₂MnBu₄].

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Exploring the Synthesis and Electronic Structure of Iron-oxo Clusters – P

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Water splitting is an important process to generate green hydrogen, however, a photocatalyst is required for this process that can promote both proton reduction as well as water oxidation.¹ Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a promising material for this process due to its high natural abundance, low toxicity, and ideal band gap of ~ 2.2 eV.² However, the large-scale realisation of this material remains a challenge. Short charge carrier distances ($\sim 2\text{-}6$ nm)³ and the need for an external bias of ~ 0.6 V to drive the overall water splitting process are problematic.⁴ Utilising ultrasmall iron(III)-oxo clusters or nanoparticles could overcome these issues. Quantum confinement effects in these ultrasmall systems can be utilised to effectively tune the band gap of the clusters based on their size, potentially removing the need for a potential bias. However, the effect of size upon the electronic structure of strongly correlated materials such as hematite is not widely explored and understood in the literature. Therefore, molecular iron-oxo clusters are interesting atomically defined analogues of bulk oxide materials, and by studying these we aim to understand the effects of size upon electronic structure.^{5,6} In this poster the synthesis of a range of iron-oxo clusters will be explored and UV-Vis analysis will be used to analyse how their electronic structure changes with size.

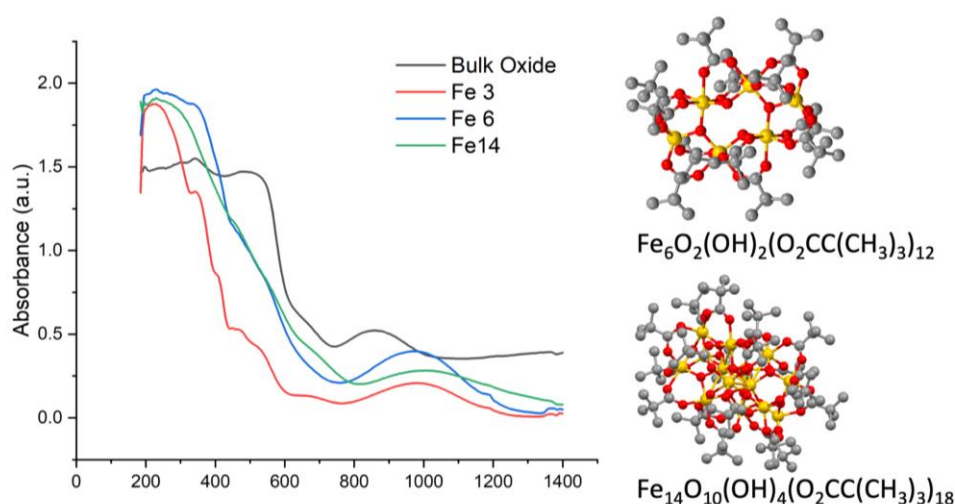


Figure 1: A comparison of the solid-state UV-Vis spectra of iron-oxo clusters of different nuclearities against bulk hematite, with SCXRD structures of the Fe_6 and Fe_{14} clusters.

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Synthesis of Novel Electrolyte Materials for Rechargeable Magnesium Metal Batteries

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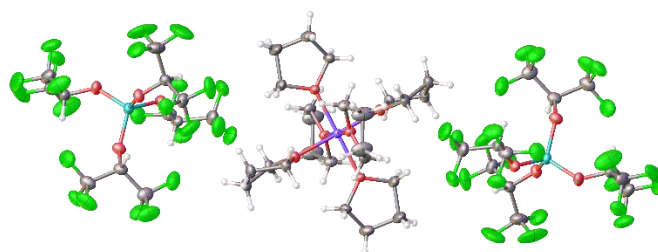


Figure 1: Crystal Structure of $\text{Mg}(\text{THF})_6[\text{Al}(\text{HFIP})_4]_2$, visualised in Olex2 software.

Lithium-ion batteries have become state-of-the-art in most devices, such as EVs, however, they no longer meet the increasing demand for the high energy density needed, i.e. range of an EV.¹ Rechargeable magnesium metal batteries (RMBs) have been identified as a promising alternative as magnesium metal is significantly more abundant, and has a high volumetric capacity (3833 mAh cm^{-3}).² However; identification of electrolytes that allow reversible magnesium plating and stripping, passivation of magnesium metal anodes, and lack of compatible cathodes pose a challenge.³ The development of new electrolyte materials for RMBs is required as the current candidates offer significant passivation, low capacities, or corrosion issues due to chloride. Weakly coordinating anions have been identified as a promising candidate for Mg electrolytes as their large size and low charge, limit interactions with the cation-reducing ion-pairing effects, and boast relatively simple synthetic routes attractive for commercial applications. Recently, electrolytes of $\text{Mg}(\text{DME})_3[\text{Al}(\text{HFIP})_4]_2$ in glyme solvents have been shown to allow reversible behaviour in cells with Mg foil and Chevrel phase Mo_6S_8 electrodes.^{4,5} Magnesium electrolytes often use glyme solvents which are highly volatile, making them non-ideal for commercial applications. In addition, the vast excess of the strongly coordinating glymes can result in the sluggish release of Mg^{2+} at the electrode surfaces. Hence, a solvent that will not compete with the ligand, improving the kinetics, is of interest. To achieve this, removal of DME from the system is critical, replacing it with more labile ligands. Therefore, we have demonstrated the synthesis of $\text{Mg}(\text{THF})_6[\text{Al}(\text{HFIP})_4]_2$, which can be used as a gateway to other interesting ligands, and in turn improve the solubility and electrochemical properties.

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Synthesis of bi- and multimetallic palladium complexes with a dinucleating pyrazolate scaffold

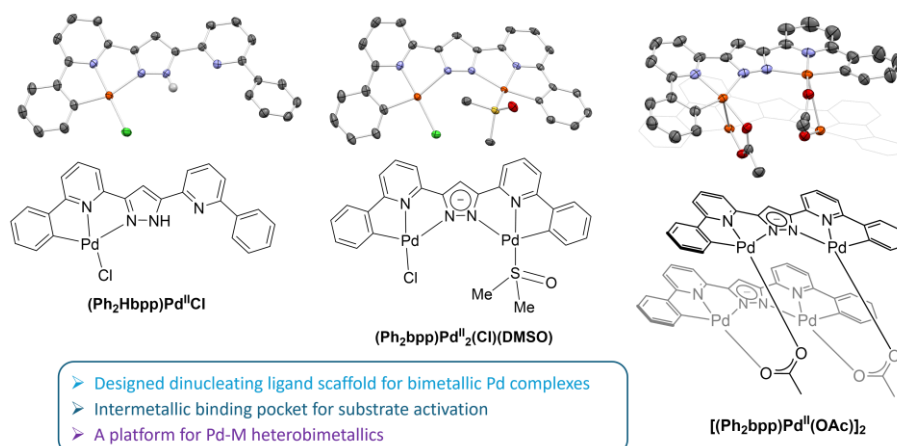
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Keyword(s): bimetallic complexes; synthetic coordination chemistry; ligand design

While transition-metal catalysts are typically based on mononuclear complexes, 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.^{2–8}

Having previously synthesised a family of dinuclear cobalt μ -peroxo complexes based on the oxidatively robust bispyridyl-pyrazolate scaffold **bpp** ligand scaffold, here we have expanded our investigations into constructing a series of homo-dinuclear Pd complexes, with an inter-metallic binding pocket prime for substrate activation. We are investigating the properties and reactivity of these complexes, with a focus on their bimetallic nature and the potential for metal-metal cooperativity. As the usefulness of palladium in a wide range of chemical transformations and catalysis is well-known, we will investigate catalytic organic transformations, such as cross-coupling reactions, or transformations *via* activation of small molecules, particularly O₂, as in the cobalt analogue. Reversible dioxygen activation may lead to catalytic aerobic oxidations of substrates such as olefines, alcohols and amines. Now that the suitability of the derivatised **bpp** scaffold with palladium has been established, we will be investigating the synthesis of Pd-M hetero-bimetallic complexes, combining palladium with catalytically active first-row transition metals, such as Fe, Co, Cu or Ni, particularly towards the greater interest of achieving a Pd/Cu molecular Wacker catalyst.



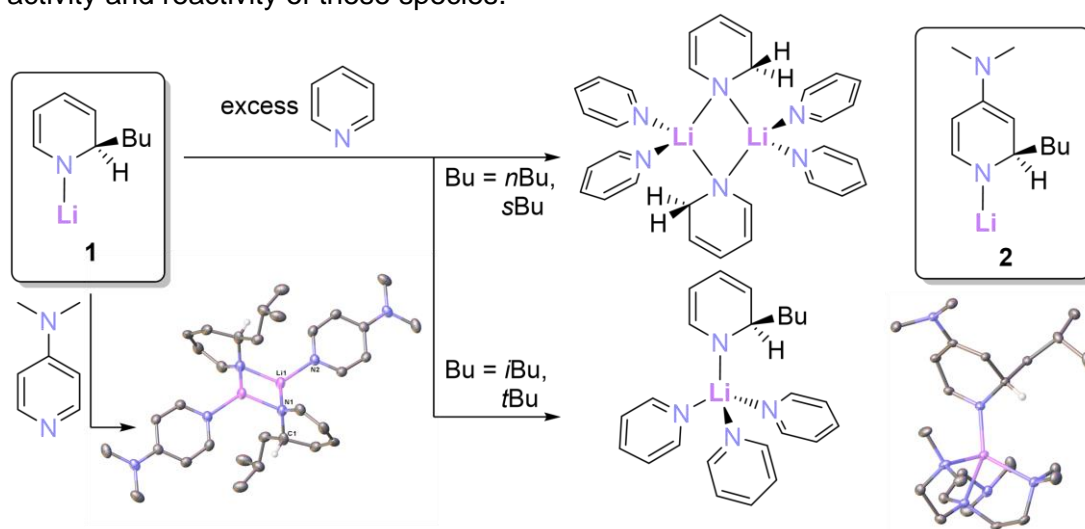
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Isomeric and Congeneric Effects in Alkali Metal Dihydropyridine Chemistry – P

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The role of alkali metal amides as synthetic workhorses is longstanding,^[1] but over the past two decades their capabilities as catalysts and pre-catalysts in their own right for an array of transformations has gradually emerged.^[2] Alkali metal (AM) complexes of 1,2-dihydropyridine derivatives in particular have long been known to mediate important organic transformations,^[3] but only with our more recent studies has a greater understanding of these intermediates and their true potential as catalysts started to be recognised. Seemingly minor changes to substitution patterns, and use of heavier alkali metals, can exhibit remarkable effects on activity and reactivity of these species.^[4-6]



Herein, we report how different isomers of the butyl group in Li-1,2-BuDHP (**1**) and Li-1,2-BuDH(DMAP) (**2**) complexes lead to different outcomes in their synthetic and catalytic reactivity, depending on their ability to act as effective surrogates of lithium hydride. Even more dramatic effects are observed upon going down group 1, whereby use of heavier alkali metals results in remarkably higher activities within the family of AM-1,2-BuDH(DMAP) complexes, when applied in transfer hydrogenation catalysis.

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New Avenues for Organometallic C-H Activation – P

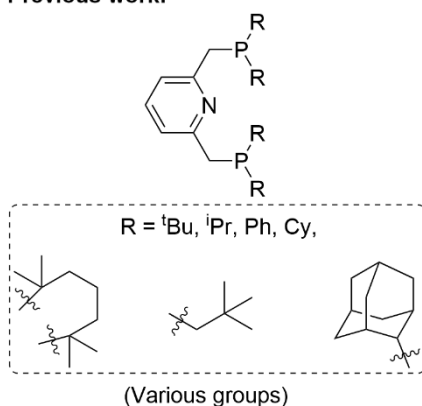
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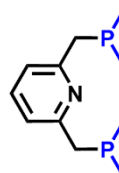
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Pincers are tridentate ligands that are typically rigid and occupy a meridional geometry. They have applications in C-H bond activation and CO₂ activation. PNP pincer ligands (named for the phosphorus-nitrogen-phosphorus arrangement of coordinating atoms) are commonly used. PNP ligands with a large amount of steric bulk on the phosphine atoms have been extensively studied, while unhindered complexes remain relatively unexplored.

Previous work:



This work:



This work aims to develop a series of sterically unhindered iridium and rhodium PNP complexes. These will be used to enable the catalytic insertion of a molecule of CO₂ into the C-H bond of an organic substrate. Iridium and rhodium are favoured due to their activity in C-H bond activation and CO₂ activation.

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Mechanism Driven Methodology Design for Iron-Catalysed Cross-Coupling - P

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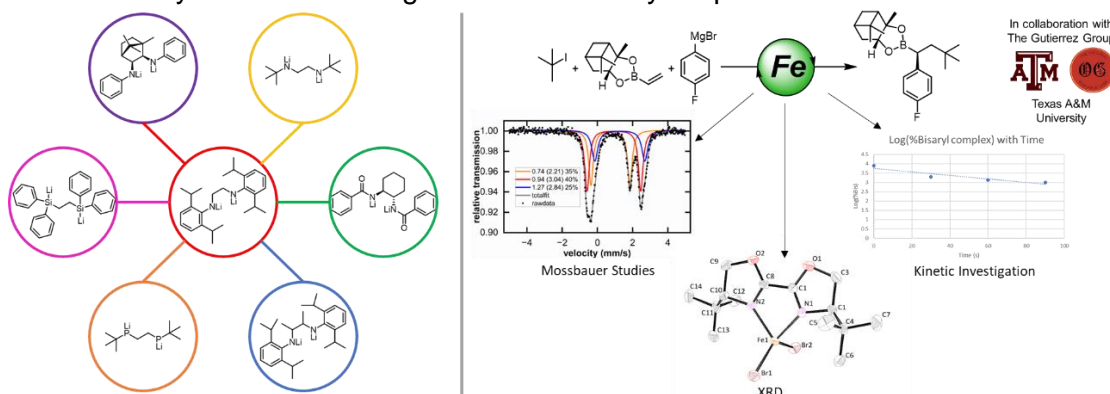
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Historically, there has been a lack of mechanistic understanding of iron-catalysed organic transformations[1]. Recent mechanistic studies by the Neidig group have begun to elucidate the unique reaction profiles of iron catalysts[2]. These insights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

Based on mechanistic work previously done in the Neidig group, the bisanionic chelating ligand motif was found as a powerful way to emulate the active iron species present in some NMP promoted iron catalysed C(sp²)-C(sp³) cross couplings[3]. Further to this, we have been interested in exploring structural variations on this ligand motif with an aim to determine the essential elements of these ligands for effective catalysis. This has yielded various new bisanionic chelating ligands for a variety of purposes, including very strongly donating lithium phosphide ligands, and chiral lithium amide ligands. The strengths of these ligands across a range of reactions, including cross coupling, are still being explored.

In collaboration with the Gutierrez lab at Texas A&M, we have been developing our mechanistic understanding of an enantioselective iron catalysed 3 component cross coupling. A range of reactive intermediates involved in the reaction have been identified, which are used in concert with DFT computation from the Gutierrez lab to identify a mechanistic pathway. Mechanistic insights have provided explanations for procedural requirements during the reaction, and insight into how the catalytic conditions target the active catalytic species.



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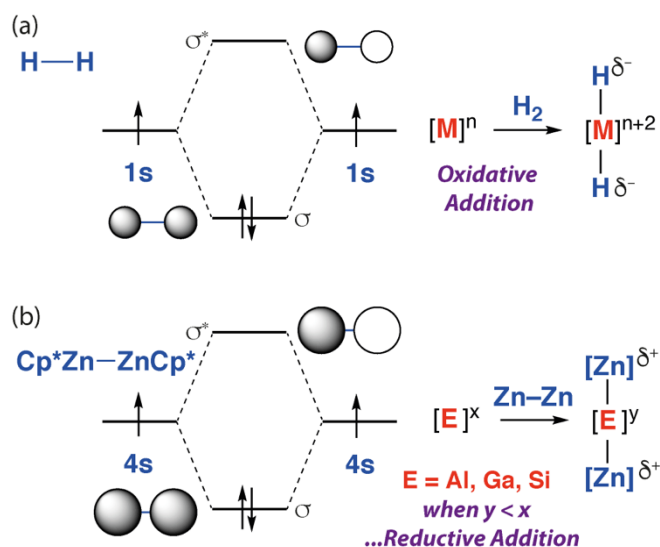
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Reductive Addition of a Zn–Zn Bond to Main Group Carbene Analogues

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Abstract: Oxidative Addition involves the addition of a substrate to a metal centre. This reaction is fundamental across synthetic chemistry and underpins numerous catalytic methods. In the textbook description of Oxidative Addition reactions, charge flow predominately occurs from the metal centre to the substrate, leading to a net increase in the formal oxidation state of the metal; this occurs with simultaneous bond breaking at the substrate. The majority of known reactions, however, involve substrates bearing relatively electronegative elements (e.g. H, C, N, O, halogen) and there has been little discussion of how addition processes may fundamentally change if substrates were constructed from more electropositive elements. Here we show that the zinc–zinc bond complex, $\text{Cp}^*\text{ZnZnCp}^*$, which is isoelectronic with dihydrogen, undergoes facile addition to the metal (or semi-metal) centres of a series of main group carbene analogues based on aluminium, gallium, or silicon. Reactions proceed with complete breaking of the Zn–Zn bond and increase in the coordination number of the central metal from 2 to 4. Based on DFT calculations and reactivity, these addition processes are not oxidative. Rather data suggest that they are better described as a reductive addition, from the perspective of the main group centre. Our findings challenge our preconceptions regarding text-book definitions and hint that when involving electropositive substrates that oxidative addition processes may not always be oxidative.



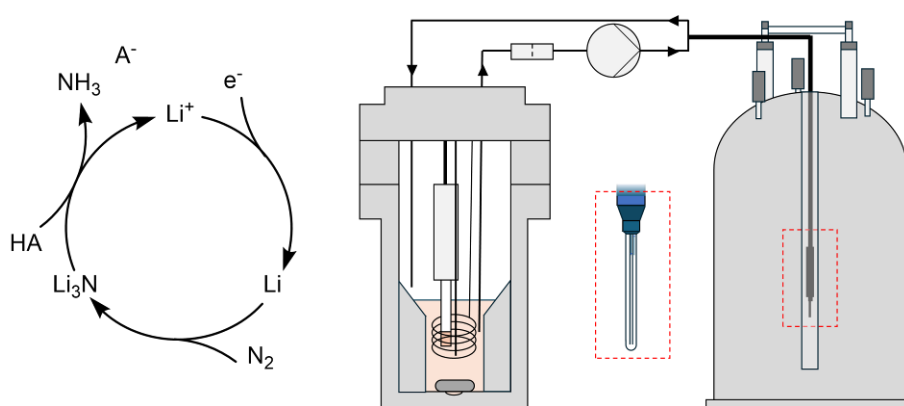
Operando FlowNMR spectroscopic study of lithium-mediated nitrogen electroreduction to ammonia

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Lithium-mediated nitrogen electroreduction to ammonia is by far the most promising alternative route to decarbonise and delocalise the industrial Haber-Bosch process. Recently, an electrolyte system of a highly concentrated imide-based lithium salt in tetrahydrofuran with ethanol as the proton source under 15 bar nitrogen has achieved a nearly 100 % Faradaic efficiency to ammonia with a yield rate of $150 \pm 20 \text{ nmol s}^{-1} \text{ cm}^{-2}$ [1]. Further understanding of the chemistry inside the system is crucial to advance the field.



Nuclear Magnetic Resonance spectroscopy in continuous flow (also known as FlowNMR) is a powerful technique to gain insights of chemical reactions in their true nature [2]. Herein, *operando* ^1H , ^7Li , and ^{19}F NMR of a robust lithium-mediated nitrogen electroreduction reaction has been monitored, revealing several intermediates and byproducts.

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Anilido-Aldimine and related titanium complexes as catalysts for CO₂/epoxide cycloadditions

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N-aryl β -diketiminate ($\{\text{ArNC(R)}_2\text{CH}^-$ or “nacnac”) ligands are widely used in organometallic chemistry, in part due to their ability to stabilise highly reactive species. Nacnac complexes with metals across the periodic table have shown applications in olefin polymerisation, hydroamination, and small molecule activation.¹ Unfortunately, these systems have a major drawback: the methine carbon atom in the ligand backbone shows nucleophilic behaviour towards substrates like CO₂.² Anilido-aldimines $[\text{o-C}_6\text{H}_4(\text{NR}_1)(\text{CH}=\text{NR}_2)]^-$, a homologue of nacnacs, have been proposed as an alternative ligand platform which blocks this site of reactivity through the introduction of a benzannulated backbone, while retaining strong bidentate metal coordination and steric and electronic tunability.³

This work explores the versatility of anilido-alimine ligands with group a titanium metal centre. We explore the coordination chemistry of these novel complexes, drawing comparisons to known nacnac and iminoacyl analogues. Several anilido-alimine ligands with a range of steric and electronic properties have been synthesised and resulting complexes have been explored as catalysts for CO₂/epoxide cycloadditions.⁴

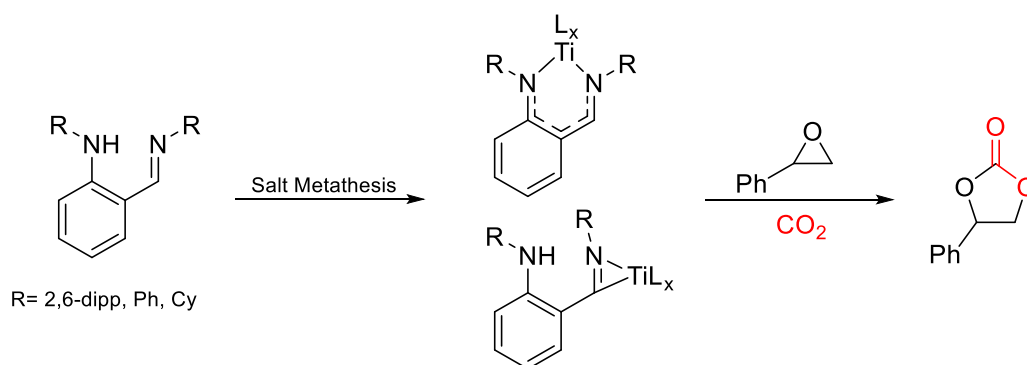


Figure 1. General synthetic route to anilido-alimine complexes and CO₂/epoxide cycloaddition.

Keywords: Anilido-aldimines, Coordination Chemistry, Catalysis, Transition Metals

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Vanadium Complexes with Hybrid Ligands for Small Molecule Activation – P

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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.

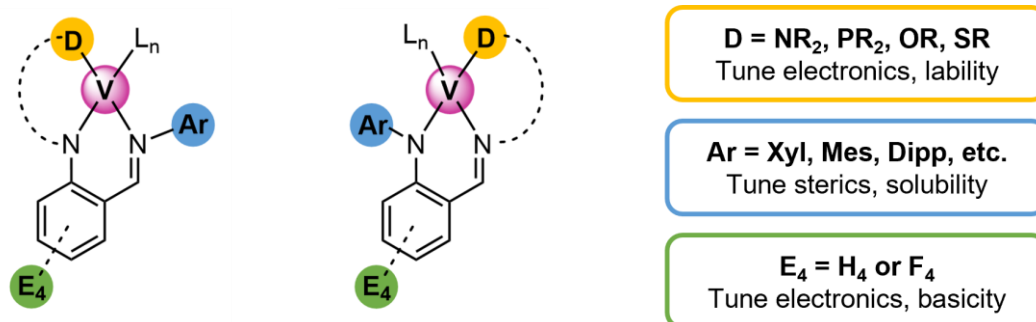


Figure 2: Proposed vanadium complexes for small molecule reactivity studies.

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B(C₆F₅)₃ Lewis acid-catalysed Thiolation of Alkenes

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Abstract:

The catalytic activity of halogenated triarylboranes has attracted considerable attention in synthetic chemistry. Their Lewis acidity, arising from the vacant *p*-orbital on the central boron atom, enables them to activate polar Lewis basic substrates. Furthermore, selectivity and reactivity can be finely tuned as the steric effects of the halogenated aryl ligands adjust their Lewis acidity. Herein, we report the B(C₆F₅)₃-catalyzed thiolation of α -alkylstyrenes and 1,1-diphenylethylene derivatives using *N*-thiosuccinimide. This method provides straightforward access to both allylic and 1,1-diarylvinyl sulfides under mild conditions, achieving yields from good to excellent with tolerance to a wide range of functional groups.

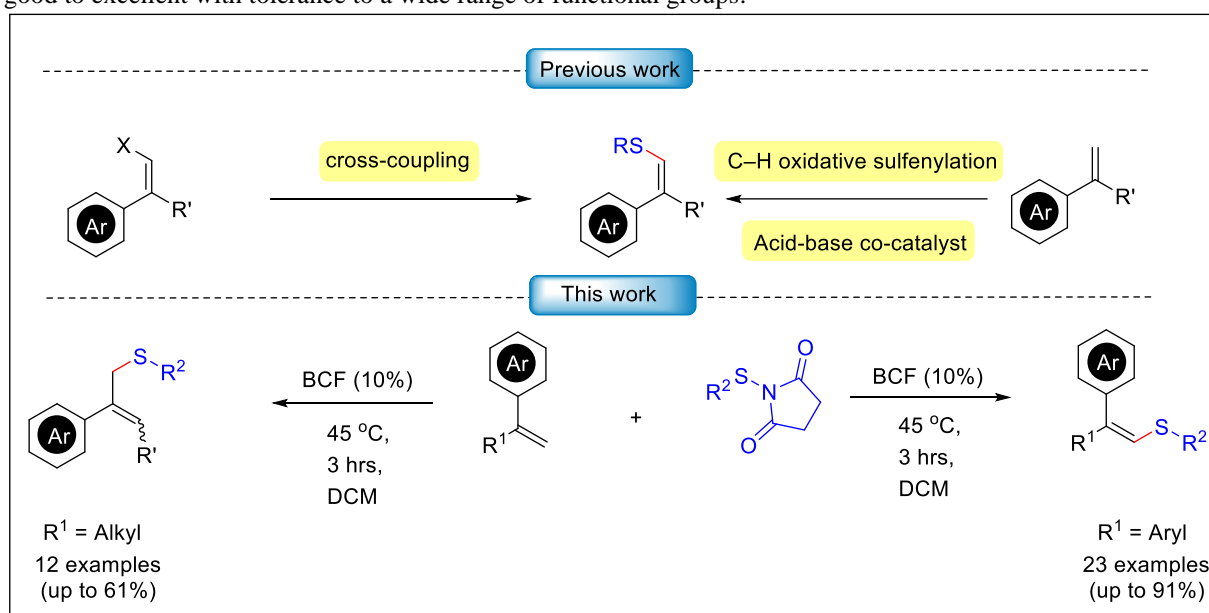


Figure 1 Catalytic reaction of B(C₆F₅)₃ towards thiolation of alkenes and the previous synthetic routes to allylic and vinylic sulfides.^{1,2,3}

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Electrodeposition of WSe₂ thin films using a single source precursor – P

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The early transition metal dichalcogenide (TMDC) semiconductors are materials with a range of high-tech applications, they adopt layered structures similar to graphene, but are notably more stable and have tunable band gaps. Layered TMDCs are typically *n*-type, but WSe₂ is notable as a *p*-type material, making it a key target for the fabrication of TMDC heterostructure devices.¹ However, this requires the development of scalable techniques to be able to fabricate functional devices with these materials.

Furthering on from our previous work producing films of MoS₂² and WS₂,³ we have recently developed the electrodeposition of an electrolyte solution of WSeCl₄, which acts as a single source precursor towards the deposition of WSe₂. This will be described alongside the details of the resulting films.

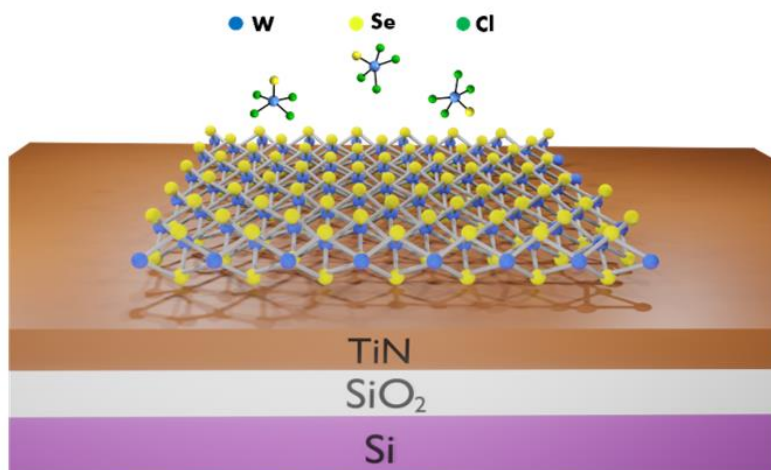


Figure 1: Illustration of the electrodeposition of WSe₂ onto a TiN electrode

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Synthesis and Characterisation of New Complexes with Functionalised Schiff Base Ligands (P)

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The presence of the imine group in Schiff Base (SB) ligands has showed its key role in their biological functions.¹ Researchers are targeting new anticancer, transition metal, drugs particularly Cu(II) complexes are being investigated due to its biocompatible properties and oxidative nature.² A three-step synthesis of novel, air-stable, alkoxy and morpholinoaniline-substituted [N,O]-donor SB ligands (**L**₁) was accomplished by condensation reactions of amines³ with various aldehydes⁴ in a 1:1 stoichiometric ratio. The unusual ring cyclised compound **2** was formed when benzaldehyde was used. Furthermore, these imines were reacted with Cu(NO₃)₂ and CuCl₂·2H₂O to give new Cu(II) complexes.⁵ The structural elucidation of SB ligands and their Cu(II) complexes were supported by their elemental analysis, FT-IR, ¹H, ¹³C{¹H}, and ¹⁹F{¹H} NMR spectroscopy and single crystal X-ray crystallographic studies.

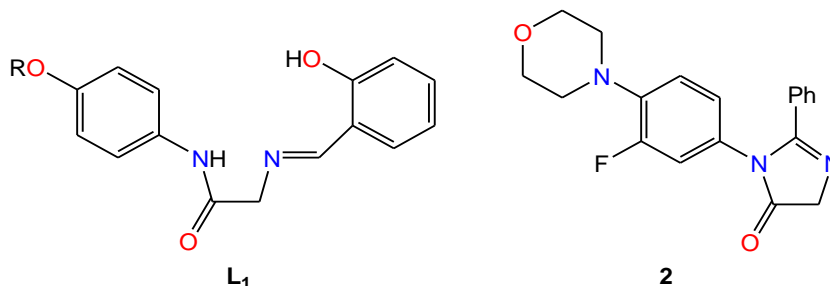


Figure 1. Schiff base ligands **L**₁ and compound **2** studied.

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

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Organozinc reagents are essential for carbon-carbon bond formation in drug synthesis,¹ yet their liquid-phase speciation and electronic structure are poorly understood. Problematically, zinc is spectroscopically quiet, mainly due to the filled 3d shell, meaning standard lab-based spectroscopies (e.g. UV-Vis, EPR, NMR) have limited use. X-ray absorption spectroscopy (XAS) is common for zinc-based compounds,² including a smattering of organozinc examples,^{3,4} but there are no organozinc studies using X-ray emission spectroscopy (XES) or resonant XES (RXES).⁵

On beamline I20 at Diamond Light Source synchrotron, high energy resolution fluorescence detection XAS (HERFD-XAS), valence-to-core XES (VtC-XES) and VtC-RXES (plus 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,⁶ allowed for the specific probing of Zn p-occupied to Zn p-unoccupied state transitions, allowing quantification of the effects of 14 different substituents on diorganozinc electronic structure and reactivity (Figure 1). This study highlights the effectiveness of X-ray spectroscopy in characterising the liquid-phase speciation and electronic structure of closed-shell diamagnetic complexes, including zinc.

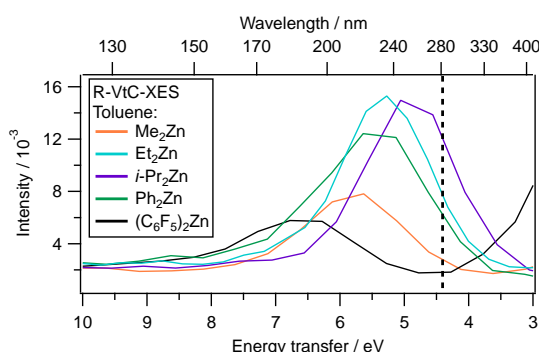


Figure 1. R-VtC-XES for Me₂Zn, Et₂Zn, *i*-Pr₂Zn, Ph₂Zn and (C₆F₅)₂Zn in non-coordinating toluene. The black dotted line represents the effective solvent cutoff for toluene using standard UV-Vis.

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The National Electron Diffraction Facility - what, where, and how for 3DED now – P

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Single-crystal X-ray diffraction has been the main-stay of structure determination since its inception. Continued powerful improvements to both hardware and software have pushed the technique to the absolute limit of the probe itself, yet there are still a host of sample types and materials for which these methods are prohibitively difficult or even impossible. This is primarily due to single-crystals large enough to study being impossible to grow, while the alternative - powder XRD - suffers from a whole range of challenges which often prohibits its use in routine structure determination.



3D electron diffraction (3DED) provides a single-crystal technique applicable to crystals orders of magnitude smaller than those used for X-ray methods. The use of electrons for diffraction mandates several considerations distinct from those of XRD, for example relating to the high vacuum environment. Even so, the advantages of 3DED still render it an invaluable addition to the structure characterisation arsenal. Besides blowing-open the above-mentioned sub-micron crystals regime, it also allows distinction of multiple crystalline phases in a mixed sample, the detection and identification of impurities, and *in-situ* elemental analysis.

Previously, 3DED for structure determination has been limited globally to a handful of expert groups with electron microscopy background, but the 3DED community is growing rapidly, and dedicated electron diffractometers are becoming commercially available. The recently established National Electron Diffraction Facility (NEDF) secured not one but two fully operational instruments, housed at the Universities of Southampton and Warwick, and now makes 3DED capability and expertise available to researchers across the UK as part of the National Crystallography Service.

This presentation familiarises the community with the new technique, share our experiences so far, and showcase the capability of the new equipment. We discuss some of the differences between 3DED and XRD which require careful consideration prior to, during, and after the experiment, as well as when assessing the data and results obtained, and flag access routes, hence increasing the visibility and accessibility of this brand-new technique.

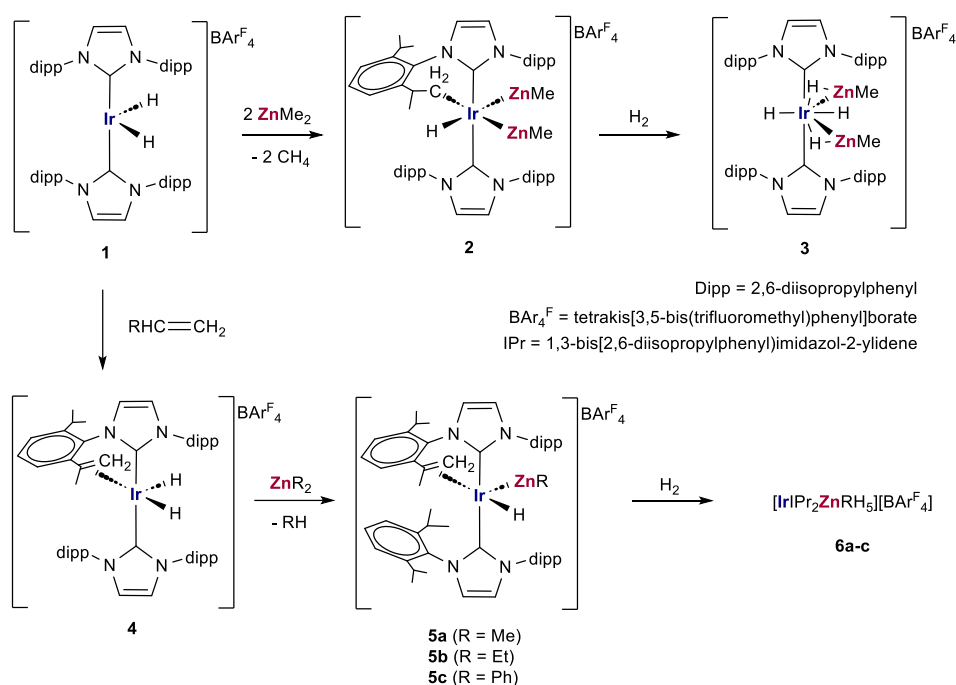
Reactivity of coordinatively unsaturated, heterometallic iridium-zinc complexes with hydrogen

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Heterometallic transition metal-main group metal (TM-MGM) complexes are of considerable interest because of the potential they hold for cooperative reactivity arising from the presence of disparate metal centres. Facile synthesis of such species is possible through the elimination of an alkane upon reaction of TM hydride and MGM alkyl reagents.¹ Previous work in the Whittlesey group has used this approach to prepare Ru-Zn complexes,¹⁻³ but we have recently found that similar chemistry is possible using Ir-H precursors. Treatment of cationic iridium dihydride **1** with ZnMe_2 leads to formation of dizinc complex **2**. Exposure of **1** to alkene followed by ZnR_2 ($\text{R} = \text{Me, Et, Ph}$) affords the monozinc species **5a-c**. Both **2** and **5a-c** react with H_2 to afford novel heterometallic polyhydride species **3** and **6a-c**.



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Mapping the Mechanism, Turn over speciation, and Effect of Acidity in the Iridium-Catalysed Direct Reduction Amination of Acetophenone (P/O)

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The direct reductive amination (DRA) of ketones using HCOONH_4 as a reductant and the Kuwata and Watanabe iridium-picolinamidato complex as a catalyst has emerged as a operationally simple yet powerful methodology for synthesizing unprotected primary amines from acidic methanolic reaction mixtures.¹ However, its working mechanism remains poorly understood. Characterizing a catalytic process is complex but essential for knowledge-based design reaction optimisation.² While reactants, co-catalysts and catalysts can be studied independently, their interplay ultimately determines the reaction outcome. Therefore, it is advantageous to study them together *in-situ*, via real-time online reaction monitoring. Owing to the non-invasive and inherent quantitative nature of nuclear magnetic resonance (NMR), we utilized the *operando* FlowNMR spectroscopic capabilities of Bath's Dynamic Reaction Monitoring Facility to gain insights into this catalytic amine formation reaction under true working conditions.³

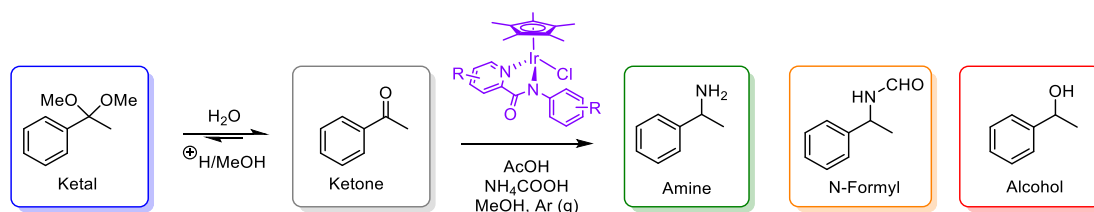


Figure 1 Reaction scheme for the DRA of acetophenone.

We reveal several aspects of catalysis in the DRA of acetophenone: parasitic hydrogen gas co-production alongside reactant consumption, catalyst distribution during turnover, an updated reaction mechanism, the role of Brønsted acids and their effect on catalytic outcomes, and a kinetic and thermodynamic investigation of amine and alcohol selectivity. The utility of our findings for applied catalysis is demonstrated through the development buffered reaction conditions, achieving competitive quantitative amine recoveries without hydrogen gas co-production. This improves overall atom economy and mitigates overpressure concerns from flammable hydrogen gas. The insights from our investigation will inform a variety of future DRA protocols using Cp^*Ir catalysts with HCOONH_4 .

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RSC Dalton Southern Conference 2024 – Poster Abstract

Title: Transition Metal Alternatives for CO₂ Hydrogenation: Supported by Pincer POCOP Ligand

Abstract: Pincer ligand bound complexes have circulated in homogenous chemistry north of 5 years, more popularly with transition metals. These specialised ligands are made up of rigid frameworks which bischelate to the metal centre and provide a great deal of stability. POCOP: (2,6-(tBu₂PO)₂-C₆H₃) is a tridentate PCP-type pincer ligand containing an anionic benzene ring backbone with symmetrically attached O tethers bound to sterically hindered phosphine groups. Already, POCOP has proven itself to be very successful in polymerisation and catalytic reactions when supporting transition metals but as it is commonly known the use of TM's as catalysts is no longer the future!

Catalytic alternatives have become more popular in research to try and mitigate the use of precious metals. Main group elements and frustrated Lewis pairs have been reported to be successful catalysts in many organic functionalisations and small molecule activations. Therefore, novel group 13 metal POCOP complexes have been synthesised and structurally characterised. Plans for carrying out CO₂ hydrogenation with these complexes are mentioned, along with some interesting results such as intramolecular frustrated Lewis pair behaviour being seen within these complexes.