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# Transparent Conductive Fluorine and Titanium Co-doped Zinc Oxide Films via Aerosol Assisted Chemical Vapour Deposition

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Aerosol-assisted chemical vapor deposition (AACVD) was employed to deposit highly transparent and conductive fluorine or titanium doped, as well as fluorine-titanium co-doped thin films on glass substrates at 450 °C. All films were characterized using various techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), UV-Vis spectroscopy, and four-point probe analysis using Hall-effect method. With thickness under 700 nm, the films were crystalline and highly transparent (81-88%). The co-doped film, comprising 1.0 atomic % fluorine and 0.70 atomic % titanium, exhibited remarkable electrical properties with a charge carrier concentration of  $3.96 \times 10^{20} \text{ cm}^{-3}$ , and charge carrier mobility of  $8.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Moreover, it displayed a band gap of 3.6 eV. Notably, compared to undoped or singly doped films, the co-doped film demonstrated significantly enhanced structural morphology suitable for applications requiring transparent conducting oxides. To the best of our knowledge, highly transparent and conductive fluorine-titanium co-doped films have been successfully deposited for the first time.<sup>1</sup>

**Keywords:** Transparent conducting oxides, Co-doped Zinc oxide, Titanium and Fluorine co-doped Zinc oxide, electronic materials, wide band gap material, nanomaterials.

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## Sodium Tris(3,5-Dimethylpyrazolyl)Borate: A Potential Alternative to Sodium Alkoxide in the Lochmann-Schlosser Base.

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The Lochmann-Schlosser super base is a mixture of organolithium (R-Li) compounds and heavier alkali metal alkoxides (M-OR', M = Na, K, Rb, Cs).<sup>1</sup> This super bases are known for their widespread reactivity in organic and inorganic synthesis.<sup>1</sup> Its reactivity is primarily driven by metal-metal exchange between R-Li and alkali metal alkoxides, a phenomenon first reported by Lochmann in 1964 and further explored by Schlosser.<sup>2</sup> The lithium heavier metal exchange is believed to involve the formation of mixed aggregates, though their structural details remain unexplored.<sup>3</sup> Recently, there has been a resurgence in exploring organosodium complexes, fueled by a shift towards sustainable alternatives to lithium-based compounds and the superiority of Lochmann-Schlosser's base is undisputable in this context.<sup>4</sup> Second-generation super bases, which incorporate branched alkoxides with R-Li, show enhanced reactivity.<sup>5</sup> However, the potential of non-aggregating molecular alternatives to alkali metal alkoxides remains largely untapped. Our exploration of the potential of alkali metal compounds of tris(3,5-dimethylpyrazolyl)borate (Tp<sup>Me2</sup>) in transmetallation reactions motivated us to investigate the reactivity of sodium tris(3,5-dimethylpyrazolyl)borate.<sup>6</sup> In this work, we present sodium tris(3,5-dimethylpyrazolyl)borate as a novel substitute for sodium alkoxides, paired with mesityllithium to create a new super base capable of deprotonating weakly acidic C-H bonds. This is demonstrated through the isolation of several cationic benzyl sodium complexes which exhibits remarkable reactivity, highlighting the potential of these systems in organic and inorganic synthesis.<sup>7</sup>

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## Exploring Compounds of Bismuth: Synthesis, Structure, and Reactivity

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Bismuth has potential to change how we achieve and how we think about catalysis. It has been described as a “green” heavy metal, its application industries may partially resolve the environmental problems related to heavy metal pollution.<sup>1</sup> Bismuth has, primarily, one major oxidation state (+3), but others are readily accessible (+1, +5).<sup>2</sup> This results in bismuth displaying properties akin to transition metals, as they possess multiple oxidation states which can be exploited in catalytic reactions. Through synthesis of new amidinate-bismuth complexes and investigating their properties, we can harness the power of bismuth and discover ways to reduce the environmental and societal costs of modern chemistry.

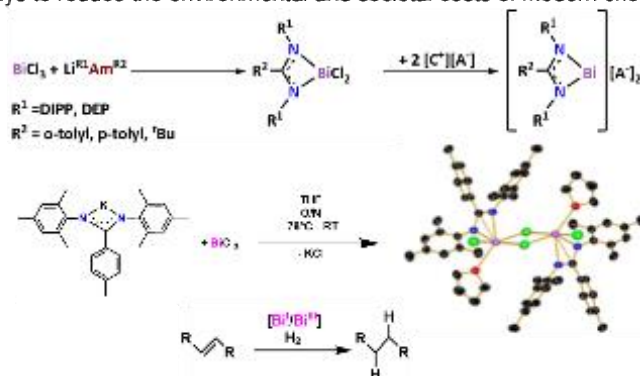


Figure 1: (top) General route to bismuth-amidinate complexes (middle) structure of new complex (bottom) bismuth redox couple for hydrogenation.

Aminidate ligands, in a similar way to BDI ligands, can be readily modified through alterations to the backbone (e.g. p-tolyl, <sup>t</sup>Bu, etc.) or the peripheral ligands (e.g. DIPP (diisopropylphenyl), mes (mesitylene), etc.).<sup>3</sup> The simple manner in which the ligands can be altered means a family of bismuth complexes has been created, allowing the influence of bite angle and % $V_{\text{bur}}$  to be investigated. These molecules have been subjected to small molecule gasses ( $\text{H}_2$ ,  $\text{CO}_2$ ) and have displayed promising results.

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## Facile, reversible hydrogen activation by low-coordinate magnesium oxide complexes

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The activation of small molecules, such as dihydrogen, for use as feedstock to reduce unsaturated chemical substrates is one of the most important chemical processes. This is due to its wide applicability in various industries, including petrochemicals, pharmaceuticals, materials, and food.<sup>1-4</sup> We report the facile and reversible activation of dihydrogen by three-coordinate nacnac magnesium oxide complexes  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2(\mu\text{-O})]$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}$  and  $\text{Dip} = 2,6\text{-diisopropylphenyl}$ ) under ambient conditions to yield a bridged hydride/hydroxide complex  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2(\mu\text{-OH})(\mu\text{-H})]$ .<sup>5-7</sup> This marks the first facile example of dihydrogen activation across a magnesium-oxygen complex.<sup>5</sup> This process has shown to be chemically reversible, either by the addition of a Lewis base such as THF or DMAP to yield the magnesium oxide adduct species  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}(\text{THF})_2(\mu\text{-O})]$  and  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}(\text{DMAP})\}_2(\mu\text{-O})]$  or by applying heat and vacuum to their solutions (for  $\text{R} = \text{Pr}$ ).<sup>5</sup> Alternative synthetic routes to yield  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2(\mu\text{-OH})(\mu\text{-H})]$  have also been explored from  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2]$  and  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}(\mu\text{-H})\}_2]$  complexes.<sup>5</sup> Preliminary catalytic hydrogenation studies have demonstrated the reversible dihydrogen uptake of magnesium oxide complexes via the hydrogenation of 1,1-diphenylethylene, where the bridged hydride/hydroxide complex  $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2(\mu\text{-OH})(\mu\text{-H})]$  acts as a labile source of  $\text{H}^+$  and  $\text{H}^-$ .<sup>5</sup> The activation of dihydrogen has also been studied via DFT calculations.<sup>5</sup> NMR spectroscopy and X-ray crystal structures will be presented.<sup>5</sup>

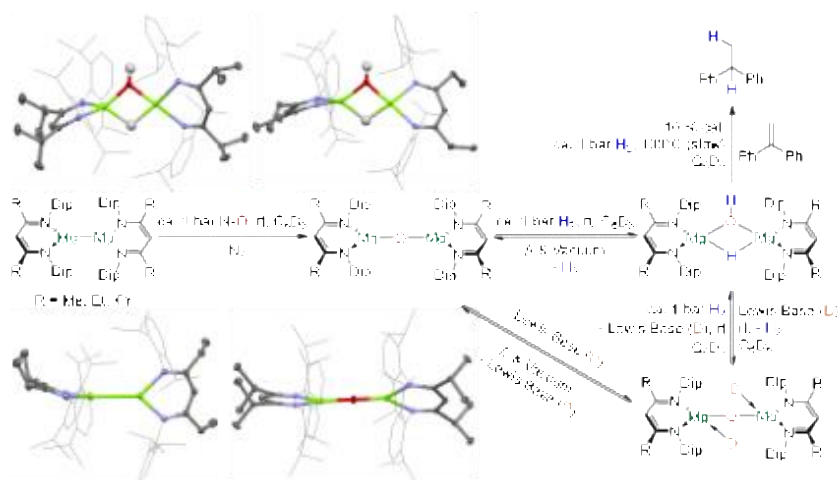


Figure 1. Synthesis of magnesium oxide complexes and reversible hydrogen activation.<sup>5-7</sup>

# FLP-mediated reductive dehydrogenation of a gallane: *umpolung* reactivity of a Ga–H bond induced by hydride abstraction

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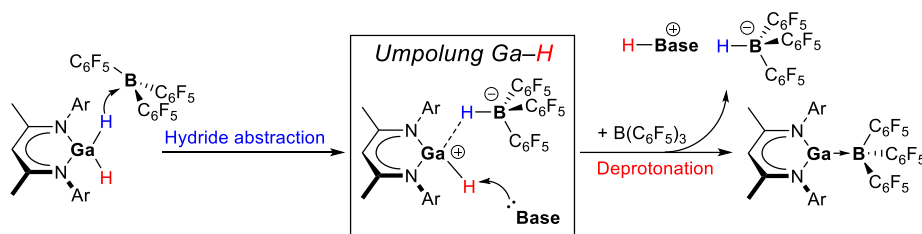
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Deprotonation is a classic reactivity pattern for archetypal transition metal hydrides, which can display appreciable Brønsted acidity. In the *p*-block, E–H bonds can be straightforwardly deprotonated for many of the relatively electronegative elements situated in groups 14–16, but not for group 13 element hydrides. Bases tend to attack the Lewis acidic triel centre, and not the negatively polarized hydride. In contradiction to this, Okuda, Maron, and co-workers reported deprotonation of gallium(III) hydride dication [LGa<sup>III</sup>H]<sup>2+</sup>, supported by coordinatively saturating tetradentate macrocycle L, to yield gallium(I) cation [LGa<sup>I</sup>]<sup>+</sup>.<sup>1</sup>

Here, we describe the dehydrogenation of  $\beta$ -diketiminatogallane [(BDI)Ga<sup>III</sup>H<sub>2</sub>],<sup>2</sup> to gallium(I)-borane complex [(BDI)Ga<sup>I</sup>→B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>],<sup>3</sup> mediated by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in either the presence or absence of a bulky phosphine (Figure 1). Mechanistic investigations using a combined experimental and computational approach suggest that initial hydride abstraction facilitates transfer of the second hydride as “H<sup>+</sup>” to the basic phosphine or non-innocent BDI ligand backbone. Thus, “deprotonation” leads to formal two-electron reduction of the gallium centre to Ga(I).

This *umpolung* Ga–H bond reactivity hints at the untapped potential of (cationic)gallium complexes as *p*-block mimics of “transition metal-like” redox reactivity.



**Figure 1.** Transfer of **hydride** and **proton** from a gallium(III) dihydride to Lewis acid and Brønsted base results in formal reduction to gallium(I), which is trapped as an organoborane adduct.

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## Organolithium and organosodium complexes: differences and similarities in their reactivity

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Organolithium complexes have served the synthetic chemistry community for over a century. Their chemistry has been well-documented<sup>1</sup>. On the other hand, organosodium complexes, though first reported as early as in the 19<sup>th</sup> century<sup>2</sup>, are still under development. In recent years, organosodium chemistry started to receive an increasing interest<sup>3</sup>, partially driven by the sustainability merit of sodium in comparison to lithium.

Yet a largely unanswered question is, shall we simply treat the organosodium complexes as a more sustainable replacement of the organolithiums? Recent studies<sup>4</sup>, including results from our group<sup>5</sup>, indicate that the answer is probably no. There is increasing evidence that the alkali metal identity has decisive effects in tuning not only their activity (fast or slow), but also their reaction patterns (e.g., nucleophilicity vs basicity).

Herein, we will introduce a few of our latest results in this regard, showcasing how the metal identity tunes the reaction pattern, i.e., the "Li vs Na" effect, in their CO and CO<sub>2</sub> activations.



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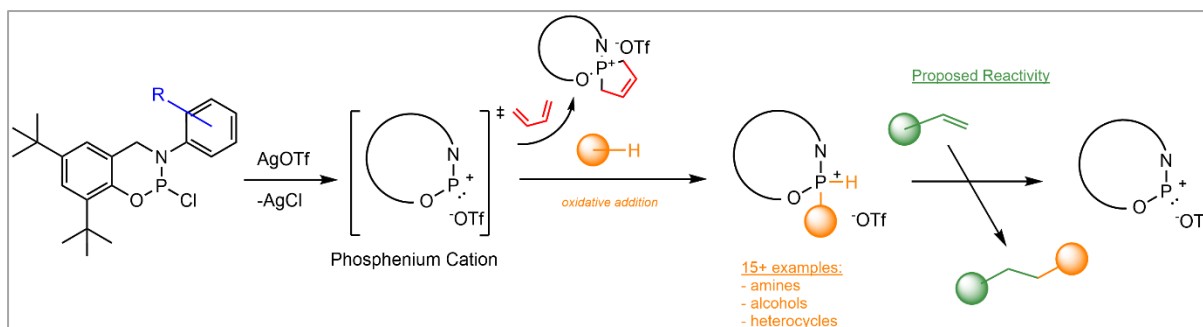
# The Oxidative Addition of Protic Substrates to Phosphorus *via* a Phosphenium Cation Intermediate

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The ability of a catalyst to accelerate a reaction means catalysts are ubiquitous in chemical processes and catalysis is now a multibillion dollar global industry.[1] Many of these processes rely on expensive and rare transition metals such as rhodium, palladium, and platinum. Given the socioeconomic difficulties in sourcing these metals, there is growing interest in finding an alternative chemical framework which can catalyse organic transformations. One promising route to a metal-free catalyst are main-group frustrated Lewis pair (FLP) complexes, which exhibit simultaneous Lewis-acidic and Lewis-basic character. These were first reported by Stephan *et al.* who demonstrated reversible hydrogen addition to the FLP [2]. This work focusses on divalent phosphenium cations, whose FLP-type reactivity derives from a lone pair and empty orbital at the phosphorus centre. These cations and related hydrides have been exploited to catalyse the hydrogenation of many different substrates such as aldehydes and olefins under mild conditions [3,4].



**Figure 1:** Scheme showing the *in-situ* generation of a phosphenium cation from novel chlorophosphines and subsequent oxidative addition of organic substrates across the cationic phosphorus centre.

In this work, chlorophosphoramidites are formed using a suite of bidentate ligands possessing differing electronic characteristics in good yields (Fig. 1). Chloride abstracting reagents such as silver triflate were used to form the phosphenium cation. The phosphenium cation was trapped *via* a [4+1] cycloaddition reaction using a 1,3-diene or 1,3-diazabutadiene [5]. *In situ* reaction of the phosphenium cation with O–H, N–H and C–H bonds resulted in oxidative addition. To date, 15+ examples have been characterised, with plans to induce reductive elimination and turnover of the catalyst.

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## Molecular Bonding Models for Quantum Materials

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Intuitive bonding models for inorganic solids with exotic electronic properties are required as ‘quantum materials’ impact an ever-wider range of technologies. Here we use two case studies to demonstrate the applicability of molecular orbital analysis of the bonding in such materials, one on high-pressure superhydrides and one on topological insulators.

Metal superhydrides, with very large H:M ratios, can be stabilized under pressure and are a rich source of high-temperature superconductors.  $\text{UH}_8$ ,  $\text{EuH}_9$ , and  $\text{LaH}_{10}$  all contain cubic  $\text{H}_8$  clusters, but in  $\text{EuH}_9$  the cubes are distorted. Atomic charge calculations allow us to assign formal charges to the metals and determine the distribution of charge over the H sublattice. MO analysis of the  $\text{H}_8$  cube shows that the ‘ideal’ geometry in  $\text{UH}_8$  and  $\text{LaH}_{10}$  is consistent with the metal charges and that  $[\text{H}_8]^{2-}$  undergoes a Jahn-Teller distortion that matches the structure of  $\text{EuH}_9$ . Phonon calculations establish the connection between the distortion and superconductivity.<sup>[1]</sup>

Topological materials have erupted as a field of study since the publication of databases that classify known materials according to their topological properties. Chemical understanding of band topology is required for us to rationally design new materials and utilize the benefits of topology, such as electrocatalysis. Here we investigate  $\text{SrAg}_4\text{Sb}_2$ , a topological crystalline insulator, with orbital projection calculations to understand the orbital origin of its non-trivial band topology.<sup>[2]</sup> We find a band inversion, the signature of a topological insulator, that we characterize as a balance between Ag-Ag  $\sigma$  and  $\delta$  bonding. The electronic structure is verified by comparison to experimental quantum oscillation measurements.<sup>[3]</sup> Ongoing work on chemical modification, magnetism, and surface chemistry will be discussed.

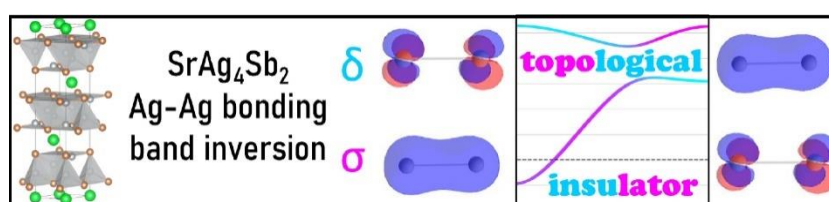


Fig. 1: Illustration of the unit cell of  $\text{SrAg}_4\text{Sb}_2$  and  $\sigma$  /  $\delta$  band inversion

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# Effect of the aerosol on AACVD (aerosol-assisted chemical vapour deposition) of transition metal dichalcogenides for catalytic applications

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Transition metal dichalcogenides (TMDCs) have been of interest in recent years because of their varying and tuneable properties. [1] They are layered nanomaterials consisting of a transition metal and a chalcogen. Reducing these materials to a single layer allows the material to have a direct band gap, improving their photocatalytic abilities.[2] There are a variety of methods that have been utilised to produce these TMDCs however a more effective technique is required to produce thin, single layer coatings. Aerosol assisted chemical deposition (AACVD) is a technique that utilises the formation of an aerosol of a non-volatile reaction precursor solution. It has the ability to produce uniform high surface area, thin coatings. [3] Transition metal diselenides have proven elusive when utilising this AACVD technique. More generally, one aspect of AACVD that hasn't been investigated is the impact of the aerosol itself on the deposition technique and how the aerosol droplet size can impact the particle size within the coatings deposited. This presentation explores the first syntheses of WSe<sub>2</sub> and MoSe<sub>2</sub> via AACVD, analysis shown in Figure 1, the preliminary results of utilising the coatings for catalytic degradation of dyes, and the preliminary results of the impact of the aerosol on this aerosol-assisted technique.

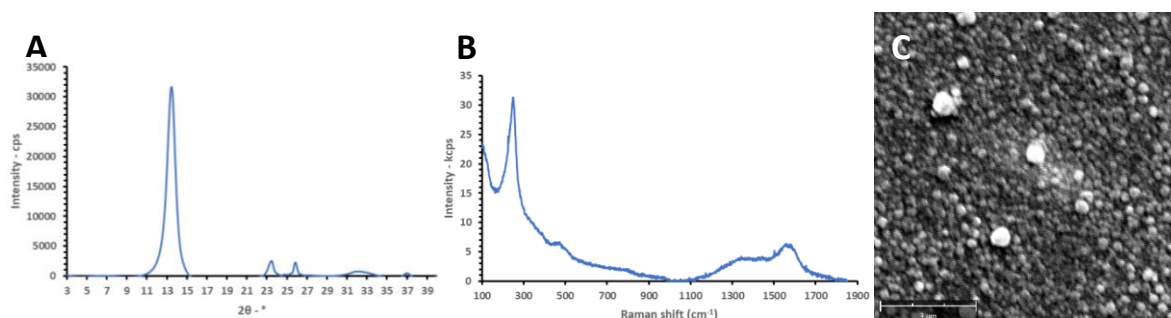


Figure 1 - Analysis of WSe<sub>2</sub> deposited via AACVD: (A) XRD analysis; (B) Raman analysis; (C) SEM analysis.

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## **d<sup>10</sup>s<sup>2</sup> post-transition metal anions: identifying and analysing their dual-mode Lewis basicity**

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Liquid-phase d<sup>10</sup>s<sup>2</sup> post-transition metal anions often have a stereochemically active lone pair, e.g. the trigonal-pyramidal trihalostannate anions [Sn<sup>II</sup>Cl<sub>3</sub>]<sup>−</sup> and [Sn<sup>II</sup>Br<sub>3</sub>]<sup>−</sup> or halobismuthate anions, that gives rise to unusual liquid-phase electronic properties and reactivity.<sup>1–3</sup> [SnCl<sub>3</sub>]<sup>−</sup> has been extensively used as a ligand in liquid-phase catalytic processes as [SnCl<sub>3</sub>]<sup>−</sup> can act as a Lewis base (*i.e.* electron donor) to form Sn-transition metal bonds and thus tune catalytic properties.<sup>3</sup> Furthermore, d<sup>10</sup>s<sup>2</sup> post-transition metal anions have potential uses in materials chemistry: optoelectronic applications;<sup>4</sup> preparation and disposal/recycling of semi-conductor materials employed within devices (energy-storage, electronic, optical)<sup>5</sup> and are present (with different structures) in halide perovskites.<sup>6</sup> However, little is known about the electronic structure of liquid-phase d<sup>10</sup>s<sup>2</sup> post-transition metal anions and how that relates to their reactivity.

Using a combination of X-ray photoelectron spectroscopy (XPS) and *ab initio* calculations, we show that liquid-phase d<sup>10</sup>s<sup>2</sup> post-transition metal anions can act as dual-mode Lewis bases.<sup>7</sup> They interact through the ligands and / or the metal centre, with the interaction mode dependent on the Lewis acid / electron acceptor identity. The metal donor atom Lewis basicity is controlled mainly by the metal identity; the ligand fine-tunes the basicity. Ligand basicity is strongly affected by changing the metal centre. Our findings give insight into the electronic structure of d<sup>10</sup>s<sup>2</sup> post transition metal anions, potentially enabling better molecular-level design of catalytic systems.

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# The role of Li...F interactions in lithium and lithium–magnesium hexafluoroisopropoxide complexes

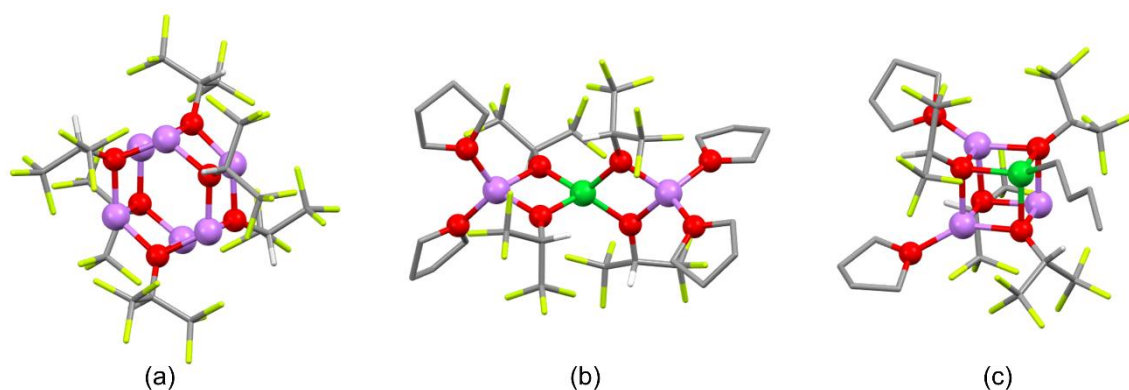
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The fluorinated alcohol 1,1,1,3,3,3-hexafluoroisopropanol (hfp) is well-established as a ligand in the design of lithium-, sodium-, and magnesium-ion battery electrolytes and additives.<sup>1</sup> During our investigations on its lithium salt derivatives, the key electrolyte precursor  $[\text{Li}(\mu_3\text{-OCH}(\text{CF}_3)_2)]_6$  (**1**) was isolated and characterised by single-crystal X-ray diffraction for the first time.<sup>2</sup> The solvent-free hexamer was found to possess a ring-stacked hexagonal prismatic arrangement (Fig. 1a) supported by Li...F interactions; notably, this is the first example of a lithium organometallic stabilised exocyclically exclusively through such interactions. To explore the behaviour of hfp as a ligand in s-block fluoroalkoxides further, we prepared the heterobimetallic lithium–magnesium complexes  $[\text{Li}_2(\text{thf})_4\text{Mg}(\mu_2\text{-OCH}(\text{CF}_3)_2)_4]$  (**2**) and  $[\text{Li}_3(\text{thf})_2(^n\text{BuMg})(\mu_3\text{-OCH}(\text{CF}_3)_2)_4]$  (**3**) (Fig. 1b, 1c). The unexpected structure of **3** is of particular interest, being based on a  $\text{Li}_3\text{MgO}_4$  heterocubane arrangement with highly unusual 3:1 Li:Mg stoichiometry and Li...F interactions analogous to those in **1**. Focusing on the solid-state structures and solution  $^7\text{Li}$  NMR spectra of **1–3**, the vastly different geometries possible for s-block alkoxide electrolyte precursors will be discussed in this talk, highlighting specifically the potential importance of Li...F interactions in molecular stabilisation.



**Figure 1.** Molecular structures of the three complexes obtained: (a) lithium fluoroalkoxide hexamer **1**; (b) lithium magnesiate **2**; (c) lithium–magnesium heterocubane **3**. Colour key: lithium–magenta; magnesium–green; oxygen–red; carbon–grey; fluorine–lime green; non-hfp H atoms omitted for clarity.

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## Experimental and computational steps towards phosphorus cations as main group catalysts

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Dependence on an ever-dwindling supply of transition metals (TMs) for their catalytic ability necessitates research into the development of candidates based on more-abundant elements.<sup>1</sup> Phosphenium cations (3), divalent phosphorus centres with a positive charge, have been shown to be effective main group catalysts in reactions such as imine reductions and hydroborations and are of interest for their potential in frustrated Lewis pair (FLP) chemistry.<sup>2</sup> The aim of this work is to determine the catalytic viability and potential scope of a number of phosphenium cations through the synthesis and subsequent analysis of catalytic candidates, with the view to provide viable alternatives to their well-established and widely employed TM counterparts.

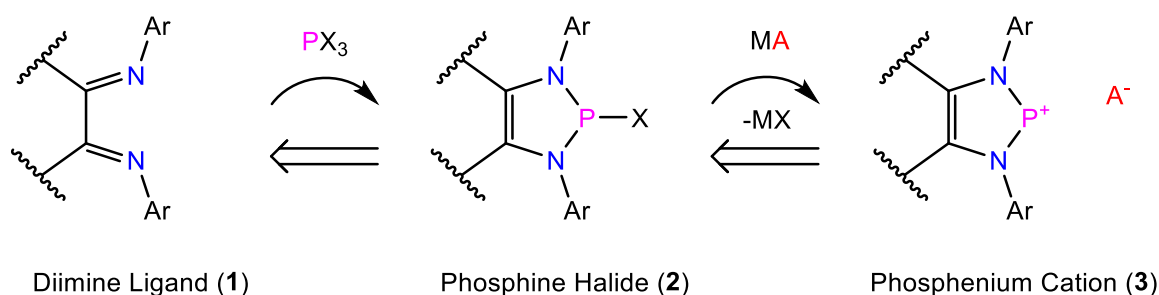


Figure 1: Synthetic route towards phosphenium cations (3)

The phosphenium cations presented here are N-heterocyclic phosphenium cations (NHPs) which contain a 5-membered aromatic ring and were isolated using a 3-step procedure (figure 1). Synthesis of  $\alpha$ -diimine ligand backbones (1), followed by halophosphine formation and subsequent salt metathesis reactions to form the phosphenium cation with a weakly-coordinating anion ( $A^-$ ).<sup>3</sup> A number of novel diimine ligands, phosphine halides (2) and phosphenium cations (3) were synthesised. Experimental and computational studies on substituent effects, Lewis acidity and reactivity towards small molecules have been carried out to understand trends in their properties. Tuning of the organic backbone has been carried out with the aim of understanding and improving catalytic viability.

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# Investigating the Role of Alkali Metal Cations in Main Group Complexes – A Computational Study

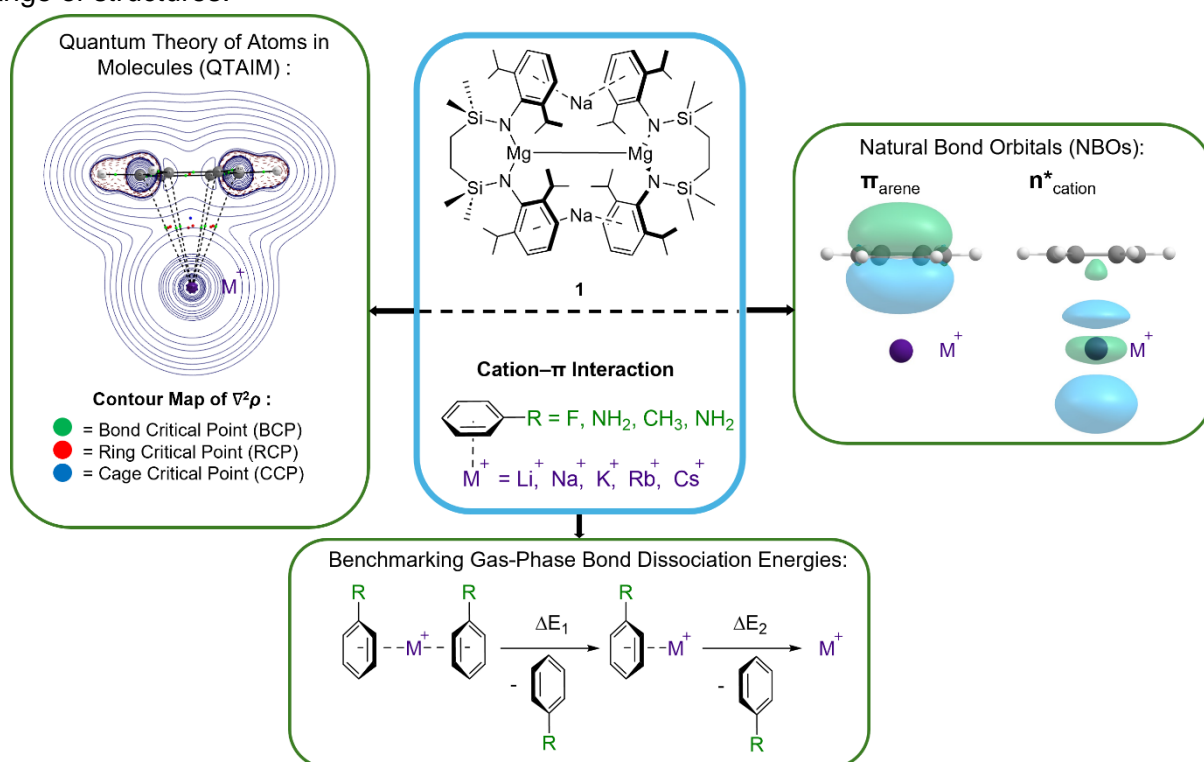
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In 2021, Hill and co-workers successfully synthesised the dimeric Mg(I) species  $\{[\text{SiNDipp}]\text{MgNa}\}_2$ ; when  $\{\text{SiNDipp}\} = \{\text{CH}_2\text{SiMe}_2\text{N}(\text{Dipp})\}_2$  and  $\text{Dipp} = 2,6\text{-}i\text{-PrC}_6\text{H}_3$  (**1**), consisting of a contiguous tetra-metallic  $\{\text{Mg}_2\text{Na}_2\}$  core. The stability of **1** and the Mg(I)–Mg(I) interaction ( $>3.2$  Å) is augmented by the presence of  $\text{Na}^+\cdots\text{aryl}$  interactions.<sup>1</sup>

To further understand these interactions, density functional theory (DFT) and electronic structure approaches are being applied to investigate the cation- $\pi$  interactions for group 1 alkali metal cations ( $\text{M}^+ = \text{Li}^+ - \text{Cs}^+$ ) with aryl groups. This study includes methodology benchmarking against gas phase collision induced dissociation (CID) experiments,<sup>2</sup> to provide bond dissociation energies, as well as natural bond orbital (NBO) analysis to assess the extent of energetic importance associated with the  $\pi_{\text{arene}} \rightarrow n^*_{\text{cation}}$  orbital interaction. Additionally, quantum theory of atoms in molecules (QTAIM) examines the bonding character of the cation- $\pi$  interaction through topological analysis of the electron density ( $\rho$ ) and Laplacian ( $\nabla^2\rho$ ) in a range of structures.



**Figure 2:** Computational approaches to study cation- $\pi$  interactions between group 1 alkali metals ( $\text{M}^+$ ) and aryl groups ( $\text{C}_6\text{H}_6$ , i.e.  $\text{R} = \text{H}$ , shown).

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## Accessing Unusual Co Multi-Metallic Complexes using Main Group Systems

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Multi-metallic compounds are the subject of significant interest due to the possibility of using multiple reactive sites cooperatively to achieve chemical transformations.<sup>1,2</sup> Bimetallic compounds comprised of main group and transition elements are of particular interest due to the contrasting electronic properties of the two metal centres.

CoCp(CO)<sub>2</sub> is known to be reduced to the bimetallic mixed oxidation state Co(0)/Co(I) radical anion [Co<sub>2</sub>(Cp)<sub>2</sub>(μ<sub>2</sub>-CO)<sub>2</sub>]<sup>•-</sup>, in the presence of weakly interacting counterions.<sup>3,4</sup> However, by using a Mg(I) dimer as the reducing agent, we can access this radical anion while coordinating the CO ligands to Mg, forming an unusual molecular square [(Nacnac)<sup>Mes</sup>Mg]<sub>4</sub>[Co<sub>2</sub>(Cp)<sub>2</sub>(μ<sub>2</sub>-CO)<sub>2</sub>]<sub>4</sub> (**1**). Further studies into the use of main group metal reducing agents reveal that alumanyl species (i.e. anionic, nucleophilic Al(I) compounds), act as stronger reducing agents, yielding trimetallic Co(0) compounds featuring the [Co<sub>3</sub>(Cp)<sub>2</sub>(μ<sub>2</sub>-CO)<sub>4</sub>]<sup>2-</sup> unit (**2**) and a central square planar cobalt centre, which has only been accessed previously using Yb metallocenes.<sup>5</sup> This poster explores the synthesis and spectroscopic properties of these unusual bimetallic Co compounds.

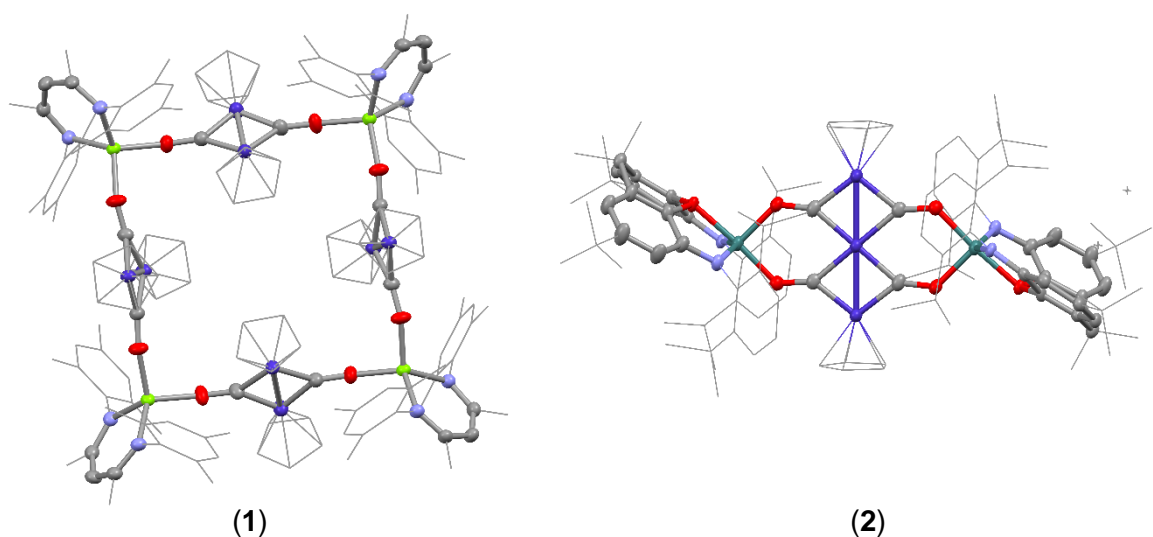


Figure: Crystal structures of Co/Mg and Co/Al compounds **1** and **2**.

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# Preceramic Polymers for Hexagonal Boron Nitride from the Catalytic Dehydropolymerisation of Ammonia Borane

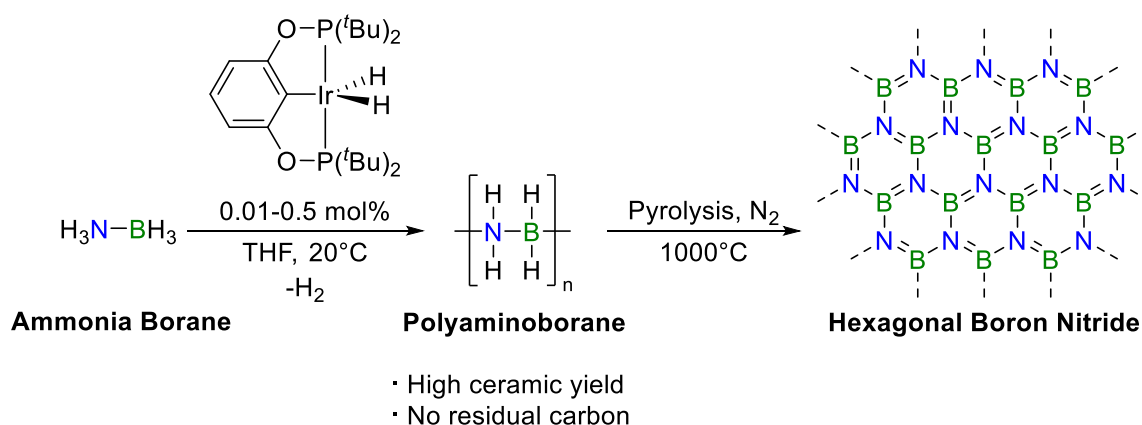
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Polyaminoboranes are isoelectronic B-N analogues of polyolefins. *N*-methylpolyaminoborane ( $[\text{H}_2\text{B-NMeH}]_n$ ) has been the focus of much of the previous research in the field, where robust catalysts are used to produce high molecular weight polymers.<sup>1</sup> The ammonia borane analogue,  $[\text{H}_2\text{B-NH}_2]_n$  has been the subject of fewer investigations, mainly due to low solubility limiting characterisation and potential uses.<sup>2</sup> It is, however, a direct precursor for hexagonal boron nitride (h-BN), a material with a range of promising applications in photonic devices, due to its optical properties.<sup>3</sup> We report a preliminary study of the synthesis and use of  $[\text{H}_2\text{B-NH}_2]_n$  as a h-BN preceramic. In this area,  $[\text{H}_2\text{B-NH}_2]_n$  offers several advantages over the methyl-containing  $[\text{H}_2\text{B-NMeH}]_n$  analogue, including higher ceramic yields and no residual carbon.



**Figure 1.** Synthesis of  $(\text{H}_2\text{B-NH}_2)_n$  and its use as a preceramic for the production of h-BN.

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## Zirconium Triethyl Complexes: Synthesis and Reactivity

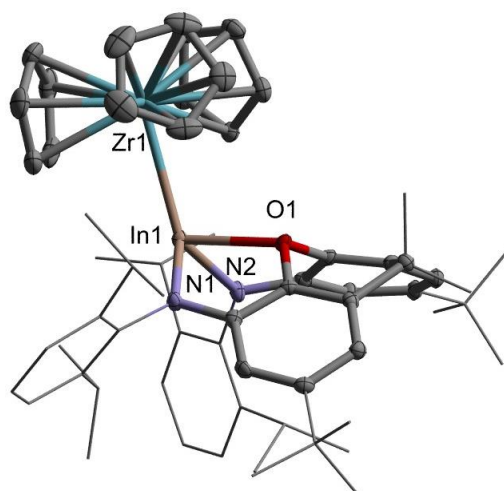
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Anionic compounds of group 13 elements (E) in the +1 oxidation state can act as X-type ligands, allowing the formation of M-E bonds from electrophilic metal complexes.<sup>1-3</sup> Very few examples of group 4-group 13 metal bonds have previously been reported, with the majority of examples being of a donor-acceptor nature.<sup>4,5</sup> Exploration of the synthesis and geometric/electronic structure of covalent group 13-group 4 bonds is therefore of significant interest. The synthesis of bimetallic triethyl complexes is potentially hindered by the reducing power of the triethyl anion. As such, drawing inspiration from the recent synthesis of a beryllium aluminyl complex<sup>1</sup>,  $\pi$ -donating cyclopentadienyl ligands/leaving groups were chosen to increase electron density at the transition metal centre, and favour metathesis over reduction. A range of triethyl (Al, Ga, In) complexes of zirconium were synthesised, using NON (4,5-bis(2,6-diisopropylanilido)-2,7-ditert-butyl-9,9-dimethylxanthene) ligated triethyl anions and  $\text{ZrCp}_4$ . The geometry of these complexes is significantly distorted compared to other bimetallic triethyl species, preferring an equatorial bonding mode within the TBP geometry at E instead of the more typical axial geometry.<sup>1,2</sup> The thermolytic and photolytic reactivity of the synthesised complexes was also explored, revealing trends relating to stability of the +1 oxidation state of E, the energies of the Zr-E bonding orbital and the orbital symmetry.



**Figure 1:** Molecular structure of (NON)InZrCp<sub>3</sub> in the solid state determined by X-ray crystallography

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## Photochemical generation of Al(I) species from Al(III) precursors

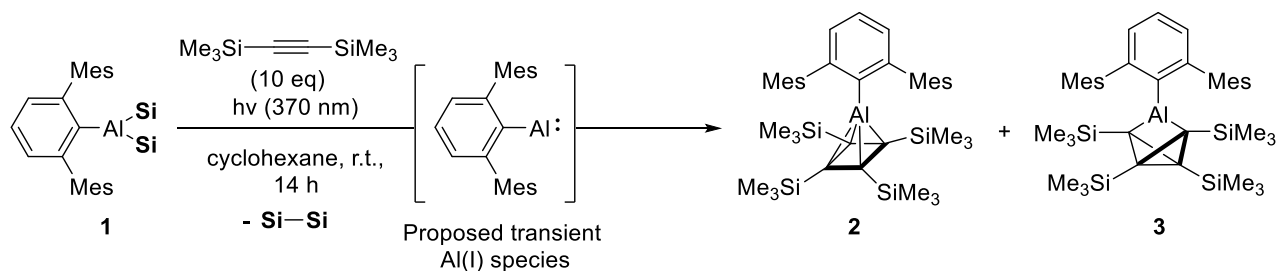
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Al(I) complexes have demonstrated rich oxidative addition chemistry. However, reductive elimination at aluminium centres is uncommon due to the inherent greater stability of aluminium in the +3 oxidation state. Synthetic routes to Al(I) species mostly involve the reduction of an aluminium halide precursor with a strong metal reducing agent.

In this work, photolysis has been employed to instigate reductive elimination at the aluminium centre of a novel *Mes*-terphenyl (2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; Mes = 2,4,6-trimethylphenyl) substituted disilylalane, <sup>Mes</sup>TerAlSi<sub>2</sub> **1** (**Si** = SiMe<sub>2</sub>Ph) in the presence of an alkyne (Scheme 1). This has led to the successful cleavage of the Al-Si bonds, suggesting the presence of a transient Al(I) species.

Compounds **2** and **3** represent the first aluminium-containing compounds of these geometrical isomers. Additionally, **2** is the first isolated tricyclic isomer, which was previously only theorized, likely due to the highly strained bis-cyclopropane system.<sup>1-3</sup> This discovery prompts intriguing questions regarding the mechanisms of their formation and bonding modes in these compounds.



Scheme 1: The formation of aluminapyramidane **2** and an aluminium tricyclic isomer **3** following reactivity of <sup>Mes</sup>TerAlSi<sub>2</sub> **1** with bis(trimethylsilyl)acetylene under irradiation. **Si** = SiMe<sub>2</sub>Ph.

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## Electrochemical characterisation of low valent aluminium species

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Aluminium tends to exist in the +3 oxidation state, both in nature and in a laboratory settings. With appropriate supporting ligands, compounds with aluminium in the +1 oxidation state can be synthetically accessed.

A broad range of ligands have been shown to support and stabilise reactive aluminium (I) centres.<sup>1</sup> In the majority of cases, the synthetic steps that take Al(III) to Al(I) are low yielding and poorly understood, with factors such as high reactivity or over-reduction to form metallic aluminium often invoked to explain the synthetic difficulties encountered.<sup>2,3</sup> The ligand effects on yield are similarly underexplored, with subtle changes in ligand framework dramatically effecting stability and yield.<sup>4</sup> In both cases, a greater mechanistic understanding would aid in understanding both of these processes.

Cyclic voltammetry has been used to investigate the mechanisms and reaction pathways in d and f block chemistry. Hence, we have attempted to apply these methods to probe how the reductions of main group complexes progress, with various ligands.

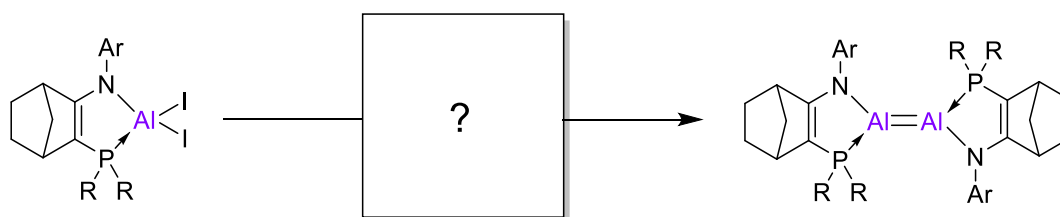


Figure 1: Reduction of an aminophosphine supported aluminium (III) species to aluminium (I)

Herein we present our electrochemical methods, the redox events detected in aluminium (I) species, and their precursors in higher oxidation states. With this we propose a novel mechanism for the reduction to aluminium (I).

With this information, we can begin to improve the methods and techniques we use to synthesize aluminium (I) compounds and begin to explain trends in and effects of the ligands we use.

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# Tethered $\beta$ -Diketiminato Magnesium Complexes

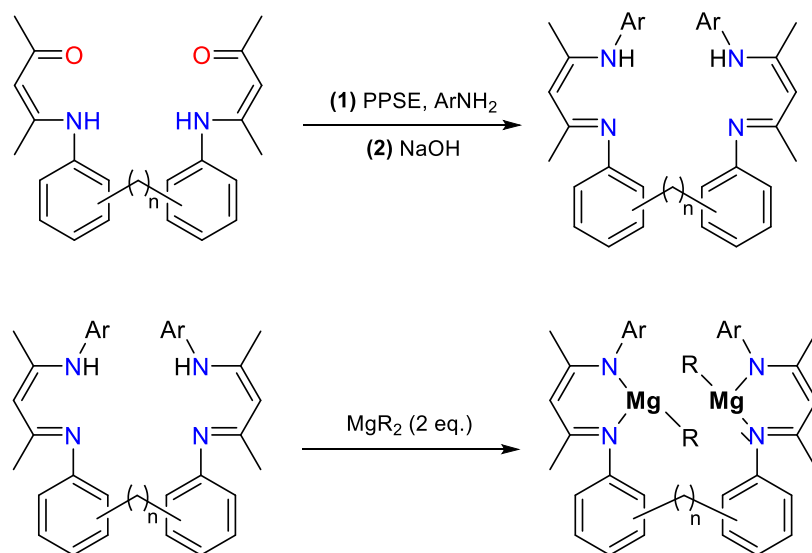
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Low oxidation state dimagnesium(I) complexes have consistently proven their ability as powerful reducing agents since their first reporting in 2007.<sup>1</sup> Their stability is attributed to  $\beta$ -diketiminato ligands, commonly known as NacNacs, providing kinetic stabilisation via sterically bulky substituents alongside their bidentate chelating ability. While a number of dimagnesium(I) complexes have been employed within organic/organometallic synthesis as reducing agents, an example of a catalytic cycle using these complexes is yet to be reported.<sup>2</sup>

Here we present the preparation and characterisation of novel tethered NacNac ligands and their application in the synthesis of dimagnesium complexes (Scheme 1). Utilising the original steric stabilisation from bulky substituents, these ligands additionally maintain a close proximity of both metal centres, in principle reducing the entropy required to form a direct magnesium bond. Variations of the R-group influence both the stability and solubility of these complexes, while structural differences within the tether optimise the inter-magnesium distance.



**Scheme 1:** Preparation of tethered Nacnac ligand and complexation with magnesium starting material.

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## Semi-Hydrogenation of Alkynes with Zinc Complexes

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Catalysts for semi-hydrogenation of alkynes often use precious metals, such as rhodium, palladium, and platinum. These are undesirable due to their toxicity, low abundance, and expensive nature.<sup>1-3</sup> Zinc is an ideal alternative as it is a non-toxic, cheap, and a highly abundant metal.<sup>4, 5</sup> Zinc complexes have been utilised as catalysts for hydrosilylations,<sup>6, 7</sup> hydroborations<sup>8, 9</sup> and more recently hydrogenations.<sup>10, 11</sup>

Here we present a series of next generation zinc complexes synthesised and applied as catalysts for the semi-hydrogenation of diphenylacetylene to afford Z-stilbene. At 23 bar pressure, Z-stilbene was selectively formed with alkene: alkane selectivity at 95:5 and Z:E ratio at 99:1.<sup>12</sup> The synthesis of less sterically bulky zinc complexes via two different routes has been attempted. New zinc complexes with reduced steric bulk catalysed the reaction to afford higher TOF and TON than the originally reported zinc catalyst.

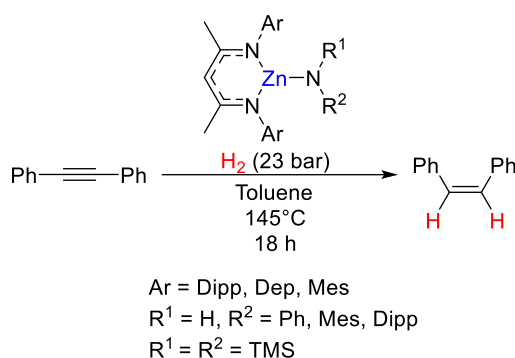


Figure 3: Reaction scheme of semi-hydrogenation of diphenylacetylene with various zinc catalysts.

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# Single-source precursors for the aerosol assisted chemical vapour deposition of tantalum oxides and tantalum oxynitrides

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Single-source precursors for the Aerosol Assisted Chemical Vapour Deposition (AACVD) of tantalum-based materials were prepared as a possible route to stable and low recombination photoelectrochemical water splitting materials.[1] A tri-tert-butanolamine ligand was employed to create tantalum alkoxide precursors such as a tantalum oxo-bridged tetramer **1** and a tantalum imido species **2**. These are capable of decomposition into tantalum oxide and tantalum oxynitride respectively, as verified by thermogravimetric analysis.

Successful depositions of the tetramer **1** were performed in a hot wall AACVD reactor to yield tantalum oxide. It was shown that higher deposition and annealing temperatures of up to 500 and 900 degrees Celsius improved the degree of order and microstructure in thin films, in accordance with literature.[2] The thin films produced were found to be amorphous, forming into large spherical nodules as displayed in Figure 1. These possessed a band gap of 4.7 eV.

Single-source precursors for tantalum oxide dopant elements such as nitrogen, aluminium and manganese have been synthesised. An electric and magnetic field assisted AACVD reactor has also been recently constructed which may be used to further alter thin film properties.[3]

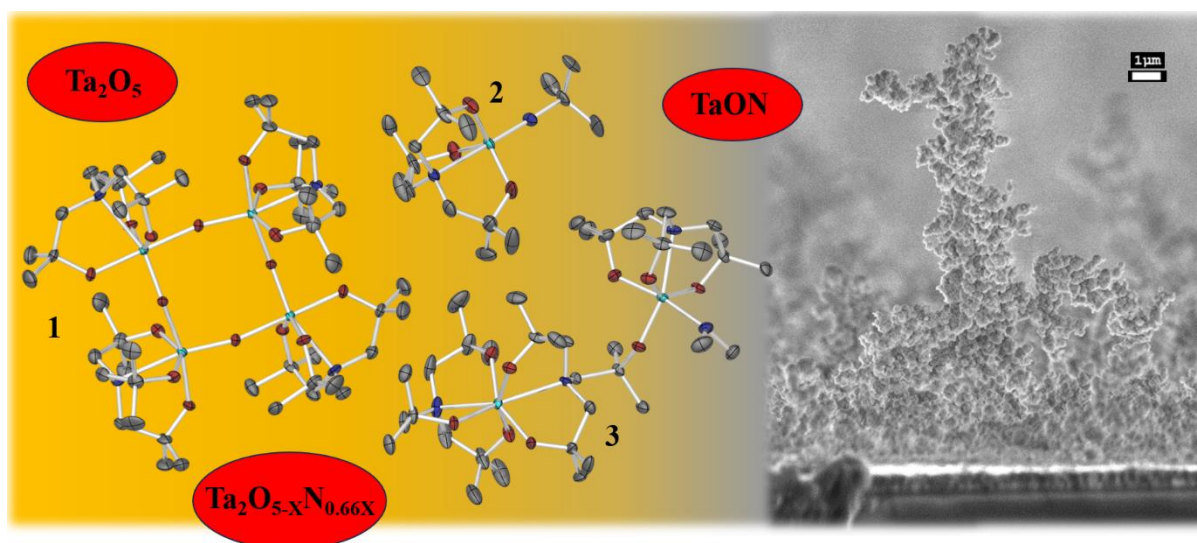


Fig. 1. To the left - tantalum oxide and oxynitride single source precursors prepared for deposition. to the right – A ‘tower’ of tantalum oxide, height ca. 15 $\mu$ m, grown from fluorine doped tin oxide.

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## Reductive or Oxidative Addition at Tin<sup>II</sup>?

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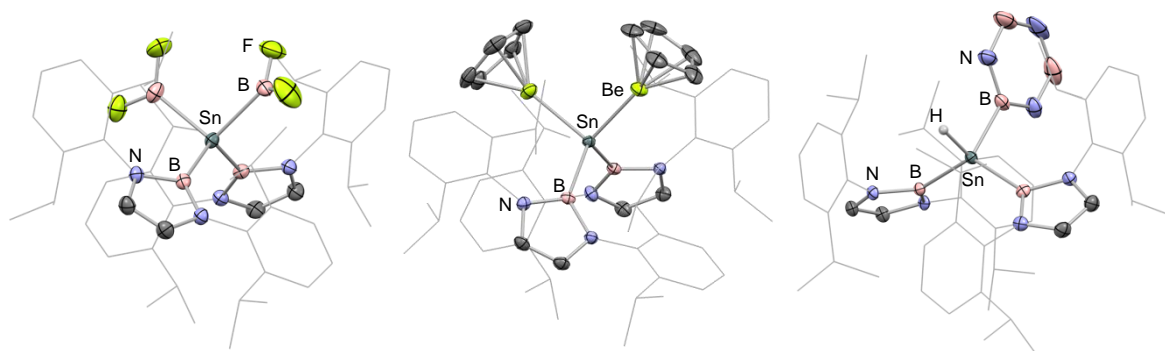
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The addition of element-element bonds to metal centres is key for a wide range of industrially important chemical transformations.<sup>1</sup> Whether these additions are deemed oxidative or reductive is dependent on the identities and electronegativities of the metal, elements, and ligands involved.<sup>2</sup> In recent decades, attention has shifted away from the more common precious metal systems to higher abundant main group metals due to their transition metal-like character.<sup>3</sup>

The chemistry and reactivity of borazine with both *p*- and *d*-block metals remains mostly unexplored, including addition of the B–H bond to any element in the periodic table.<sup>4,5</sup> Moreover, addition of both B–B and Be–Be bonds to a single main group metal site has yet to be reported, despite the former being of potential great importance to the development of main-group mediated borylation reactions.

Here, we report B–H bond activation in borazine, as well as the addition of B–B and Be–Be bonds at the tin centre of a bis(boryl)stannylene. NMR spectroscopic studies, in combination with single-crystal X-ray diffraction (Figure 1) allow for unambiguous structural determination of the novel complexes, clearly demonstrating addition of the E–E bonds to the Sn<sup>II</sup> centre. Quantum chemical calculations suggest that some of these processes may be better described as ‘reductive addition’ as the tin centre remains highly electron rich after addition.



**Figure 1.** Solid-state structure of  $[B]_2Sn(BF_2)_2$ ,  $[B]_2Sn(BeCp)_2$  and  $[B]_2Sn(Bz)H$  ( $[B] = B(NDippCH)_2$ ,  $Dipp = 2,6\text{-}i\text{-Pr}_2C_6H_3$ ). Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

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## Development and application of single source precursors for semiconducting transition metal dichalcogenide thin films

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Transition metal dichalcogenides (TMDCs), are highly anisotropic 2D materials, analogous to graphene, except with tuneable band-gaps. They are comprised of  $ME_2$  (M = metal; E = S, Se, Te) repeating subunits. TMDC's are attracting significant interest to fill the global demand for smaller and more efficient next-generation electronic and optoelectronic devices. This requires few-layer, crystalline growth on the micron scale with defect-free layers and interfaces and is technologically extremely challenging.<sup>[1]</sup>

Electrodeposition is a scalable, cost effective and area-selective deposition method which avoids requirements for post-deposition patterning or subsequent material transfer. Achieving this for TMDCs would represent a significant technological advance, and with careful design, could allow semiconductor materials to be directly grown into pre-designed or flexible substrates, allowing production of wearable devices or small devices for Internet of Things applications.

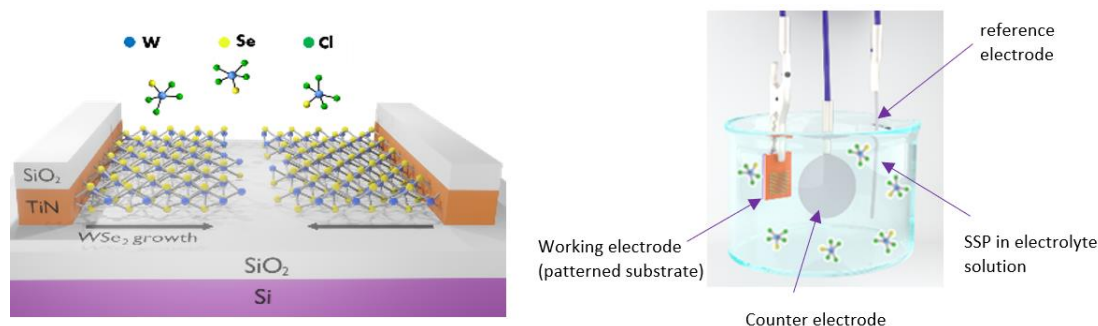


Figure 1: Schematic for the TMDC film growth (left) and for electrochemical deposition cell (right).

We have developed bespoke single source precursors (incorporating M and E into the same molecular entity) for the electrodeposition of mono/few-layer  $MoS_2$  from  $[MoS_4][nBu_4N]_2$  and  $WS_2$  from  $[WS_2Cl_4][Et_4N]_2$  directly onto patterned graphene.<sup>[2, 3]</sup> Our interdisciplinary team has also recently reported the growth of few-layer  $WSe_2$  from the edge of a thin nano-band electrode, over an insulator channel, allowing for direct *in-situ* measurements of the electronic properties, and with potential for use in devices.<sup>[4]</sup>

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# Unconventional strategies for “precious-metal-like” redox catalysis using the main group

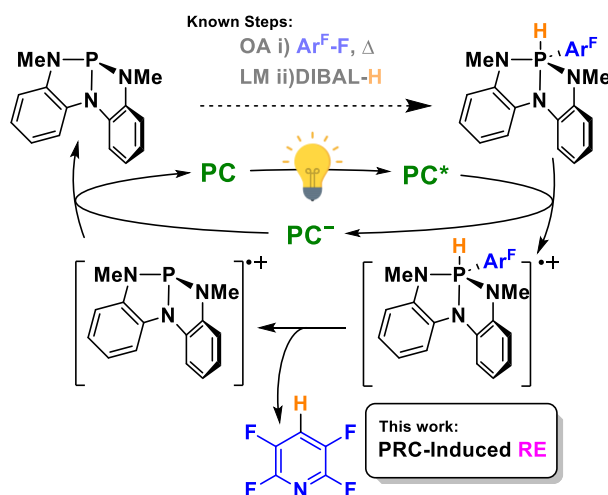
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Precious metal (PM) catalysis, while vital to the modern chemical industry, is fraught with sustainability issues, and, in many contexts, currently has no viable alternative. Replacement with main group catalysis is an attractive prospect for reasons of both sustainability and cost. However, there are still major challenges in replicating the elementary steps of the prototypical PM catalytic cycle. This is particularly true of reductive elimination, which typically provides the key bond forming step in such cycles.<sup>1</sup>

We suggest photoredox catalysis (PRC) as a solution to driving facile reductive elimination at main group centres. Herein, we describe the first investigation into the use of PRC for this purpose. In this concept, transient oxidation of a redox active supporting ligand bound to a main group element is used to induce reductive elimination and a successful proof of concept demonstration has been achieved using a constrained phosphorus pincer complex as a model.<sup>2</sup>

In a separate project, an alternative strategy has also been investigated in which the net outcomes of PM like catalysis are mimicked, rather than the underlying chemical steps themselves. Using orthoquinones, an unconventional set of elementary steps allows oxidative coupling of triphenylphosphine to enable catalytic functionalisation to difluoro products as well as further stoichiometric investigations to synthesise imidophosphorane products. Chemical and electrochemical oxidation methods are used to regenerate the starting quinone from the in-situ formed catecholates to complete the synthetic cycle. This provides the starting point for the development of fully catalytic  $2e^-$  redox cycles that do not require a transition metal.



PRC-induced reductive elimination at a T-shaped phosphine to complete a stoichiometric hydrodefluorination cycle.

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## Exploring the Alkyne Insertion Chemistry of an Aryl(silyl)stannylene

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Stannylenes, the heavier tin analogues of carbenes, have seen recent research attention for their capacity for small molecule activation. In particular, electron-rich stannylenes featuring bulky aryl and silyl ligands are known to react with a wide range of bonds.<sup>1–3</sup> However, the activity of such species towards multiple bonds has been comparatively less well-explored compared to that of single bonds, despite an understanding of this reactivity being important for the development of novel main-group catalysts.<sup>4,5</sup>

Following the 2022 report of a novel electron-rich aryl(silyl)stannylene,<sup>6</sup> a range of alkyl- and aryl-substituted alkynes have been shown to undergo irreversible insertion into the Sn-Si bond in a selective manner, resulting in a *cis* arrangement of Sn and Si groups around the C-C double bond. In the products resulting from asymmetric alkynes, the more sterically bulky group is bound to the same carbon atom as Sn. Reversible insertion occurs for the substrates 3-hexyne and trimethylsilylacetylene. The thermodynamic parameters for these reactions have been determined by variable temperature NMR and a general mechanism for all insertions has been elucidated computationally.

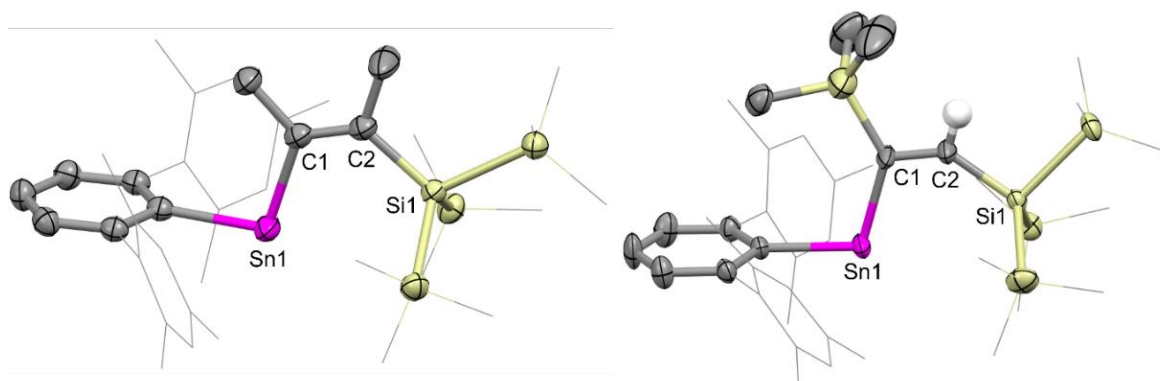


Figure 1. Product of irreversible 2-butyne insertion (left) and reversible trimethylsilylacetylene insertion (right). Both feature a *cis* arrangement of Sn and Si groups around the C-C double bond, where in the latter case the more sterically bulky SiMe<sub>3</sub> group is adjacent to Sn.

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## CO<sub>2</sub> as a versatile precursor to higher-value industrial feedstocks using Group 14 complexes

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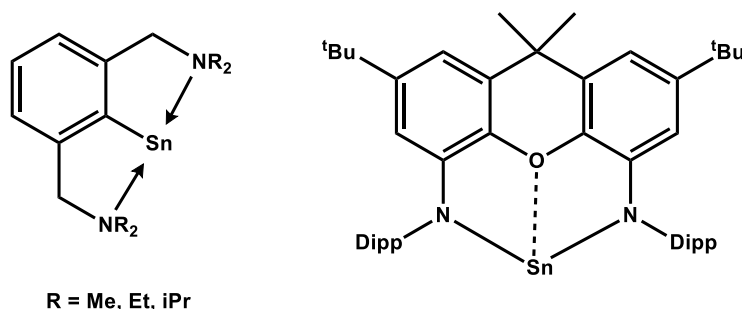
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The chemical transformation of CO<sub>2</sub> as a synthon for the construction of more complex molecules provides a key, under-explored possibility to address climate change. Chemical activation of CO<sub>2</sub> has the potential to lower atmospheric CO<sub>2</sub> concentrations while simultaneously alleviating dependence on fossil fuels by producing value-added commodities from a renewable source of carbon.<sup>1</sup> Target commodities include methanol, formic acid, and formaldehyde, all of which may be used as synthetic building blocks to more complicated molecules.

The key to overcoming the strong thermodynamic stability of CO<sub>2</sub> lies in efficient and selective catalysts. The group 14 elements have ambiphilic properties owing to their vacant p-orbital and s-orbital lone pair.<sup>2</sup> Therefore, by careful ligand design, the reactivity of the ensuing catalyst can be tuned for electrophilic or nucleophilic behaviour.

We have explored the synthesis of two classes of catalysts bearing group 14 elements, and the subsequent reactivity of each with CO<sub>2</sub>.



**Figure 1:** Catalysts investigated for the controlled reduction of CO<sub>2</sub>.

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## Exploring the reactivity of a Dewar-1,3,5-triphosphabenzene

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The discovery of kinetically stabilised phosphalkynes<sup>1,2</sup> has paved the way for synthesising 1,3,5-triphosphabenzene *via* stoichiometric, metal-mediated cyclotrimerisations. Whilst the reactivity of 1,3,5-triphosphabenzene has been well-documented,<sup>3</sup> the Dewar valence isomer remains less explored due to limited synthetic routes and thermal instability with respect to isomerisation. The Webster group previously reported the gram-scale synthesis of 2,4,6-tris(triphenylmethyl)-Dewar-1,3,5-triphosphabenzene **A** from the [Fe(salen)]<sub>2</sub>-μ-oxo catalysed cyclotrimerisation of triphenylmethylphosphalkyne.<sup>4</sup> Unlike the *tert*-butyl counterpart, triphenyl-substituted Dewar-1,3,5-triphosphabenzene is thermally stable and moderately air and moisture stable – providing a platform to explore reactivity. Here, we present diverse transformations of **A** with bulky alkali-amide salts, including unique ArC(sp<sup>3</sup>)-H functionalisations.

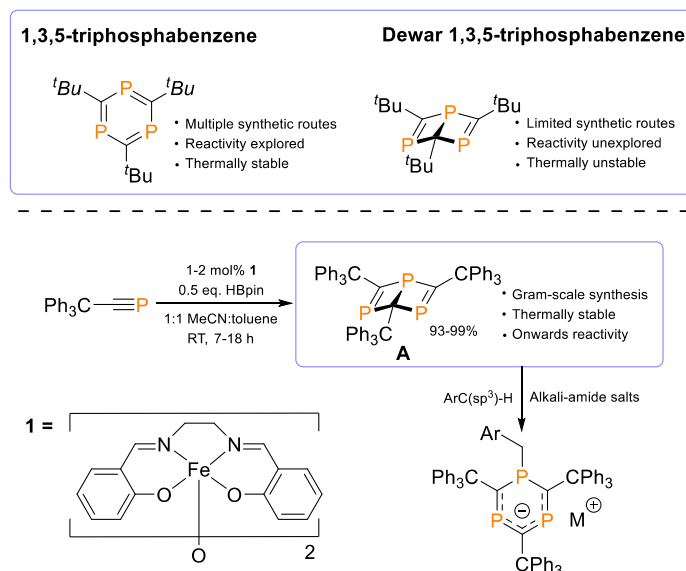


Figure 1. Comparison of 1,3,5-triphosphabenzene and Dewar-1,3,5-triphosphabenzene valence isomers. An iron catalysed synthesis of Dewar-1,3,5-triphosphabenzene.

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# Bismuth precursors for the atomic layer deposition of p-type Bi<sub>2</sub>O<sub>3</sub>

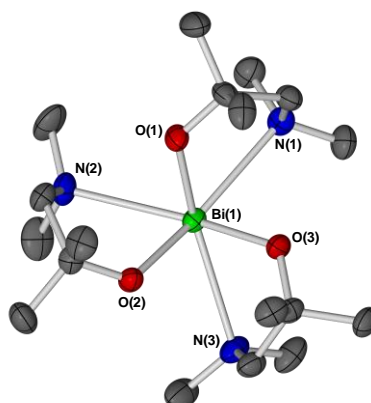
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Bismuth(III) oxide (Bi<sub>2</sub>O<sub>3</sub>) is a known p-type semiconducting material with a relatively wide band gap. As a result of its wide band gap, relatively good environmental stability (chemical and thermal) and high carrier mobility, Bi<sub>2</sub>O<sub>3</sub> is a promising material for use in electronic and optoelectronic devices and therefore has potential applications in fields such as photocatalysis and gas sensing.<sup>1,2</sup> Studies have identified seven different crystalline forms of bismuth oxide: α-Bi<sub>2</sub>O<sub>3</sub>, β-Bi<sub>2</sub>O<sub>3</sub>, γ-Bi<sub>2</sub>O<sub>3</sub>, δ-Bi<sub>2</sub>O<sub>3</sub>, ε-Bi<sub>2</sub>O<sub>3</sub>, ω-Bi<sub>2</sub>O<sub>3</sub> and η-Bi<sub>2</sub>O<sub>3</sub> and depending on the method of preparation, thin-films of Bi<sub>2</sub>O<sub>3</sub> can be either n-type or p-type, making Bi<sub>2</sub>O<sub>3</sub> amphoteric.<sup>1,3</sup> The current lack of commercially viable p-type metal oxide materials available hinders technology dependent on p-type metal oxide thin-film transistors and Bi<sub>2</sub>O<sub>3</sub> could be a promising p-type metal oxide material.

Therefore, developing potential bismuth(III) atomic layer deposition (ALD) precursors that could be used to deposit Bi<sub>2</sub>O<sub>3</sub> thin-films is of interest. A number of bismuth(III) alkoxide and amide complexes have previously been investigated as ALD precursors for the production of Bi<sub>2</sub>O<sub>3</sub> thin-films.<sup>4,5</sup> Here we report the synthesis and development of several homoleptic bismuth(III) alkoxide and aminoalkoxide complexes, which were analysed using NMR spectroscopy, single-crystal X-ray diffraction and thermogravimetric analysis (TGA). Of these complexes, [Bi(OC(Me)<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub>] has shown the most favorable TGA data and is currently the best candidate for further ALD studies.



**Figure. 1.** Molecular structure of the prospective ALD precursor [Bi(OC(Me)<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub>]. The thermal ellipsoids are shown at a 50% probability level. The hydrogen atoms are excluded for clarity.

*This work was supported by the EPSRC and Pragmatic Semiconductor.*

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# The Synthesis and Reactivity of Low Oxidation State Indium Complexes

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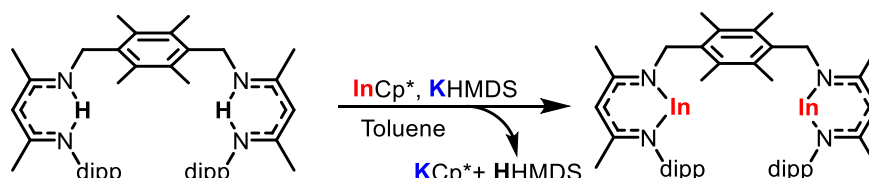
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With the rising interest in the implementation of main group based catalysts, the exploration of both s and p-block metal complexes to promote transition metal like redox reactivity has become an increasingly important field of research. The highly reactive nature of many low oxidation state group 13 complexes, particularly based around aluminium, is now very well documented – with many examples of impressive activation reactions having been demonstrated thus far. [1,2] Despite this, the significant instability of their electron rich states typically limits the reversibility that is observed once oxidation has taken place. [3]

The increasing contribution of the inert pair effect for the lower triel elements serves to significantly stabilise their monovalent states, thus reducing the total energy separation from their natural (III) form. [4] The aim of this project is to explore the synthesis and reactivity of the Indium(I) counterparts of well-known Al<sup>I</sup> based reagents, with the intent of uncovering any potential reversible character promoted by its increased stability in the +1 state.

We present a new synthetic route for the formation of  $\beta$ -Diketiminato (BDI) based In<sup>I</sup> complexes and its implementation in the formation of a series of novel bis-In<sup>I</sup> complexes. The reactivity of these compounds towards small molecules such as H<sub>2</sub>, CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> is also explored.



New synthetic route for the formation of BDI stabilised In(I) complexes

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# Competing Pathways for Hydrosilylation of Alkyl and Aryl Ketones Catalyzed or Mediated by $\text{PAr}_2^+$ Species?

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In this study we use computational modelling to investigate the role of phosphirenium ions, (**I**, Figure 1) as a source of reactive phosphonium cations,  $\text{PAr}_2^+$  without heteroatom substituents. The  $\text{PAr}_2^+$  species can then initiate Lewis Acid catalysis, for example the hydrosilylation of alkyl ketones.<sup>1</sup> This involves the nucleophilic attack of ketone on the phosphonium catalyst to give **III<sub>P</sub>**, followed by hydride transfer and silyl group migration to give **V<sub>P</sub>**. However, when investigating electronic substituent effects on the  $\text{PAr}_2^+$  species it was found that catalysis diverges between alkyl and aryl ketones after formation of adduct **V<sub>P</sub>**. For alkyl substrates, another unit of ketone displaces the hydrosilylated product and results in subsequent reformation of the active catalyst **III<sub>P</sub>**. An alternative pathway for hydrosilylation of aryl ketones involves cleavage of the C-O bond in adduct **V<sub>P</sub>** resulting in a phosphonium silyl ether and a carbocation (**I<sub>C</sub>**). This pathway highlights the possibility of two competing catalysts for hydrosilylation, either a carbocation (**I<sub>C</sub>**) or silylium ion<sup>2, 3</sup> (**I<sub>S</sub>**) with process **I-V<sub>P</sub>** acting as initiation steps. The degradation of **V<sub>P</sub>** and formation of **I<sub>C</sub>** is dependent upon the ketone substrate, but also the electronic nature of the  $\text{PAr}_2^+$  species. This work discusses the divergent catalysis from **V<sub>P</sub>** between aryl and alkyl ketones and will also explore important side-reactions such as deoxygenation<sup>4</sup> of aryl ketones.

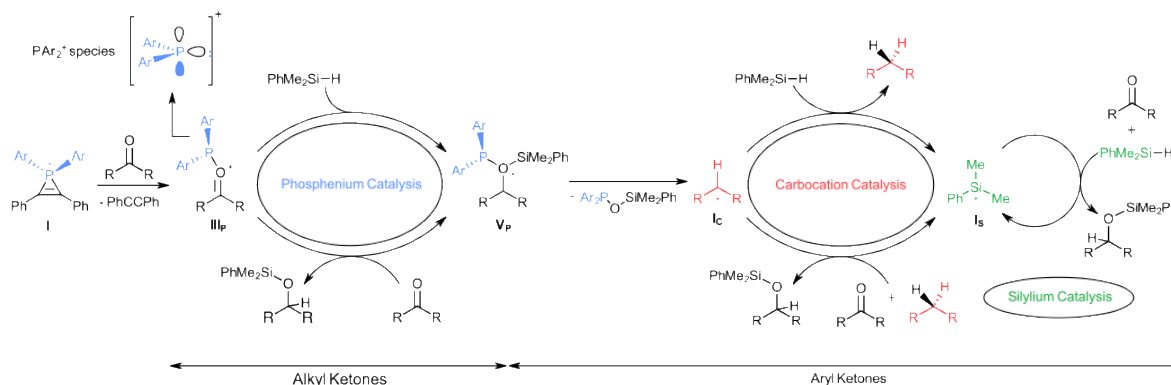


Figure 4. Divergent catalysis for the hydrosilylation of alkyl and aryl ketones.

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# Low oxidation state aluminium complexes *via* reduction of aluminium iodides

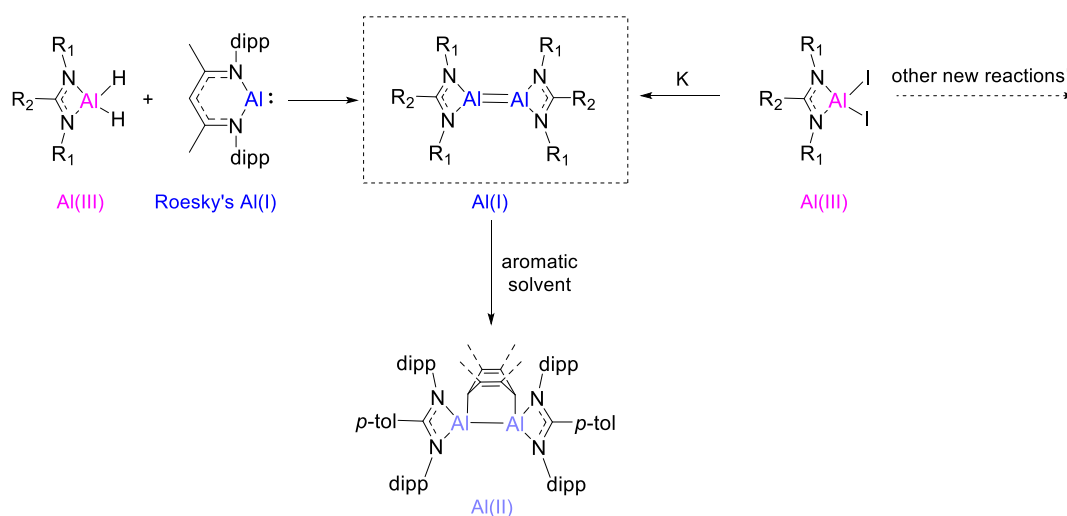
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Chemical catalysis has historically been dominated by complexes of precious transition metals, particularly those in the platinum group. However, dwindling global supplies of these metals and problems of sustainability make it necessary to find alternatives. Aluminium has recently appeared as an attractive target to this end; in low oxidation-states it has closely spaced vacant acceptor and filled donor orbitals, which can allow it to mimic some transition-metal reactivity.<sup>1</sup>

A range of low oxidation state 'masked dialumenes' with differing arenes have been synthesised, following the initial report of an adduct with benzene.<sup>2,3</sup> These masked dialumene complexes imply the formation of a highly reactive Al=Al bond *in situ*, which activates the reaction solvent.<sup>4</sup> This route uses the synthetically challenging monomeric Al(I) first reported by the Roesky group (Figure 1).<sup>5</sup> To make the synthesis more scalable, an alternative route has since been explored starting from aluminium(III) iodides. These can be reduced in a stepwise fashion, through a discrete Al(II) complex to the proposed Al(I). This allows reactions on a larger scale to form the intended products, and implies a range of exciting new reduction reactions to try.



Reaction scheme showing two routes to forming a transient Al(I) complex

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## Lighting Up Group 13 Metals: Excited State Reactivity towards Sustainable Redox Catalysis

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Main group (MG) elements have recently been raised as benign and inexpensive alternatives to transition metals in organometallic chemistry.<sup>1</sup> However, this growth has not been accompanied by a thorough investigation into the potential merger of p-block elements and light-induced organometallic processes in catalysis. This is surprising, as challenging light-induced two-electron processes in MG metallic centres, such as reductive elimination, have been reported, however, remain rare.<sup>2</sup> Thus, the merger of MG chemistry and visible light induced events for excited state reactivity is a powerful strategy to develop sustainable and catalytic technologies and unveil a new landscape of sustainable reactivity.

This project focuses on the photoinduced organometallic chemistry of Group 13 (G13) elements, including Aluminium (Al) and heavier analogues, like Indium (In). Inspired by Himmel's work,<sup>3</sup> it aims to unveil the potential of G13 species to undergo oxidative addition under visible light irradiation. This is crucial for low-valent In species,<sup>4</sup> which are highly stable due to the inert pair effect,<sup>5</sup> and possibly utilisable with Al in reactivity with stable molecules such as N<sub>2</sub> and Csp<sup>3</sup>-H bonds.<sup>6</sup> Low-valent In species have been isolated and experimentally and theoretically characterised (Figure 1), showing promising electronic structures and reactivity to be applied in photoinduced organometallics. The ultimate goal of this project is to develop a catalytic cycle based on the E(I)/E(III) redox couple. This innovative approach could revolutionize chemical transformations, reducing reliance on precious transition metal catalysts and minimizing environmental impact.

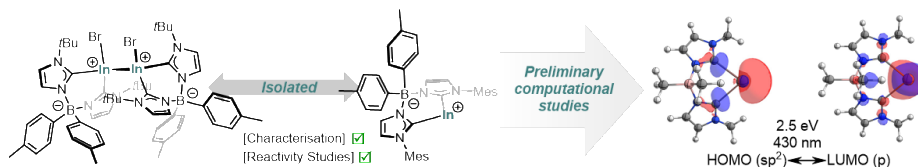


Figure 1. Isolated bis(NHC) supported low valent In species for potential applications in photocatalysis.

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## Exploring the organometallic reactivity and applications of bis(NHC)-supported pnictidenes

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Noble metals like Pd and Rh are essential in the chemical industry due to their ability to substrate coordination and organometallic redox events in catalysis.<sup>1</sup> However, their supply and price instability have recently spurred interest in main group elements, which show potential for mimicking two-electron processes of transition metals.<sup>2</sup> Within this realm, antimony (Sb) presents itself as a versatile element with multiple oxidation states ranging from -3 to +5, but remains underexplored in the field of redox catalysis.<sup>3</sup>

With the aim of studying the reactivity of low valent pnictidenes, we isolated and characterized novel Sb(III) complexes supported by anionic bis(NHC) ligands. Reduced Sb(I) species showed promising stoichiometric oxidative addition reactions with multiple small molecules. Interestingly, such compounds have shown to be excellent catalysts for the hydrodefluorination of polyfluorinated (hetero)aromatic scaffolds. Furthermore, their catalysis in the synthesis of thiosilanes, show potential in the application of these pnictidenes for on-demand release of dihydrogen. This work highlights Sb's ability to undergo organometallic processes and their potential applications within catalysis and hydrogen storage/release.

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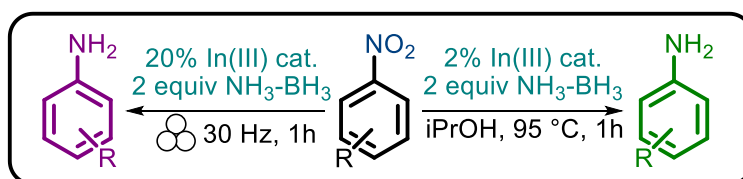
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## Solvothermal and mechanochemical indium-catalysed transfer hydrogenation of nitroarenes to anilines using ammonia-borane.

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Chemoselective hydrogenation of nitroarenes is an imperative reaction in fine chemical industry as it is a key reaction in the synthesis of both pharmaceuticals and dyes.<sup>1</sup> However, most catalysts for this transformation are based on noble metals. Noble metals often use hydrogen gas to complete this transformation which requires specialised equipment and can be expensive to dispense and store.<sup>2</sup> Using ammonia-borane (AB) as a mild H<sub>2</sub> alternative, we report the indium-catalysed transfer hydrogenation (TH) of nitroarenes to the corresponding anilines under mild conditions at low catalytic loadings (< 2mol%). Notably, our system utilises air and moisture tolerant indium Lewis acids that can catalyse the reaction *via* both solvothermal methods, using isopropanol as the solvent, and mechanochemically *via* ball milling. Furthermore, we undertake a substrate scope containing various other reducible functional groups and compare the activity and selectivity between solvothermal and mechanochemical methods for our system. The application of our system toward the synthesis of bioactive molecules is also attempted.



**Figure 1:** General synthetic method for solid-state and solution phase transfer hydrogenation of nitroarenes via In(III) catalysts.

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## Mechanochemical Synthesis of Organosodiums

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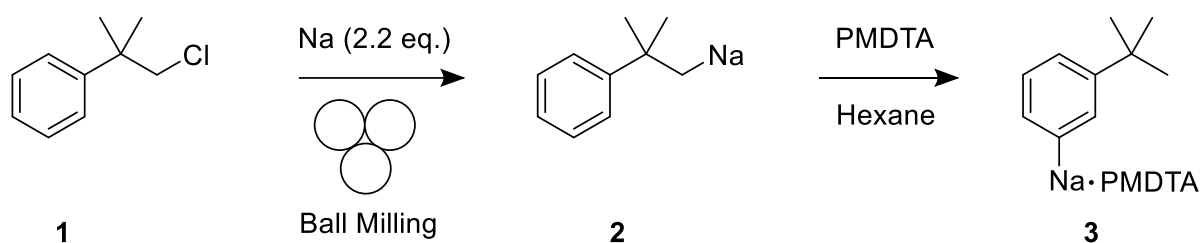
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Organolithium reagents are widely utilised reagents in organic synthesis. However, the relatively low crustal abundance (0.002% for Li vs 2.36% for Na) and increasing demand for lithium necessitates exploration of more sustainable alternatives. Organosodium compounds present a lower-cost, more sustainable, alternative to organolithiums and have distinct reactivity.<sup>1</sup> Currently, two methods are used to synthesise organosodiums: 1) Transmetallation from organolithiums. 2) Sodium-halogen exchange using a sodium dispersion. It would therefore be advantageous to develop a route to access organosodiums that does not require lithium, or the use of a sodium dispersion, which presents practical difficulties.<sup>2</sup>

This poster will describe our recent work employing mechanochemistry to develop a sustainable synthesis of organosodium reagents. Our approach allows the reaction of cheap, easily handled, sodium lumps with alkyl halides (e.g. **1**) with little to no solvent. We will describe the optimization and generality of this new methodology to form a variety of different organosodiums (e.g. **2**), including the effect of exogenous ligands upon aggregation states, stability and structure (probed in solution by NMR and in the solid state by X-ray crystallography). Moreover, a curious  $sp^3$ - $sp^2$  sodium shift process (e.g. **2**  $\rightarrow$  **3**) will be discussed. This new methodology opens the door for future studies into the preparation and synthetic utility of these highly reactive reagents.



The mechanochemical synthesis of neophylsodium, **2**, and subsequent rearrangement on addition of PMDTA to give **3**.

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## Gallium-68 Encapsulated Inorganic Nanoparticles for PET and Fluorescence Imaging

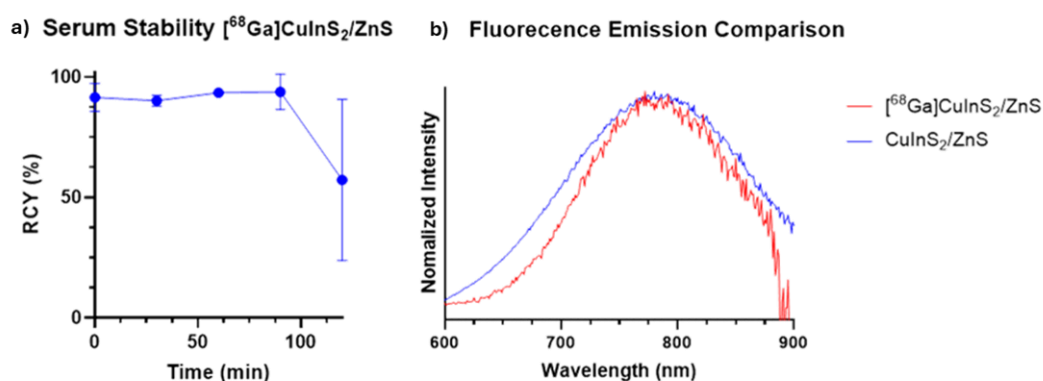
Aisleen S. Whelan<sup>ab</sup>, Thomas W. Price<sup>a</sup>, H lio M. Gil<sup>a</sup>, Laur ne Wagner<sup>a</sup>, Samantha Y.A. Terry<sup>a</sup>, Mark Green<sup>a</sup>, Sean Woodall<sup>b</sup>, Graeme J. Stasiuk<sup>a</sup>

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Dual-modal imaging, combining PET and fluorescence, offers great potential for enhancing tumour detection and image-guided surgery using one molecule. Quantum dots (QDs), with their high brightness, stability, and tuneable optical properties, serve as an ideal platform for these applications.<sup>1,2</sup> This work focuses on encapsulating gallium-68 within Copper Indium Sulphide/Zinc Sulphide (CuInS<sub>2</sub>/ZnS) QDs to enable simultaneous PET and fluorescence imaging, allowing for staging and surgical guidance on the same day. CuInS<sub>2</sub>/ZnS QDs were synthesized using a microwave method, which ensures rapid and uniform heating for efficient core-shell formation. Gallium-68 was incorporated into the QD core during synthesis. The QDs were characterized using fluorescence analysis, UV-Vis absorbance, and dynamic light scattering to confirm optical properties and size distribution. Serum stability was assessed via instant thin-layer chromatography (iTLC). The emission peaks of CuInS<sub>2</sub>/ZnS and [<sup>68</sup>Ga]CuInS<sub>2</sub>/ZnS QDs remained at approximately 780 nm, indicating that gallium-68 integration preserved fluorescence properties. iTLC demonstrated effective gallium-68 encapsulation with a radiochemical conversion of 44%. Serum stability studies revealed gallium-68 retention above 90% for over 90 minutes (92% at 0 min, 94% at 90 min) before decreasing to 58% at 120 minutes, maintaining robust stability over two half-lives. This work successfully demonstrates gallium-68 encapsulation within CuInS<sub>2</sub>/ZnS QDs for dual-modal imaging. The preserved fluorescence and high stability highlight their potential for improving tumour detection and surgical outcomes, streamlining imaging procedures, and reducing patient burden.



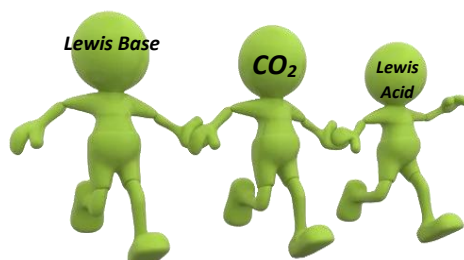
a) Serum Stability of gallium-68 Encapsulated QDs Over Two Half-Lives b) Comparison of Normalized Fluorescence Emission for QDs and gallium-68 Encapsulated QDs

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## Transition Metal Alternatives Towards CO<sub>2</sub> Activation and Conversion

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Transition metal alternatives have become more popular in research to mitigate the use of precious metals in catalysis and small molecule activation. Main group elements have emerged as sensible replacements due to their potential high reactivity and abundance. Recycling CO<sub>2</sub> towards useful small molecules is a highly desirable process to veer away from the continued use of damaging fuels for many industrial procedures.<sup>1</sup>

I have been investigating the use of *p*-block hydrides and frustrated Lewis pairs for the activation and conversion of CO<sub>2</sub>. A frustrated Lewis pair is a mixture containing a Lewis acid and Lewis base which cannot form a classical adduct due to steric hindrance. In this work, I will be presenting a range of synthesised main group Lewis acids varying in Lewis base pairs, group 13 metal centres and ligand backbones.<sup>2,3</sup> Differences in Lewis acidity and ligand design have been studied in relation to CO<sub>2</sub> activation. Plans for carrying out CO<sub>2</sub> hydrogenation with these complexes are mentioned, along with some interesting results such as intramolecular frustrated Lewis pair behaviour being seen within these complexes.

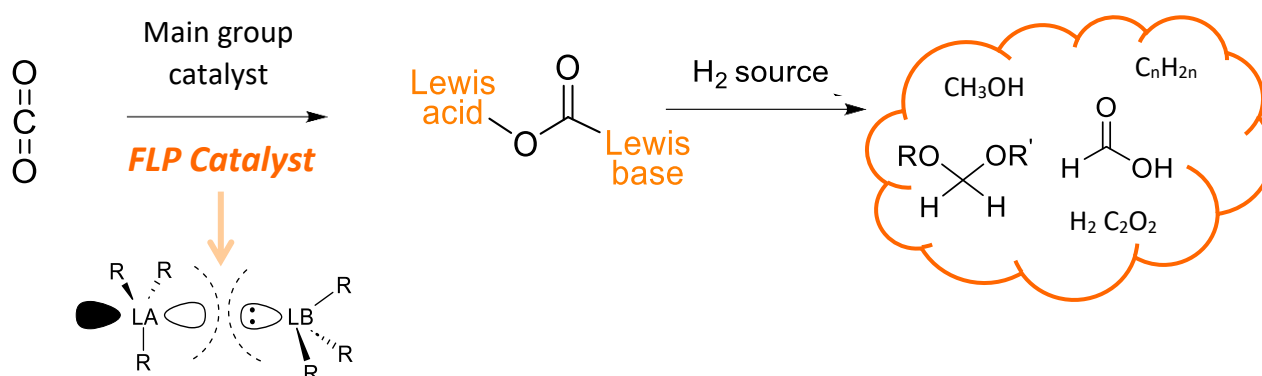


Figure 1: An example showing main group catalysis being carried out with frustrated Lewis pair catalysts for the activation and conversion of CO<sub>2</sub>

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## TADF at the extreme (of visible): using Lewis acids to tune fluorophores for 3<sup>rd</sup> generation OLEDs

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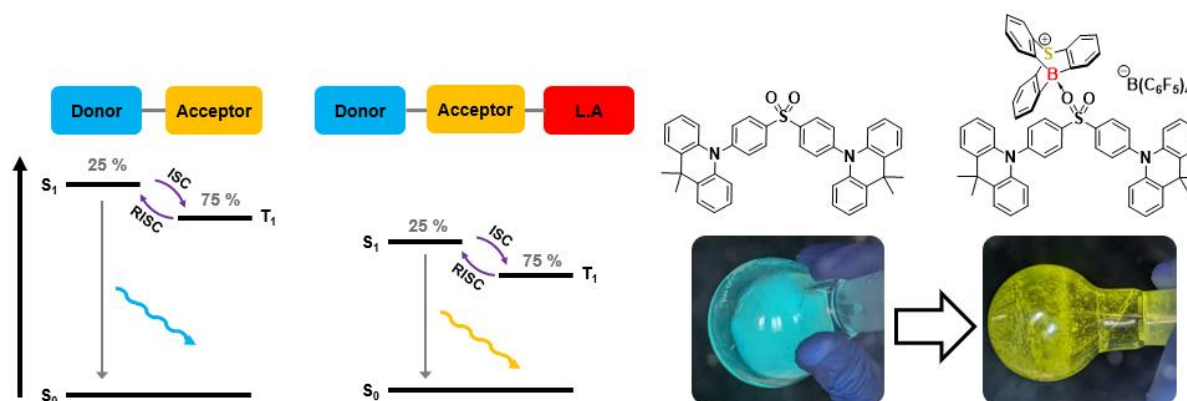
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The utilisation of thermally-activated delayed fluorescence (TADF) in the design of OLED fluorophores is a rapidly evolving research area in the pursuit of ever more energy efficient devices.<sup>1</sup> TADF allows for organic systems to harvest the triplet state that results from electronic excitation via a reverse intersystem crossing (RISC), therefore increasing external quantum efficiency.<sup>2</sup> Compared to blue and green, red and near-IR emitters are an underdeveloped area of TADF research.<sup>1</sup> One of the reasons for this is that the engineering of low-lying  $S_1$  states typically requires significantly expanded  $\pi$ -conjugated systems, increasing synthetic complexity.<sup>3,4</sup> Extended  $\pi$ -conjugation also makes  $\pi$ - $\pi$  stacking more likely, which can facilitate non-radiative decay.<sup>1</sup>

It has been previously reported that Lewis acids can lower the LUMO and  $S_1$  energy of donor-acceptor fluorophores upon Lewis adduct formation with the acceptor moiety.<sup>5</sup> Herein our group reports the bathochromic shift of TADF emission by the Lewis adduct formation of fluorophores with a range of strong Lewis acids. For example, triptycene-derived pyramidalised-boron Lewis super acids provide excellent electrophilicity coupled with the formation of bench-stable adducts.<sup>6</sup> This opens up the possibility of tuning the emission spectrum of existing TADF fluorophores.



**Figure 1.** Left: The visualization of a reduced HOMO-LUMO/ $S_0$ - $S_1$  gap upon TADF fluorophore Lewis adduct formation. Right: The observed redshift of fluorescence observed when the fluorophore is coordinated to 9-sulfonium-10-boratriptycene.

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# Monomeric $\alpha$ -Silyl Organolithium and Organosodium Complexes mediated CO and CO<sub>2</sub> Activations

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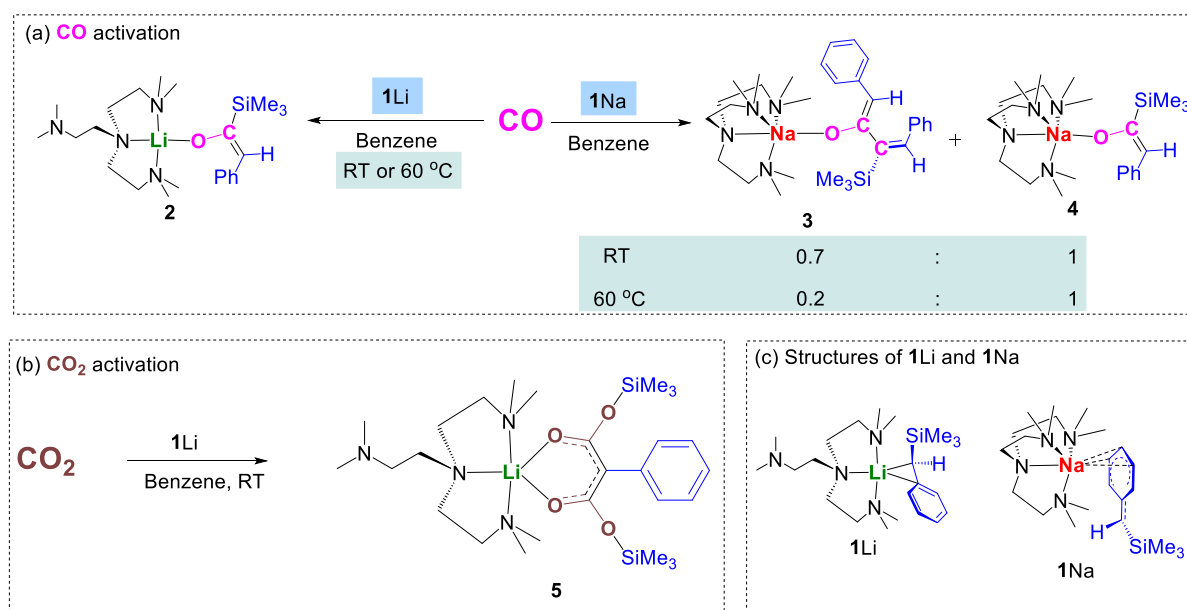
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**Keywords:** Organolithium, Organosodium, Reactivity, Carbon monoxide, Carbon dioxide

The activations of key C1 feedstocks, carbon monoxide (CO) and CO<sub>2</sub>, by transition-metal, p-block and Group-2 metal complexes have been well-documented<sup>1,2</sup>, but less common for group-1 alkali metal complexes, especially for organosodiums. Herein we report reactions between CO/CO<sub>2</sub> and monomeric lithium/sodium silyl benzyl complex, [(Me<sub>6</sub>Tren)AM(CHPhSiMe<sub>3</sub>)] (AM = Li: **1Li**; AM = Na, **1Na**). For CO, metal identity-dependent reaction patterns were observed. For CO<sub>2</sub>, an unusual silyloxo-substituted acetylacetonate complex was isolated, which is new for CO<sub>2</sub> activation. Computational reaction pathway analysis unveiled the reaction mechanisms at an unprecedented level.



**Figure 1.** activation reactions of (a) CO and (b) CO<sub>2</sub> and (c) structures of **1Li** and **1Na**.

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