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Titanium catalysts for sustainable phosphine synthesis from PH₃.

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Organophosphines are ubiquitous in organometallic chemistry and are one of the most powerful tools chemists have for catalysis. However, routes to primary and secondary phosphines are often low yielding, laborious and often exhibit poor functional group tolerance. Here we investigate whether titanium complexes can catalyse the hydrophosphination of alkenes with the simplest P1 source, PH₃. It has been shown that PH₃ could be formed *in situ* from the acid digestion of Zn₃P₂, providing a safer route to the manipulation of this P1 feedstock.¹ Furthermore, the Webster group has recently highlighted the success of this method to synthesise a variety of iron phosphine and phosphido complexes.² Examples of phosphine complexes with the early transition metals are scarce, with only a handful of examples.³

With Ti(IV) and Ti(III) dimethyl complexes (Figure 1), the stoichiometric reactivity of PH₃ can be followed using NMR, EPR and XRD. Supported by isotope labelling experiments we propose the formation of a titanium phosphinidene and phosphanide. Which would be the first example, irrespective of metal, of a terminal PH-phosphinidene being generated without the need for a sterically protecting, elaborate ligand system. Early results with alkenes show promise for hydrophosphination to form organophosphines.

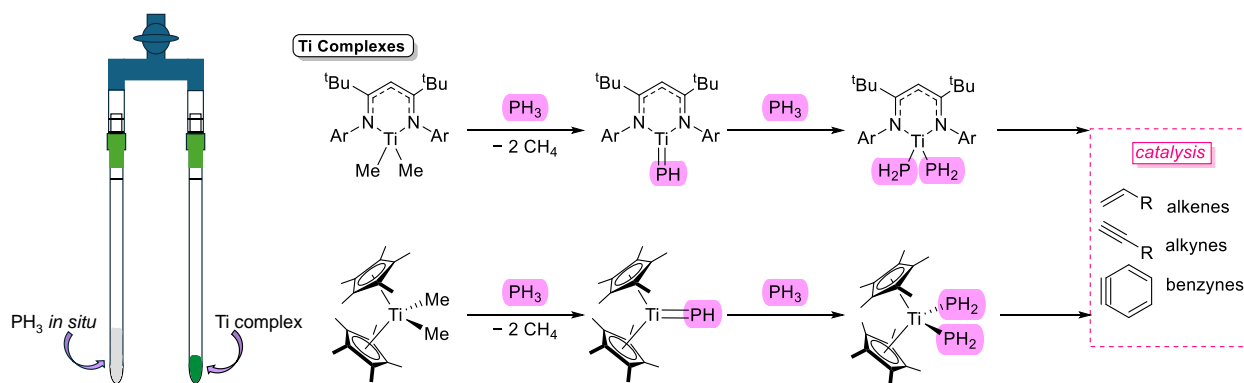


Figure 1. Synthesis of titanium phosphinidenes and phosphanides from *in situ* PH₃ generation.

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Tailoring Conductivity in Metal-Organic Frameworks: A New Approach for Synthesizing the Elusive Fe(II) Analogue of ZIF-8 for Energy Storage

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The ever-growing demand for efficient and sustainable energy storage solutions necessitates the exploration of novel materials with exceptional properties. Metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs) have captivated researchers due to their combination of high porosity, vast surface area, and structural tunability. These attributes position them as promising candidates for various energy storage applications. However, a significant hurdle impeding the utilization of ZIFs in this domain is their inherently poor electrical conductivity. A compelling strategy to overcome this limitation involves the strategic incorporation of iron (Fe) within the ZIF structure, leveraging its superior inherent conductivity compared to commonly used metals like zinc (Zn) and cobalt (Co)¹. The Fe(II) analogue of ZIF-8 (Fe(II)) represents a particularly intriguing material for electrical energy storage applications due to its anticipated enhanced conductivity. However, its synthesis using traditional methods has proven to be a significant challenge. MUV-3 is the recently reported Fe(II) analogue of ZIF-8. This material was synthesized using a solvent-free method and exhibits different sorption properties compared to ZIF-8 due to the presence of Fe(II) centers². This study delves into the exploration of anodic electrodeposition as a viable method for synthesizing MUV-3. This technique offers precise control over the deposition process, enabling the creation of thin films and tailored morphologies – properties highly desirable for energy storage.

The synthesized materials were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm their crystallographic identity and morphology. The obtained XRD patterns were compared against established reference data for MUV-3³. Similarly, the SEM images were analysed to ensure consistency with the expected characteristics of MUV-3. Our investigation yielded promising results. The electrodeposition process successfully resulted in the formation of a material exhibiting XRD patterns that closely resembled those of reference MUV-3 (Figure 1A). Importantly, unlike the MUV-3 crystals obtained through the solvent-free synthesis, the electrodeposited material (Figure 1B) displayed enhanced stability in air. The synthesized MUV-3 electrode showcased promising supercapacitor performance, exhibiting a specific capacitance of 12 F g⁻¹ at a current density of 0.02 A g⁻¹. The precise control offered by electrodeposition holds immense promise for tailoring the morphology and properties of the resulting MOF, potentially leading to the development of highly conductive electrode materials.

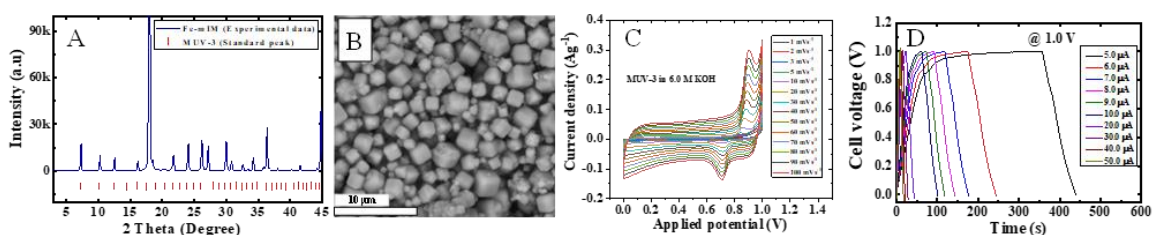


Figure 1 - (a) XRD pattern of the synthesised MUV-3 (Fe and mIM) coating compared with experimental data and standard reference peak. (b) SEM image of MUV-3 (Fe and mIM) coating obtained using DMF (c,d) Cyclic voltammograms and galvanostatic charge discharge profile of binder free MUV-3 electrodes in 6M KOH in a symmetric coin cell.

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Phosphirenium catalysed reduction reactions

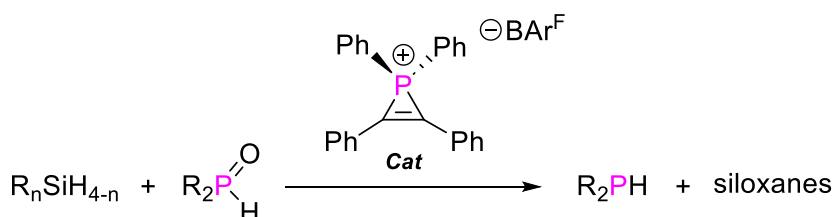
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Phosphirenium ions are low valent phosphorus-based cations isoelectronic with singlet carbenes and represent an underutilised motif in catalysis.^{1,2} Previous work in the Webster Group has established the use phosphirenium ions as a 'masked' source of phosphirenium ions in the catalytic hydrosilylation of carbonyl compounds.³ Computational study of this reaction carried out in collaboration with the Macgregor Group suggested the involvement of a phosphirenium-carbonyl intermediate as an active catalytic species. Recent investigations have focused on exploring more challenging catalytic reactions, such as the reduction of phosphine oxides using organosilanes to afford phosphines - this is a transformation rarely reported using main group element catalysis.⁴ The reduction of secondary phosphine oxides using primary silanes can be achieved using catalytic quantities of phosphirenium under mild reaction conditions with high yields (Scheme 1).



Scheme 1 – Phosphirenium catalysed reduction of secondary phosphine oxides with silanes.

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Borates vs. Aluminates: comparing the anion for lithium-ion batteries

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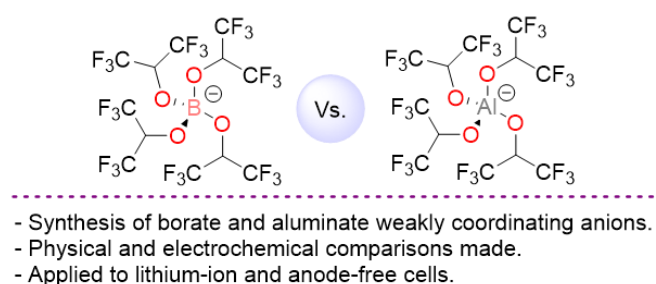
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As underpinned by the Paris Agreement 2015, the world aims to limit global temperatures rising above 1.5 °C above pre-industrial levels. To achieve this vital climate target, suitable energy storage solutions are required, where lithium-ion batteries lead the way. In the pursuit of increasing energy density, current research efforts focus on electrode development, while the electrolyte is overlooked. This is despite the electrolyte playing a key role in the practical accessible capacity, safety and overall lifetime of the battery.¹

Lithium hexafluorophosphate (LiPF₆) is the current benchmark electrolyte salt, as it is the best compromise of ionic conductivity, thermal stability, chemical stability and cost compared to other salts.² However, LiPF₆ has a low tolerance to moisture, decomposing to give LiF, POF₃ and HF.³ The toxicity of HF causes severe safety concerns, can detrimentally affect battery performance and makes end-of-life battery recycling challenging and dangerous.

This oral presentation will showcase how main group chemistry can help solve problems faced in energy storage. The use of borate and aluminate anions as electrolyte salts for both lithium-ion and next-generation anode-free batteries will be presented.⁴ The syntheses and solid-state structures of Li[B(hfip)₄]·2DME, Li[Al(hfip)₄]·DME and Li[Al(hfip)₄] (hfip = hexafluoroisopropoxy, DME = 1,2-dimethoxyethane) will be shown and their physical and electrochemical properties compared. The application of using these electrolyte salts in both lithium-ion batteries and copper vs. lithium cells will then be discussed and the question of which anion performs best answered.



Structures of [B(hfip)₄]⁻ and [Al(hfip)₄]⁻ anions used in the electrolyte for lithium-ion batteries.

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Mechanochemical synthesis of a sodium anion complex [Na⁺([2.2.2]Cryptand)Na⁻]: an investigation into its formation and reactivity

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

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

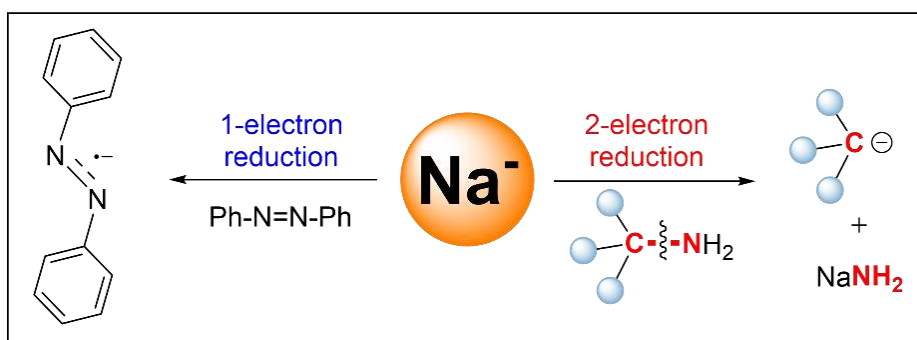


Figure 1: One and two-electron reductions of organic substrates enabled by the sodide [Na⁺([2.2.2]cryptand)Na⁻].

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Organic room temperature phosphorescence from BN-substituted xanthene derivatives

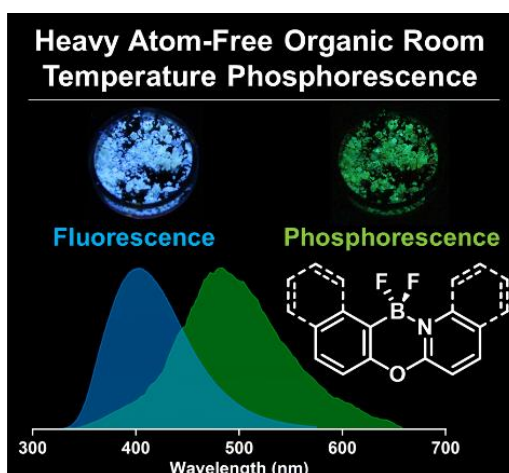
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Capable phosphors are sought after in the fields of bioimaging and organic electronics for their long excited state lifetimes and triplet state emission.¹ Organic room temperature phosphorescence (ORTP) offers phosphorescence without the use of cryogenic temperatures or expensive transition metals. Most ORTP materials rely on well-studied structural motifs (aryl carbonyls, sulfones, boronic acids), polymer matrices, or the inclusion of heavy main group elements.^{2–4} We report the unexpected ORTP of a series of BN-substituted xanthene derivatives. The inclusion of a heteroatom-rich scaffold, combined with stabilizing C–H...F interactions in the solid-state result in heavy atom-free organic phosphorescence at room temperature in an ambient atmosphere. Recent results concerning the synthesis and photophysical properties of these compounds will be discussed, and experimental results will be compared alongside theoretical calculations.



Images and spectra of fluorescence and phosphorescence from a BN-xanthene derivative.

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Anilido-alimine group 4 complexes as catalysts for CO₂/epoxide cycloadditions

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Anilido-alimine ligands [*o*-C₆H₄(NR₁)(CH=NR₂)][−] are homologues of the ubiquitous N-aryl β-diketiminato ({ArNC(R)}₂CH[−] or “nacnac”) ligands. The benzannulated backbone of the anilido alimine removes the notorious methine carbon on nacnacs, which is susceptible to nucleophilic behaviour in the presence of substrates like CO₂, all while retaining strong bidentate metal coordination and steric and electronic tunability.¹ Anilido-alimine complexes of metals across the periodic table show unique reactivity and have been utilised as catalysts for a range of polymerisation reactions, as well as organic transformations.² Anilido-alimine complexes possess two metal coordination modes: a κ² [N,N] mode and an η² [C,N] iminoacyl mode. The latter of which is highly uncommon in organometallic complexes, with just one previously reported structure.³

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

Towards the efficient capture and utilisation of carbon dioxide, a selection of titanium complexes have been taken forward as catalysts for CO₂/epoxide cycloaddition. The cyclic carbonate product formed is a key small molecule transformation in which CO₂ can be converted into useful chemical building blocks towards green solvents, lithium-ion battery electrolytes and bulk chemical processes.⁴ Here we report the first use of η² titanium iminoacyl complexes as catalysts for the cycloaddition of CO₂ and a terminal epoxide under mild, solvent-free, conditions exclusively producing the corresponding cyclic carbonate with remarkable conversion.

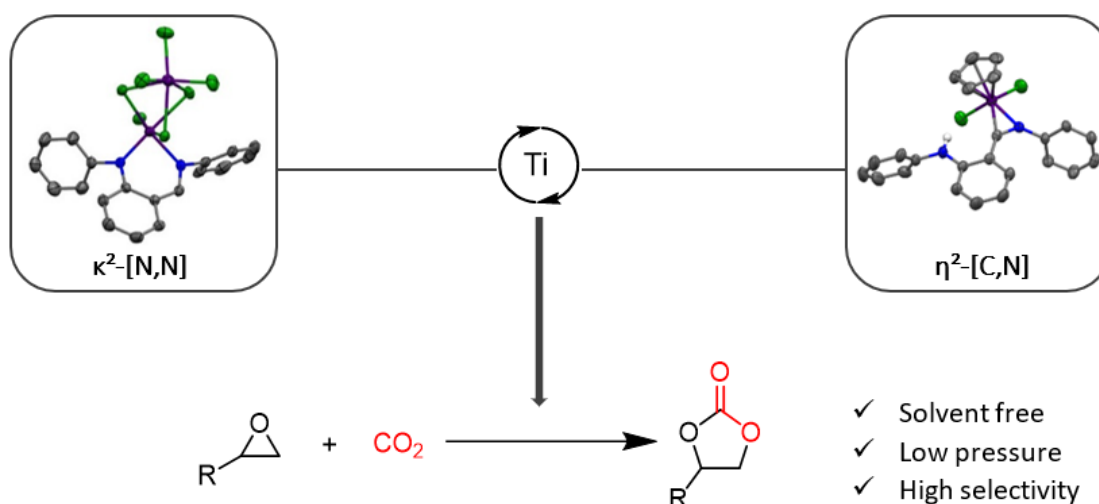


Figure 1. Overview of titanium complexes taken forward in CO₂/epoxide cycloadditions.

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Reversible CO₂ insertion into the silicon–nitrogen σ -bond of an N-heterocyclic iminosilane¹

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The rising atmospheric concentration of the greenhouse gas carbon dioxide (CO₂) is an urgent pressing global concern. The reversible capture and release of carbon dioxide (CO₂) is a critical challenge for sustainable carbon storage and valorisation.^{2,3}

This study demonstrates the reversible insertion of CO₂ into the silicon–nitrogen (Si–N) bond of an N-heterocyclic iminosilane (IPrNSiMe₃). Utilizing solution-phase thermodynamic investigations, the reaction was found to be thermoneutral and reversible under ambient conditions. Solid-state studies revealed CO₂ storage stability up to 133 °C, with release triggered upon heating. Structural and spectroscopic analysis confirmed the formation of a zwitterionic intermediate, elucidating the mechanism through both experimental and computational approaches.

Key findings include thermodynamic parameters obtained via variable temperature NMR and mechanistic insights supported by density functional theory calculations. The oxophilicity of the silane substituent was identified as a key factor enabling the reversibility of CO₂ capture. Our work presents a novel pathway for CO₂ storage and release with implications for carbon capture technologies and catalyst design.

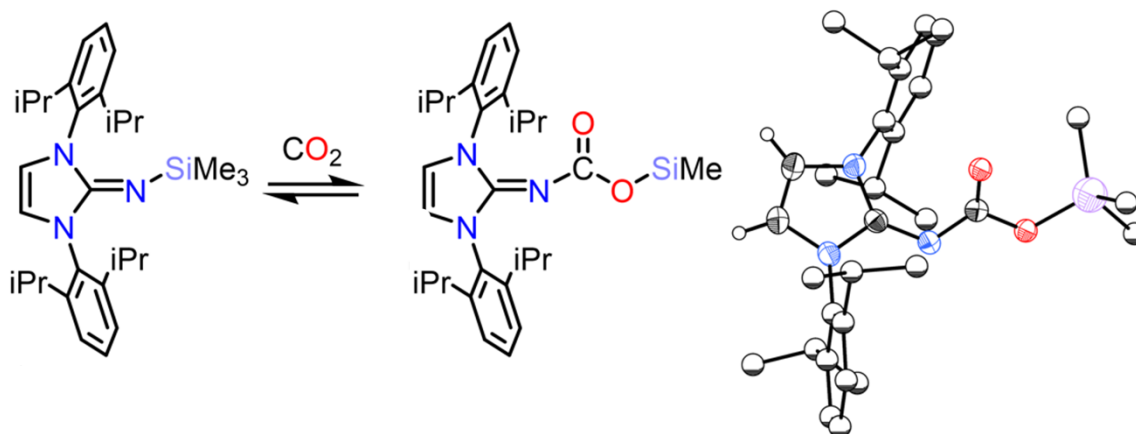


Figure.1 Left: Equilibrium between IPrNSiMe₃ and IPrNCO₂SiMe₃. Right: The crystal structure of IPrNCO₂SiMe₃

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Catalytic Nitrous Oxide Degradation with Group 15 Clusters

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The ever-increasing concentration of nitrous oxide (N₂O) in the atmosphere is no laughing matter. With an estimated greenhouse warming potential 300 times greater than CO₂ and a lifetime of ~114 years N₂O is a leading contributor to ozone depletion.¹ From a chemical perspective transfer of O and generation of N₂ from N₂O is significantly thermodynamically favourable, however due to N₂O high kinetic inertness only a handful of synthetic homogenous catalysts, primarily reliant on transition metals, have been found to mediate N₂O degradation.²

Pnictogen clusters are interesting candidates for catalysis due to their structural relationship to bulk heterogenous materials and previously we reported pnictogen clusters as competent reduction catalysts.^{3–5} Building onwards from this work, herein we report the use of pnictogens clusters in the transition metal-free catalytic reduction of N₂O (Figure 1). The mechanism has been explored experimentally and computationally, revealing evidence of an unprecedented pnictogen –1/+1 redox cycle. Besides reduction of N₂O, transfer of the O atom to sulfur and disulfides was achieved. Further the pnictogen clusters studied were also found to reduce nitro compounds (RNO₂) to afford valued primary amines.

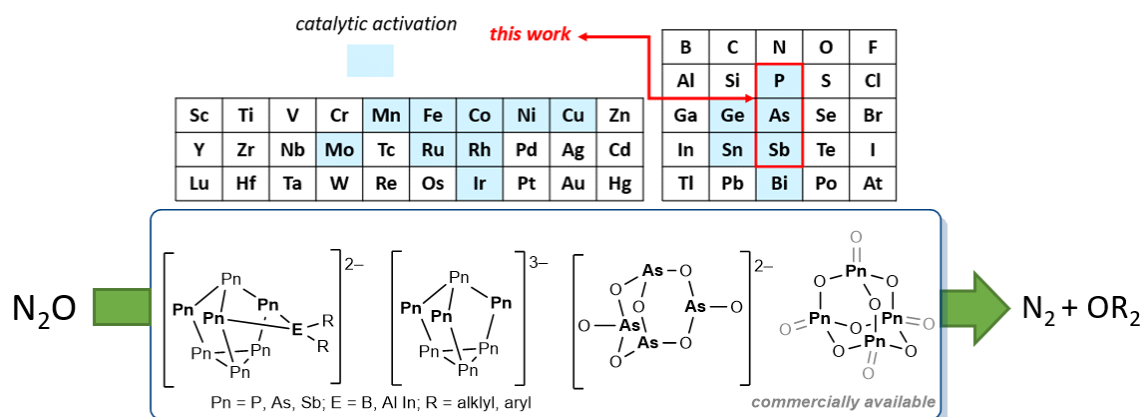


Figure 1. Homogenous catalysts based on these elements mediate N₂O reduction. General structures of the cluster catalysts studied in this work.

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Giving fluorine atoms a second life *via* a circular fluorine economy: The chemical upcycling of fluorochemicals

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Fluorine-containing molecules and materials are embedded in modern society and improve our quality of life. For example they find applications as refrigerants, insulating materials, active pharmaceutical ingredients, agrochemicals, and polymers.¹ Nearly all current fluorine-containing compounds are created from the mineral fluorite (CaF_2) through generation of the toxic intermediate hydrogen fluoride (HF ; figure 1a).^{1,2} The use of HF can, under certain circumstances, be bypassed *via* mechanochemical activation or aqueous fluoride extraction of CaF_2 , but fluorochemical production and usage is still following a linear manufacturing process.^{2,3} In addition to the necessity of mining CaF_2 , fluorine-containing products face also increasing pressure to limit environmental contaminations as well as stricter regulations.^{4,5} Sustainability is therefore an urgent key issue for this crucial sector. Here we present a new concept for the synthesis of fluorinated molecules through the upcycling of fluorocarbons (figure 1b). Industrially relevant hydrofluorocarbons (HFCs), fluoroethers including anesthetics and battery additives, poly(fluoroalkyl) substances (PFAS) including perfluorooctanoic acid, along with fluoropolymers like poly(vinylidene difluoride) are treated with a base under anhydrous conditions. This causes a rapid defluorination and the generation of an *in situ* reactive metal fluoride. The fluoride harvested from these materials can then be used to prepare a plethora of fluorinated organic and inorganic molecules in the same vessel, while forming bonds like $\text{C}_{\text{sp}2}\text{-F}$, $\text{C}_{\text{sp}3}\text{-F}$, Si-F , Ge-F , P-F , S-F and I-F . This concept represents an important step in the development of a future global circular economy for fluorine.

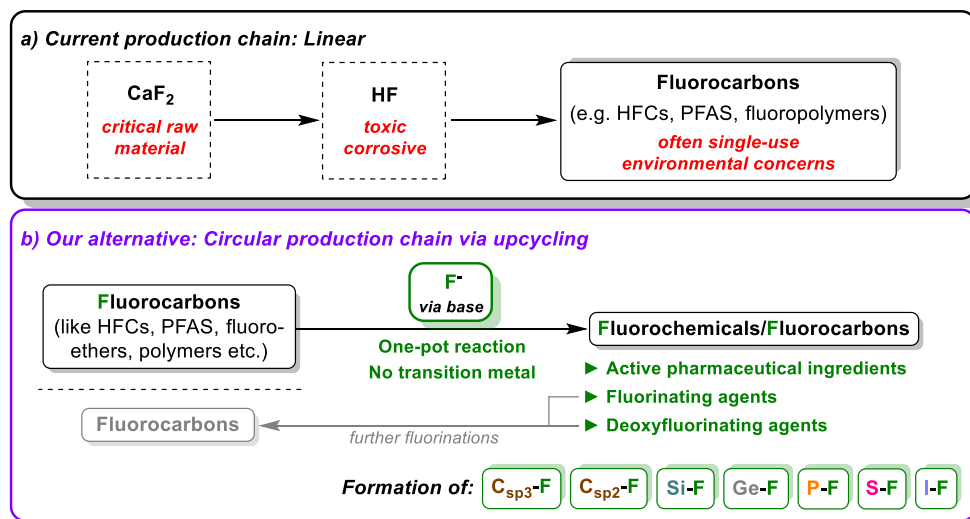


Figure 1: Synthesising fluorochemicals *via* a) contemporary methods and b) method presented here.

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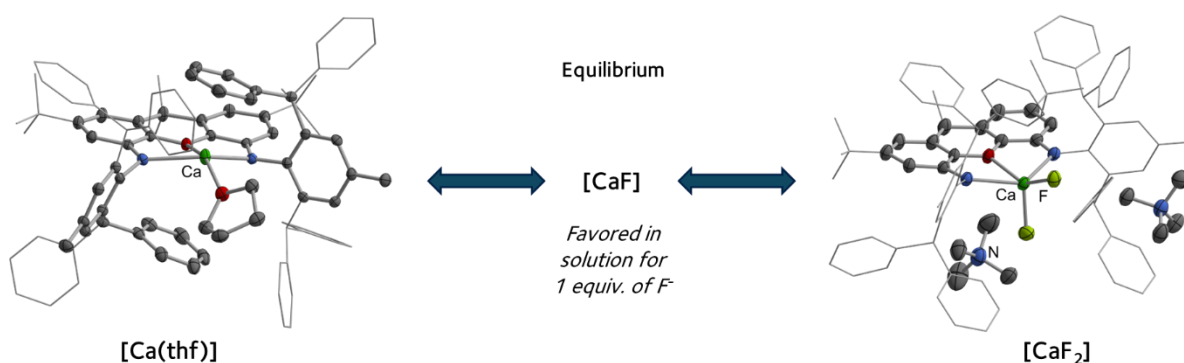
Terminal monomeric calcium mono- and difluorides as fluoride shuttles?

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Calcium fluoride is the ultimate source of all fluorochemicals^{1,2}. Current synthetic approaches rely on the use of HF, generated from naturally occurring fluorspar and sulfuric acid. Methods for constructing E–F bonds directly from CaF₂ have long been frustrated by its high lattice energy, low solubility, and impaired fluoride ion nucleophilicity. Little fundamental understanding of the reactivity of Ca–F moieties is available to guide methodology development; well-defined molecular species containing Ca–F bonds are extremely rare, and existing examples are strongly aggregated and evidence no nucleophilic fluoride delivery^{3,4}. Building on our previous work⁵ in which we showcase the synthesis, characterization and nucleophilic fluoride delivery of a range of well-defined complexes with structurally diverse Ca–F units, we now focus on the synthesis of true terminal Ca–F_x (x = 1,2) moieties. We show that these monomeric, terminal Ca–F complexes display interesting dynamic properties, with equilibria in solution that are not always reflected in the solid state. The terminal nature of the Ca–F motifs, in combination with the dynamic properties of the fluoride ligands, allows for reversible fluoride shuttling and enables their reactivity in nucleophilic fluoride delivery.



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

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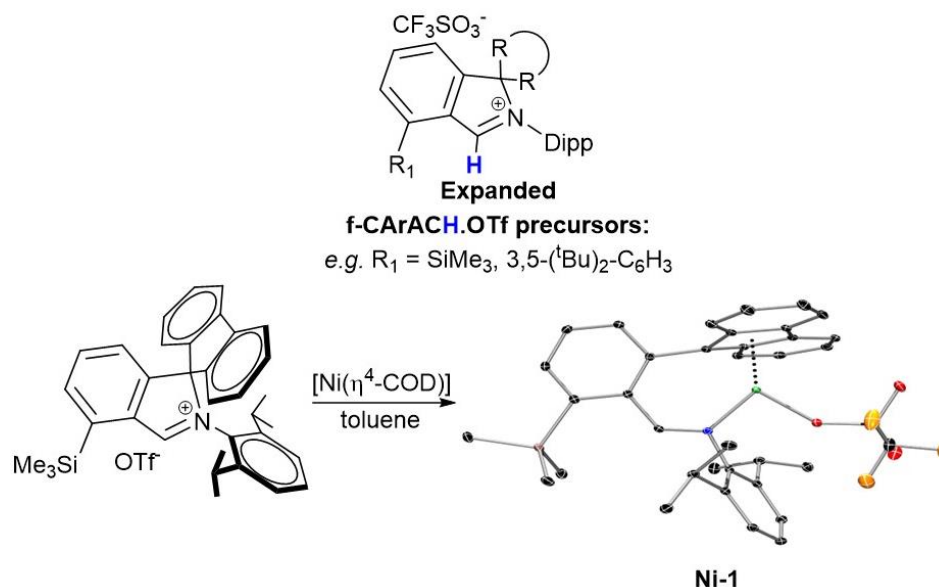
A New, Convenient Way of Accessing Ni(II) and Ni(I) Complexes via C – N Oxidative Cleavage

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Fused Cyclic Aryl Amino Carbenes (*f*-CARACs¹), have attracted interest as supporting ligands for transition metal complexes with potential applications in photonics² and catalysis³. As part of our research efforts to expand the *f*-CARAC scaffold to modulate their stereo-electronic properties, we have successfully synthesised, in good to moderated yields, a series of new isoindolinium salt precursors *f*-CARACH.OTf which incorporate in the ligand architecture bulky arenes and silyl groups (**Scheme 1**). Attempts to introduce the carbene *via* their reaction with [Ni(η^4 -COD)₂] led instead to the unprecedented fission of a C–N ligand backbone bond as a result of the oxidative insertion of Ni (e.g. complex **Ni-1**, **Scheme 1**). The isolation of **Ni-1** and similar congeners, in good to excellent yields, offers insight into the paucity of Ni complexes featuring *f*-CARAC ligands, and has allowed us to access a syn-bimetallic Ni(I)-Ni(I) complex *via* its reduction with Na(Hg).



Scheme 1: Expanded *f*-CARAC ligand scaffolds (*top*) and reaction scheme leading to **Ni-1** as a result of the oxidative cleavage of a C–N bond (*bottom*). Color code: C black, N blue, Ni green, Si brown, S yellow, O red, F orange.

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Reversible Ligand Activation in Solid-State Molecular Organometallic Chemistry

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Over the last two decades, metal-ligand cooperation (MLC) has shown to be of great utility at promoting a wide range of chemical transformations.^{1, 2} Here, we show that MLC can be extended to single-crystal to single-crystal (SC-SC) organometallic reactivity,³ using a stable rhodium(III) σ -alkane complex (**1**),⁴ supported by a structurally responsive diposphine ligand (Figure 1).⁵ Complex **1** reacts with D₂ gas in the solid-state, selectively enriching the ligand framework with deuterium, through metal-ligand cooperation. A σ -complex-assisted-metathesis pathway is suggested to operate, enabling retention of the rhodium(III) oxidation state, and is consistent with the selectivity of this H/D exchange process.⁶

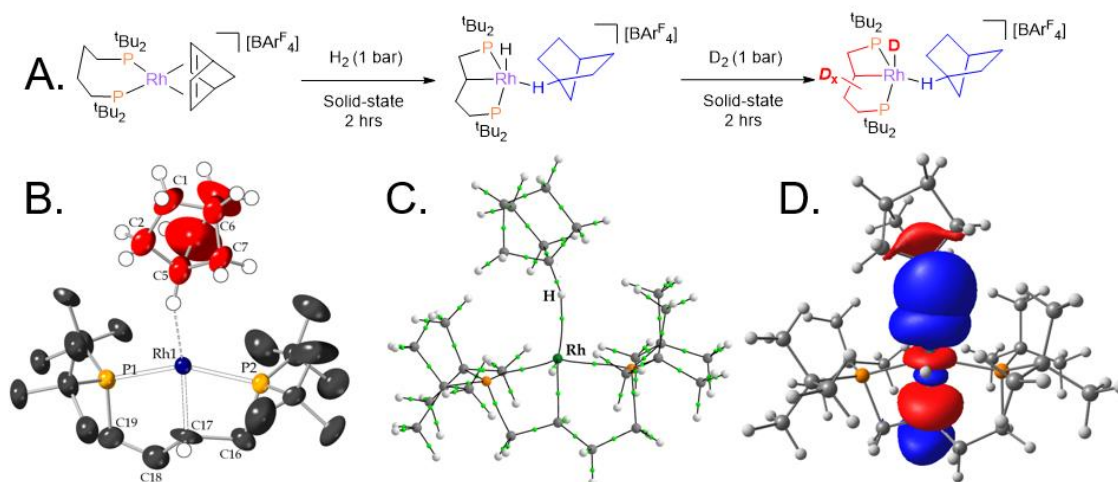


Figure 1: **A.** Synthetic procedure to yield a rhodium(III) σ -alkane complex (**1**) through a SC-SC transformation and selective H/D exchange under D₂ gas. **B.** Solid-state structure of **1**. **C.** QTAIM plot of **1**. **D.** NBO donor/acceptor orbitals involved in the $\sigma_{C-H} \rightarrow Rh$ σ -donation.

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Applications of boryloxide ligands in lanthanide chemistry: diversifying the coordination landscape

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The ‘hard-hard’ combination of anionic O-donors and trivalent lanthanide (Ln) ions is reflected in the vast literature on Ln-alkoxide, -aryloxide, and -siloxide complexes, many of which have found practical uses in materials science and catalysis.¹ In contrast, boryloxide ligands (Figure 1, *left*) are much less common in lanthanide chemistry and their coordination chemistry with lanthanides remains underexplored.^{2,3} Aiming to address this knowledge gap, the complexation behaviour of the bulky boryloxide ligand [DippBO][−] with erbium and ytterbium is being investigated in our laboratory, with a view to the synthesis of low-coordinate single-molecule magnets (SMMs). In this presentation, the structural and dynamic magnetic properties of a series of trigonal bipyramidal complexes with the general formula [Ln(OB^{Dipp})₃L₂] (Ln = Er, Yb; L = THF, pyridine) will be discussed, along with multireference calculations on selected systems.

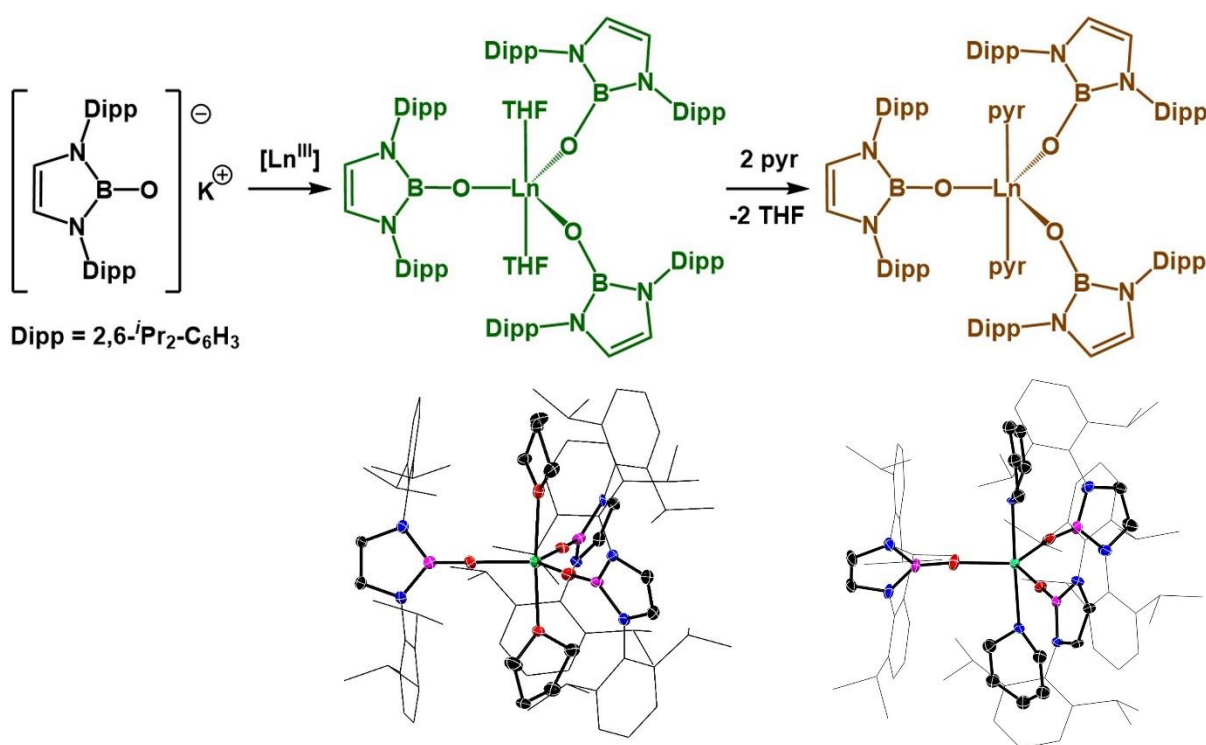


Figure 1. Ln^{III} (Er^{III}/Yb^{III}) complexes of the boryloxide ligand

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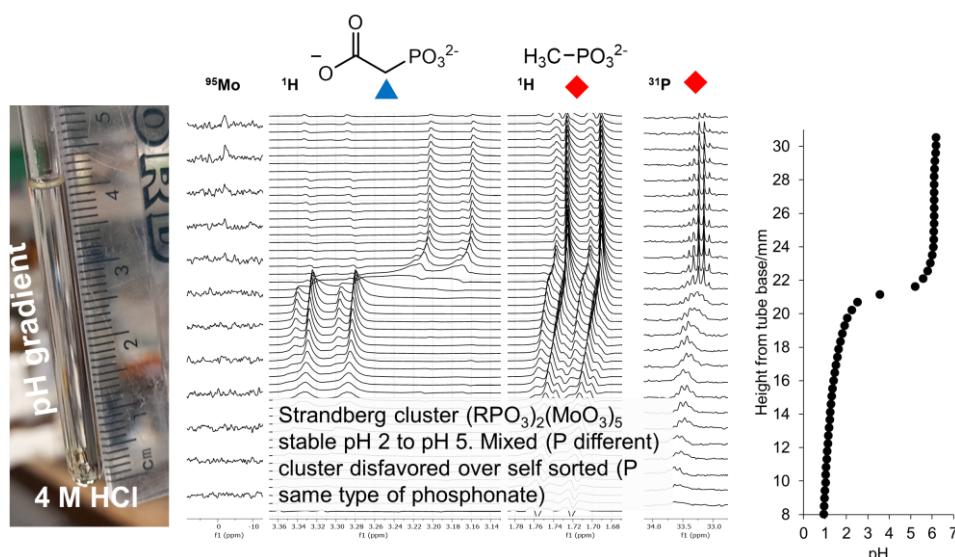
Exploring the pH-dependent self-assembly of polyoxometalates in organic media using multinuclear chemical shift imaging NMR

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We demonstrate a high throughput technique that permits the *in-situ* study of the pH-sensitive self-assembly of polyoxometalates (POMs) and their speciation in a range of solvents. POM speciation is well studied¹ and computationally modelled² in aqueous solution, however, for solubility/stability reasons almost all synthesis of chemically functionalised POMs is conducted in organic solvents. The gaps in our understanding of POM self-assembly in these solvents hugely restrict POM functionalisation to top-down approaches and limit our ability to design POMs to fully exploit form and function. As part of unrelated work, we have developed highly efficient methods to determine the acid dissociation constants (pK_a) of pharmaceutical ingredients in organic media.^{4,5} We create pH gradients in standard 5 mm NMR tubes and record NMR spectra at different spatial positions along the gradient using chemical shift imaging (CSI) techniques, thereby studying a system across a wide pH range simultaneously in one sample; a highly efficient approach that can nowadays be applied on any modern spectrometer. As a first study with POMs, we have followed the self-assembly of phosphates¹ and phosphonates (Scheme 1) with sodium molybdate to give Strandberg³ and other polyoxometalate clusters, reproducing known speciation in H₂O¹ and enabling the rapid testing of new systems. Our technique promises to be a highly efficient tool to address important questions regarding the behaviour of polyoxometalate clusters in organic media. We are also exploring the pH-dependent interaction of POMs with DNA and proteins.



Scheme 1. Analysis of POM self-assembly using multinuclear CSI NMR along pH gradients

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Isomer Selective Self-Assembly of Coordination Cages from Low Symmetry Ligands

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Coordination cages are host architectures¹ of interest for applications in catalysis, sensing and stabilisation of reactive species, amongst others. The vast majority of coordination cages reported employ symmetrical ligands to facilitate the self-assembly process, as lower symmetry ligands have the potential to form mixtures of isomeric products (Fig. 1).² Control of this self-assembly process, however, would allow access to more structurally sophisticated architectures, with implications for advanced functionality and guest-binding selectivity.³

We have been interested in developing design strategies to bias the formation of particular cage isomers from the self-assembly of unsymmetrical ligand scaffolds. Towards this, we have successfully used various design strategies including covalent tethering,⁴ geometric design⁵ and coordination-sphere engineering.⁶ We have also developed high-throughput computational methodologies to aid in the design of such systems, reducing costly trial-and-error synthetic discovery.⁷ Ongoing work is focused on extending our toolbox of design principles for accessing structurally complex, low-symmetry coordination cages, and exploiting the observed correlation between experimental and computational results to allow in silico analysis for effective computational forecasting to aid in the design of future systems.

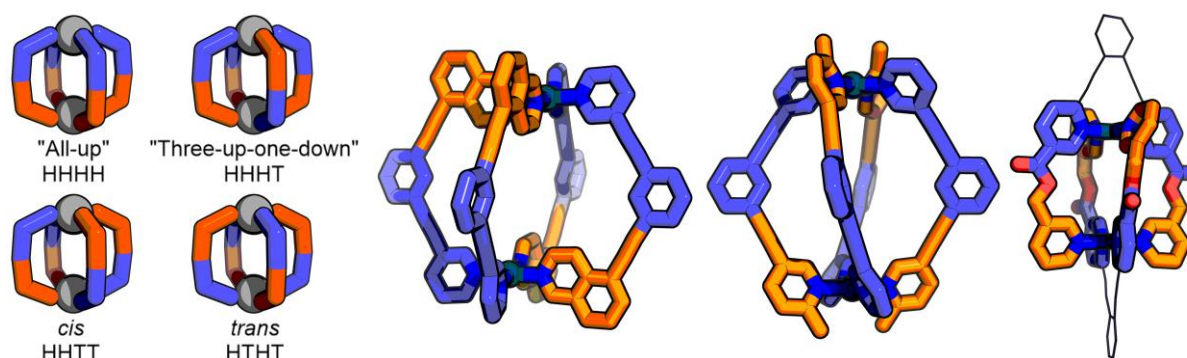


Fig. 1 Pd₂L₄ coordination cages assembled from unsymmetrical ligands can form four potential isomers. These systems can be steered away from statistical mixtures through the use of geometric design, coordination sphere engineering and covalent tethering strategies to direct the selective formation of particular isomers.

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Coordinating a New Approach to Drug Detection: Functional Metal Complex Based Ionic Liquids

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Presumptive drug tests are ubiquitous in clinical and forensic laboratory settings. They usually have excellent sensitivity and good to very good specificity.¹ For many commonly used tests, metal complexes either act as a catalyst for redox reactions or coordinates to the target drug molecule. These microchemical reactions have undergone rigorous validation² to ensure that they can produce reliable results among different illicit materials and doping agents, but they have seen little in the way of chemical development or innovation. Many presumptive tests also use concentrated acids such as sulphuric acid as the carrier solvent which present challenges in handling, preparation, safety and shelf life. Here we present a new class of presumptive tests combining similar microchemical reactions combined with intrinsic ionic liquids properties to increase promising properties for testing such as, solubilising power and shelf stability. Thus far, we have developed ionic liquid-based tests for numerous illicit materials, fig. 1, based on known tests such as the Scott's test for cocaine, Mandelin and Froehde tests which are multipurpose tests, Simons tests for primary and secondary amines, and the Chen-Kao test for phenylalkylamines. Investigation of their chemical, physical and reaction properties have been undertaken to compare to traditional presumptive tests current used in the sector.

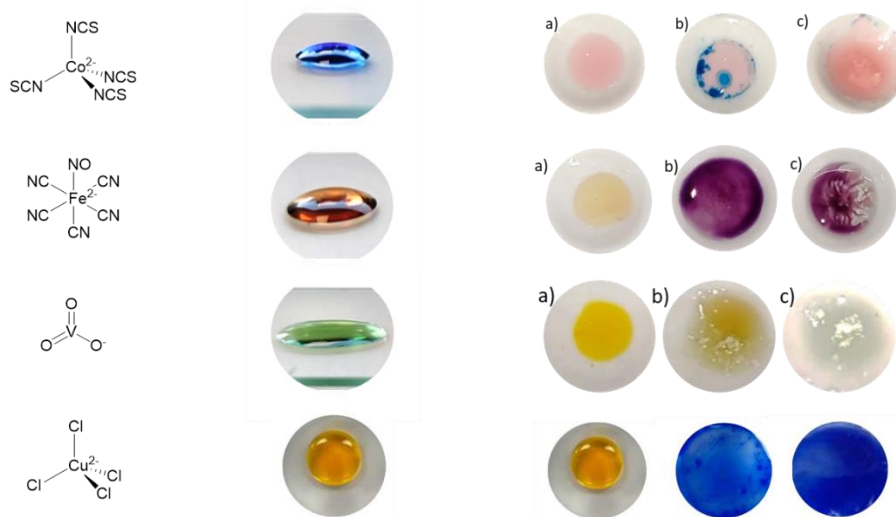


Figure 1: Active chemical structure of novel ionic liquids tests (left) with positive spot tests(right).

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