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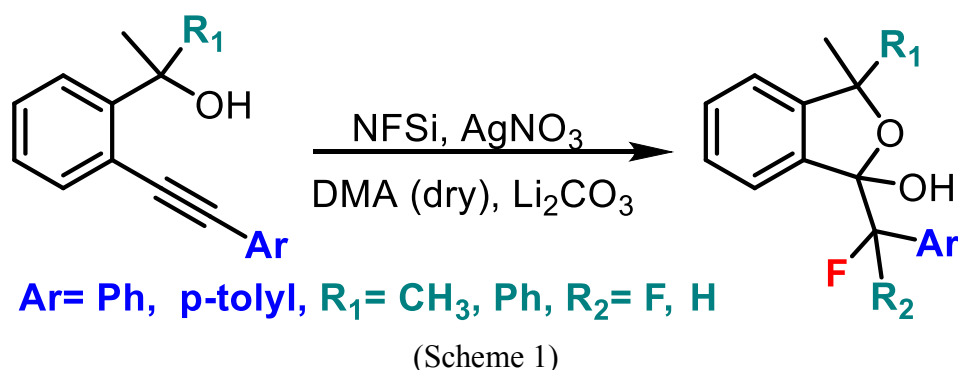


POSTERS

Silver-catalysed fluorocyclisation of alkyne-substituted tertiary alcohols – P

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Fluorinated heterocycles are highly desirable targets for the pharmaceutical industry because heterocyclic compounds often form the core structure in drug candidate molecules and the incorporation of fluorine can enhance their biological activity [1]. The aim of this research was to design new fluorocyclisation procedures for aromatic alkynes containing tertiary alcohol groups that act as the internal nucleophiles (Scheme 1) [2, 3]. Here, the electrophilic reagent NFSi, in the presence of 10% silver nitrate as a catalyst, has been successfully applied to give new benzofurans. Either mono- or di-fluorinated products can be formed, dependent upon the reaction conditions and the R1 substituent.



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Addition of C–F Bonds to a Mg(I)–Mg(I) Bond_P

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The activation of strong carbon-fluorine bonds is of significant interest, not least because around 20 % of synthetic compounds produced in pharmaceutical and agricultural chemistry contain at least one fluorine atom [1].

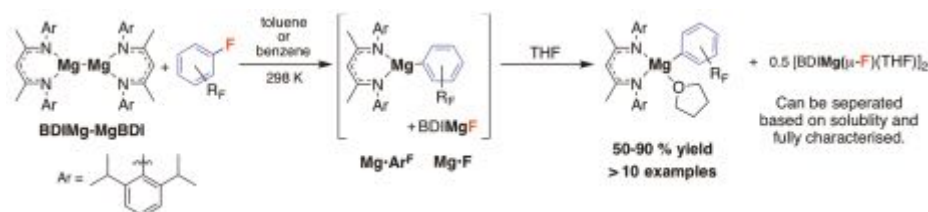


Figure 1: General synthetic approach towards the synthesis and isolation of new $\text{Mg}\bullet\text{Ar}^{\text{F}}$ complexes.

We became interested in the highly reactive, low-valent magnesium complex **BDIMg–MgBDI** (Figure 1) in the context of C–F bond activation. First reported in a landmark paper by Jones and Stasch, the Mg–Mg complex has previously been shown to activate an array of substrates via oxidative addition across the Mg(I)–Mg(I) bond [2, 3]. Here, we show that **BDIMg–MgBDI** reacts with aromatic sp^2 C–F bonds resulting in the formation of two new magnesium species from a single reaction; **Mg•Ar^F** and **Mg•F** (Scheme 1). The scope of C–F bond activation includes a range of perfluorinated and partially fluorinated arenes. **Mg•Ar^F** can be seen as discrete ‘Grignard type’ compounds and the reaction a homogeneous analogue of Grignard formation [4].

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Frustrated Lewis Pair Carboranes – P

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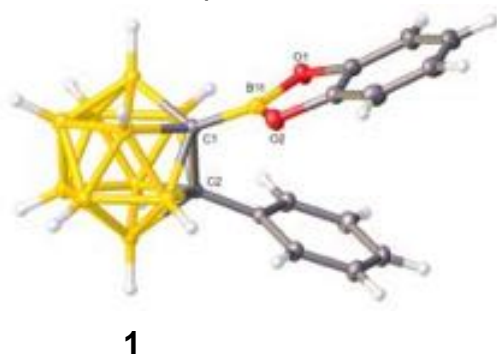
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Frustrated Lewis pairs (FLPs) have become important systems for performing transition metal-free catalysis.^{1,2} Typically, $B(C_6F_5)_3$ (or analogues) is used as the Lewis acid and phosphines (PR_3) are used as the Lewis base.¹ Two key variants are: having one molecule as the Lewis acid and one as the Lewis base (intermolecular FLPs) or installing both functionalities on the same molecule (intramolecular FLPs). Carborane cages have not so far been investigated for use in FLP chemistry despite several useful properties including:

1. High chemical stability;
2. The potential for tuning the distance between FLP fragments through different carborane isomers or clusters of different geometries;
3. The electron withdrawing nature of the carborane benefitting the Lewis acid site;
4. Tunability of different substituents on the cage including both the acid or base sites.

This work describes the incorporation of the Lewis acidic boron-catechol (1,3,2-benzodioxaborolyl) centre onto several carborane backbones, e.g. **1**. These compounds were characterised spectroscopically and



crystallographically and are the first examples of boron-catechol units on carborane cages. These Lewis acidic carboranes were then combined with several Lewis bases to form FLP systems which show catalytic activity towards Michael addition reactions at least as good as non-carborane based metal-free catalytic systems.³

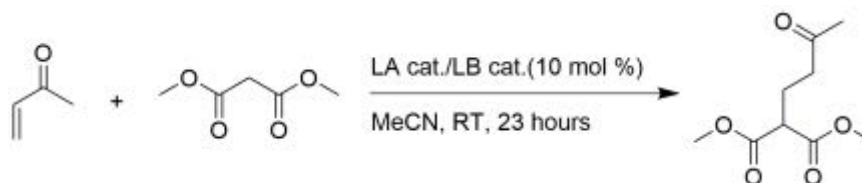


Figure 1 Michael addition of dimethyl malonate and 3-buten-2-one with Lewis acid and Lewis base catalysts (10 mol%) at room temperature in acetonitrile.

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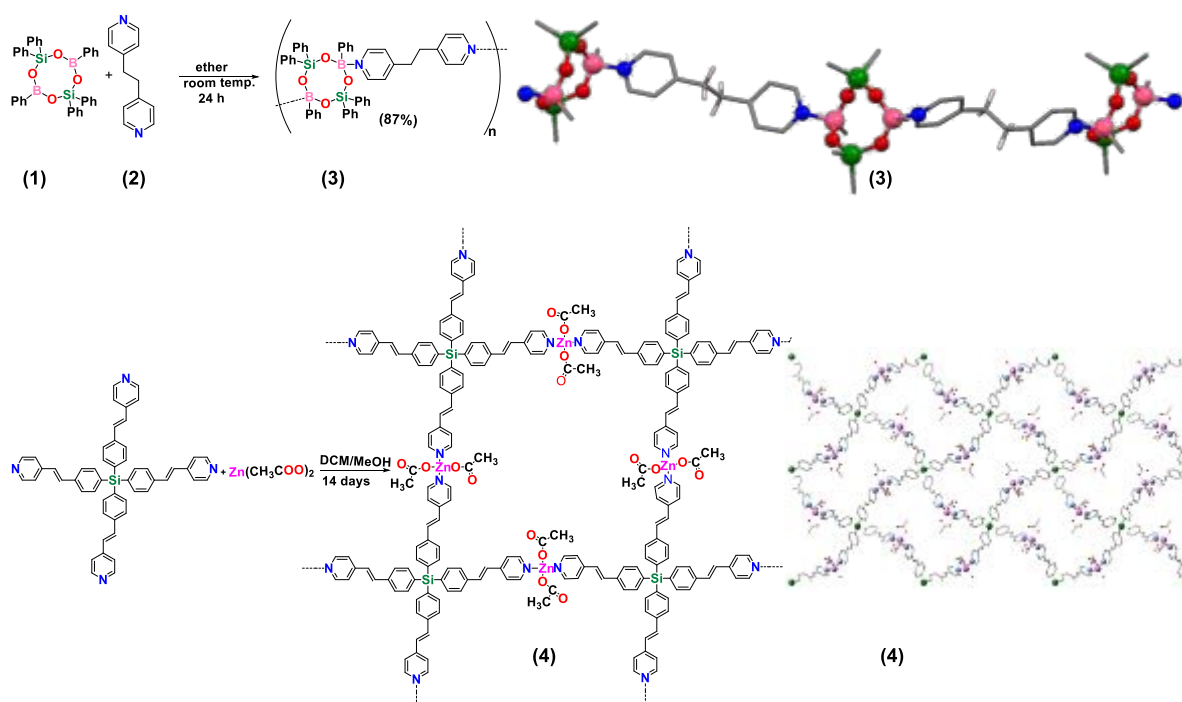
Silicon-Containing COFs and MOFs for CO₂ Capture – P

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Globally, anthropogenic use of fossil fuels as the major source of energy for domestic and industrial applications¹ has led to an increase in the concentration of CO₂ in the atmosphere, thus increasing global warming.² The concentration of CO₂ in the atmosphere can be curbed by capturing it at source. This study is being piloted in order to explore the potential of novel silicon-based Covalent Organic Frameworks (COFs) and Metal-Organic Frameworks (MOFs) for CO₂ capture and to avert its emission into the atmosphere after the burning of fossil fuels.³ Silicon containing Lewis acid e.g. **(1)** has been coordinated with a range of nitrogen containing Lewis bases e.g. **(2)** to give a series of 1D polymers such as **(3)** below. In addition, a number of novel silicon based tetrakis-, tris- and di- aryl-pyridines and aryl-carboxylic acids have been synthesized, characterized and then reacted with metal ions e.g. Zn(CH₃COO)₂ to give a 2D Metal-Organic Framework (MOF) **(4)**



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Catalytic reduction of C=O bonds by group 13 catalysts: inner sphere vs outer sphere mechanisms - P

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There has been much scientific focus in recent years on the catalytic reduction of CO₂. This is partly due to environmental factors, but also due to its nontoxic and inexpensive nature as a potential C1 chemical feedstock. A number of recent efforts have concentrated on the development of Main Group catalysts which are capable of effecting this transformation, due to their reduced cost, toxicity and increased abundance relative to transition metals. A particularly successful method is the catalytic reduction of C=O functionalities by insertion into a metal hydride bond. For CO₂, there have been a variety of single site systems reported that are capable of accomplishing this, with one of the most efficient being a Nacnac-stabilized gallium hydride system, {HC(MeC^{Dipp}N)₂}Ga(^tBu)H, reported by the Aldridge group, which has attained turnover frequencies of up to 2.5 h⁻¹ at 10 mol% and 60°C.¹

Given the observed propensity of Group 13 hydrides for such reactivity, a variety of β-diketiminate systems of the type {HC(XC^{Dipp}N)₂}M(R)H (M = Al, Ga; X = Me, NMe₂) have been developed and their reactivity towards CO₂ probed. Through systematic investigation of both stoichiometric and catalytic reactivity, insight has been obtained into the effects that metal, the metal bound R group and the NacNac backbone X group have on (i) the insertion of CO₂ into the metal hydride bond and (ii) the metathetical regeneration of the hydride.

A report of the use of related systems for the catalytic hydroboration of carbonyl-containing organic compounds,² led us to initiate an investigation of the mechanism by which this reactivity occurs. Based on this work and our CO₂ reduction chemistry, we find that the pathways for the reduction of CO-containing compounds by aluminium and gallium hydrides are different. The weaker nature of Ga-O bonds allows for an inner-sphere metathetical process for regeneration of the metal hydride, while for aluminium an outer-sphere mechanism pertains, thereby avoiding the thermodynamic sink represented by the Al-O bond.

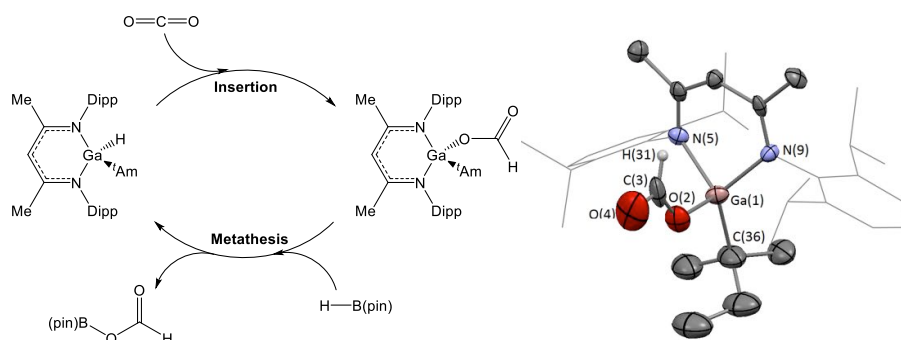


Figure 1: Reported mechanism for the reduction by pinacolborane of CO₂ catalysed by (Nacnac)DippGa(^tAm)H (left) and the molecular structure of the formate intermediate.

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Heterobimetallic derivatives of bis(carborane) – P

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Bis(*o*-carborane, the simplest bis(carborane) species, is composed of two *ortho*-C₂B₁₀H₁₁ clusters linked by a carbon-carbon bond. Recent developments in its synthesis have led to a surge of interest surrounding the chemistry of this molecule. In the Welch group, we have explored both single- and double-deboronation followed by homometalation to yield either metallacarborane/carborane¹ (**1**) or metallacarborane/metallacarborane² (**2**) products respectively. Herein, we focus on the natural progression of this chemistry to target mixed metal derivatives.

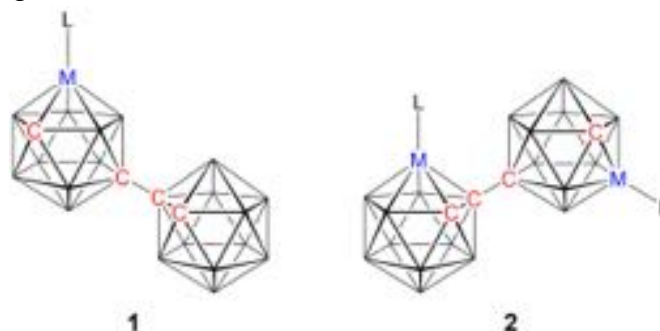


Figure 1 Structures of 2,1,8-MC₂B₉H₁₀-1',2'-C₂B₁₀H₁₁ (**1**) and 3,1,2-MC₂B₉H₁₀-2',1',8'-MC₂B₉H₁₀ (**2**). Metal fragments ML = CoCp or Ru(*p*-cymene)

Using the CoCp derivative of **1** as a starting point, deboronation of the second cage was developed using 'wet' fluoride which has been shown to be a mild alternative to the standard KOH/EtOH deboronation method. Subsequent metalation of the [CoCpC₂B₉H₁₀-*nido*-C₂B₉H₁₁]⁻ anion led to the isolation of the first example of a heterobimetallic bis(carborane) derivative (**3**). An analogous species using Ru(*p*-cym) as the initial metal fragment has since been prepared. Ongoing work is focused on expanding the scope of this reaction with the intention of incorporating two catalytically-active metal fragments to generate a tandem catalyst.

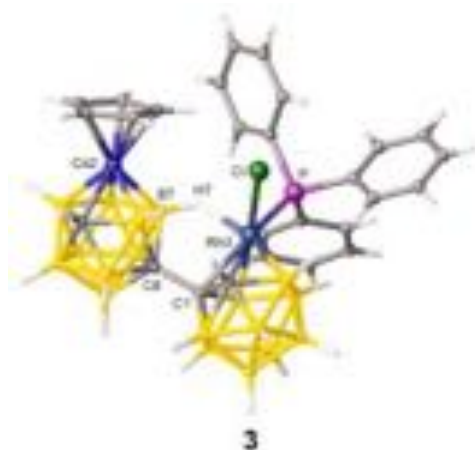


Figure 2 Molecular structure of 2,1,8-Co(Cp)C₂B₉H₁₀-3',1',2'-Rh(PPh₃)C₂B₉H₁₀ (**3**).

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Expanding the range of unsymmetrical diboranes – P

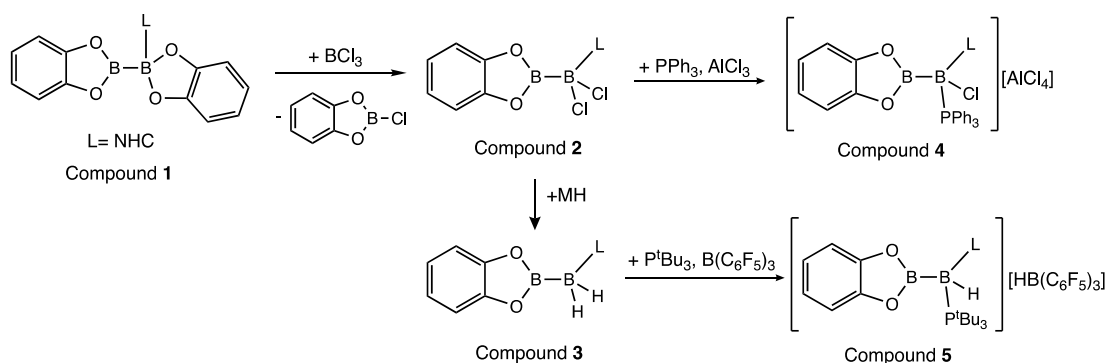
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Diborane(4) compounds have received considerable interest recently, particularly, examples that possess two distinct boron moieties,¹ these unsymmetrical diborane(4) species can be easily achieved by adding a neutral or anionic Lewis base to a (RO)₂B-B(OR)₂ precursor, quaternising one boron centre. This leads to the polarisation of the B-B σ bond and these mixed sp²/sp³ species can then react as a source of nucleophilic boron with an array of carbon electrophiles even in the absence of precious metal catalysts, providing a powerful route for forming C-B bonds.²



However, the reactivity of diborane(4) species as strong electrophiles has been limited to highly reactive species, such as B₂Cl₄, that require complex synthesis due to low thermal stability.³ Our initial goal is the development of a simple route to readily functionalisable unsymmetric diborane(4) compounds that are more stable than B₂Cl₄ and can be readily converted to strongly electrophilic diborane(4) species. We have recently achieved the synthesis of **2** in two steps from previously reported compound **1**.⁴ This route combines a NHC adduct of (RO)₂B-B(OR)₂ with BCl₃ to form **2** cleanly after removal of (RO)₂BX by-product. Compound **2** is a highly useful precursor and herein we present our studies into the substitution of chloride using metal hydrides to generate compound **3**, and the formation and reactivity of the di-boro-monocations of compounds **2** and **3**. The latter are readily accessible by adding AlCl₃ and B(C₆F₅)₃ to **2** and **3**, respectively, and with addition of a Lewis base to the putative di-boro(4) mono-cations compounds **4** and **5** can be isolated.

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Conjugated Polymers and Oligomers with BN or BP Units in the Main Chain Prepared by Silicon/Boron Exchange Polycondensation – P

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Although the isoelectronic relationship between BN and CC units has been well-recognized and exploited, particularly, to tune the properties of polycyclic aromatic hydrocarbons,¹ BN (or BP)² units as linkages in polymers are relatively unexplored.^{3,4} For this purpose, we have developed a highly efficient polycondensation strategy using silicon/boron exchange under mild conditions.⁵ This enabled the synthesis of the first poly(*p*-phenylene iminoborane) (**BN-PPV**), i.e., a BN analogue of poly(*p*-phenylene vinylene) (PPV), with an average molecular weight of $M_w = 44,500$.⁶ We recently extended this approach to the preparation of BP-containing oligomers **BP1** and **BP2**.



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Siloxane-Based Linkers in the Construction of Porous 3D MOFs and Hydrogen-Bonded Assemblies – P

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While the silicon-oxygen bond is prevalent in well-known porous materials including zeolites, organosilicas, POSS hybrids and so on, there is a dearth of literature concerned with incorporating Si-O functionality in metal-organic frameworks, and incorporation of a siloxane-based linker into a porous 3D-connected MOF has not been reported to date. To this end, three highly-connected organosilicon polycarboxylic acids (Figure 1) have been prepared and applied in the construction of MOFs. **L1-H₆** itself crystallizes as an unusual interpenetrated 3D hydrogen-bonded framework. Reaction of **L1-H₆** with Zn(II) gave **MOF 1** – a 3D MOF incorporating Si-O-Si functionality with the rare **fsy** topology (Figure 2). Cleavage of **L1-H₆** gives a silanol-based triacid **L2-H₃** which is shown to give a coordination polymer (**MOF 2**) with Zn(II) consisting of 2D layers which assemble by hydrogen-bonding to afford a 3D supramolecular structure with **flu** topology. The trisiloxane **L3-H₆** crystallizes through hydrogen-bonding to give 2D corrugated layers. Reaction of **L3-H₆** with Zn(II) afforded **MOF 3** – a 3D MOF built from infinite Zn-based rod nodes cross-linked by **L3**.

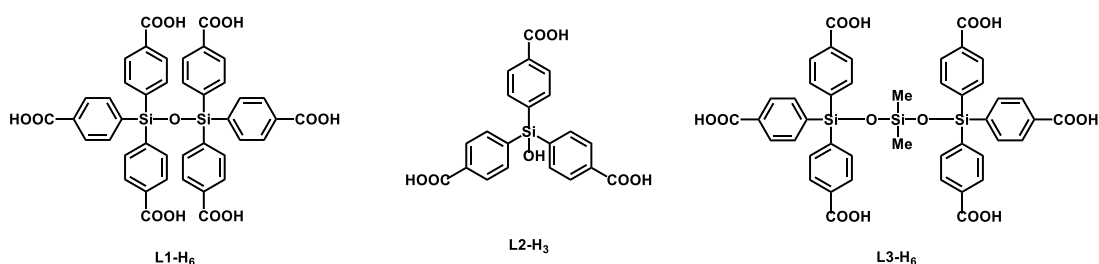


Figure 1: Structures of carboxylic acid linkers used in the preparation of MOFs.

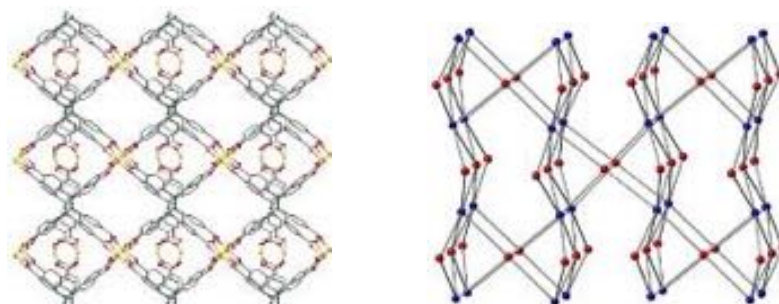


Figure 2: (Left) MOF 1 viewed along 010 direction. (Right) Schematic of **fsy** topology in MOF 1.

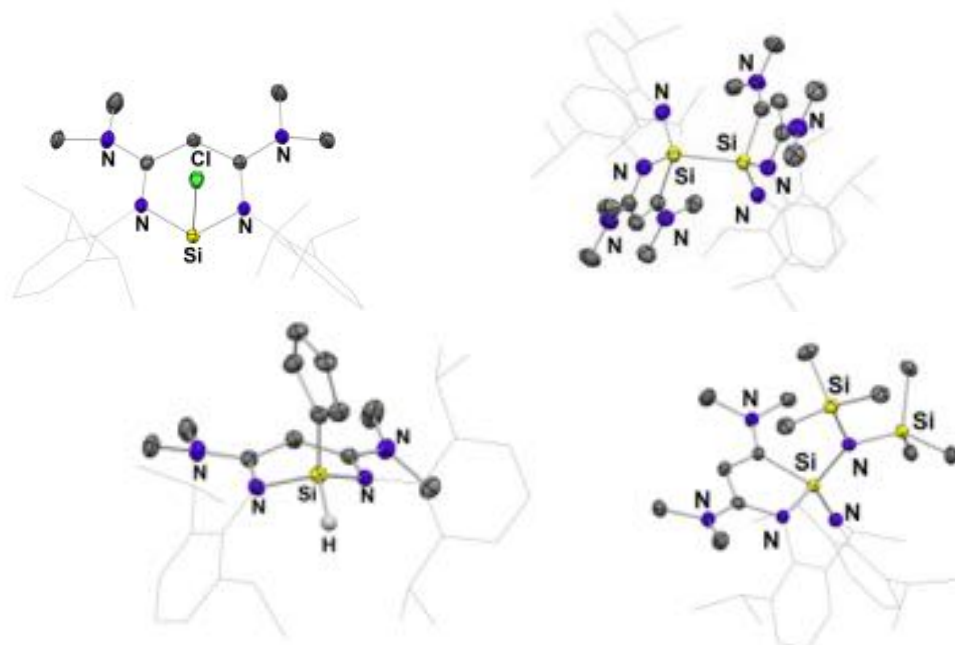
A novel beta-diketiminate stabilised chlorosilylene: Synthesis and reactivity studies

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The past ten years have witnessed significant advances in the chemistry of divalent silicon compounds – both as heavier analogues of carbenes, and as reactive entities in their own right (e.g. for the activation of E-H bonds).¹ Moreover, chloro-silylenes have been shown to be suitable precursors to various landmark compounds, such as monovalent Si^I and hydrido-silylene complexes.^{2a,b} Based on the well-established beta-diketiminate (“Nacnac”) ligand family, which has been widely employed in stabilizing reactive sub-valent species,³ we have utilized our recently-developed amino-functionalised Nacnac (“N-nacnac”) system⁴ in isolating and characterizing the first example of a beta-diketiminate supported chlorosilylene.

Preliminary reactivity studies have revealed unusual behaviour for this novel chlorosilylene, which demonstrates the tendency for thermodynamically-favoured molecular rearrangements towards the higher oxidation states of silicon. Notable examples include the isolation of a Si^{III}-dimer from the reduction with potassium graphite (for which the *in situ* EPR spectrum suggest the initial formation of a silicon-centred radical species), and two different rearrangement patterns upon salt metathesis from Si^{II} to Si^{IV}.



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Reactivity of the 2-phosphaethynolate anion towards amino acids

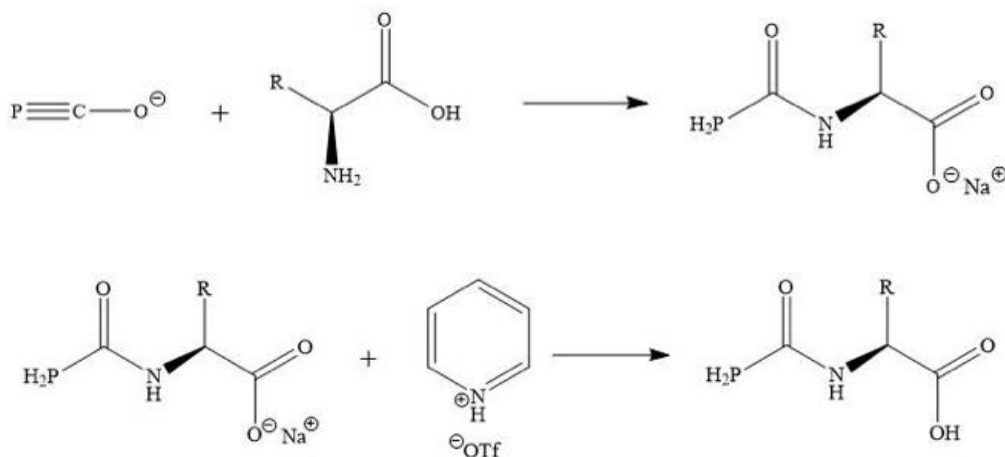
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The 2-phosphaethynolate anion (PCO^- , a heavier analogue of cyanate), was first reported in 1992 as a lithium salt by Becker and co-workers.¹ However, given the inherent reactivity of this salt, this novel anion was not extensively studied. Recently, the synthesis of more stable salts has been reported by using heavier alkali metal counter cations.^{2–5}

In 1828, Wöhler reported the synthesis of urea by the reaction between silver cyanate and ammonium chloride. Inspired by this seminal study, we recently explored the reactivity of PCO^- towards ammonium salts. This research resulted in the synthesis of phosphinecarboxamide ($\text{PH}_2\text{C}(\text{O})\text{NH}_2$), a heavier analogue of urea, which is both air and moisture stable, unlike most primary phosphines.^{6, 7}

In this study, we describe the formation of phosphinecarboxamides from the reaction between PCO^- and amino acids to yield sodium salts, and subsequent protonation by reacting the salt with an acid, as shown in the image.



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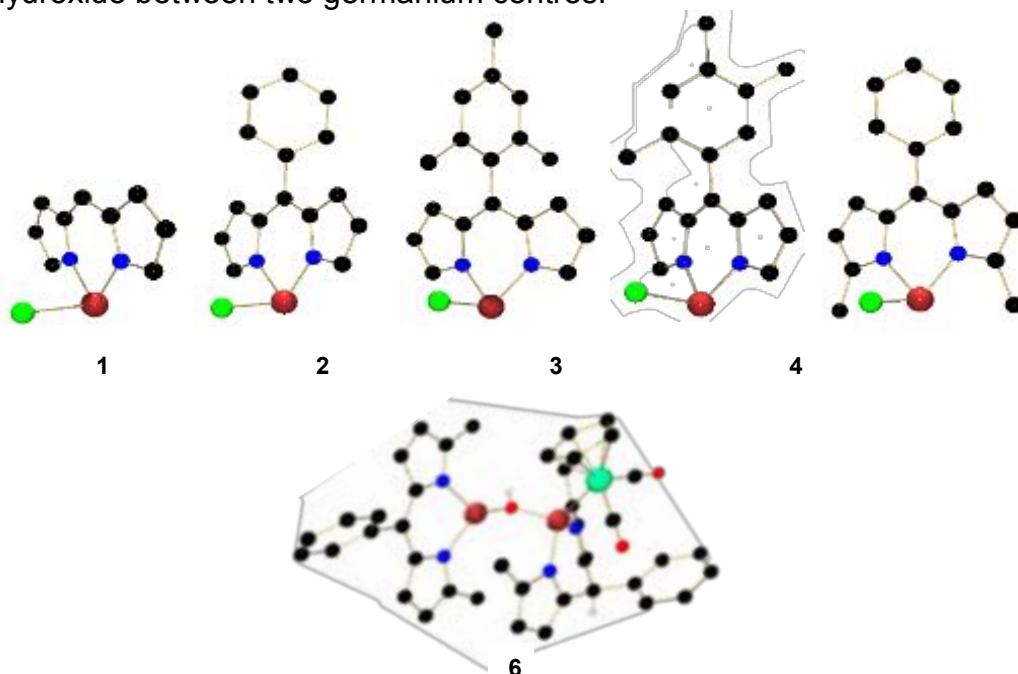
Synthesis, Reactivity, and High Pressure Studies of Germanium Analogues of BODIPY_P

Charlotte E. Gidman^a, Alexandra L. Gower, Ashley L. Payne, John R. Brook, Jasper E. H. B. Smith, William Lewis, Neil R. Champness, and Deborah L. Kays.

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Since their discovery in 1968, boron dipyrromethene dyes (also known as BODIPY) have been of much interest to the scientific community due to their fluorescent properties. Substitutions on the *alpha*, *beta*, and/or *meso* position of the dipyrryn scaffold allows changes in their fluorescent, electrochemical and physical properties [1]. In the last 25 years main group analogues of BODIPY have been investigated, with only two examples of dipyrryns bearing group 14 metal centres having been synthesised in the last 8 years [2,3].

The lack of group 14 dipyrryns in the literature has promoted an interest in the synthesis of novel germanium analogues of BODIPY (**1-5**). High pressure crystallographic studies have been performed on **3** which shows a phase change of the solid state structure from P2₁/c to P-1 at pressures above 35.85 kbar. Reactivity of these germanium complexes *via* salt metathesis reactions have also been explored, reactions of **5** with KFp led to the formation of **6**, where introduction of a water molecule to the complex resulted in a bridging hydroxide between two germanium centres.



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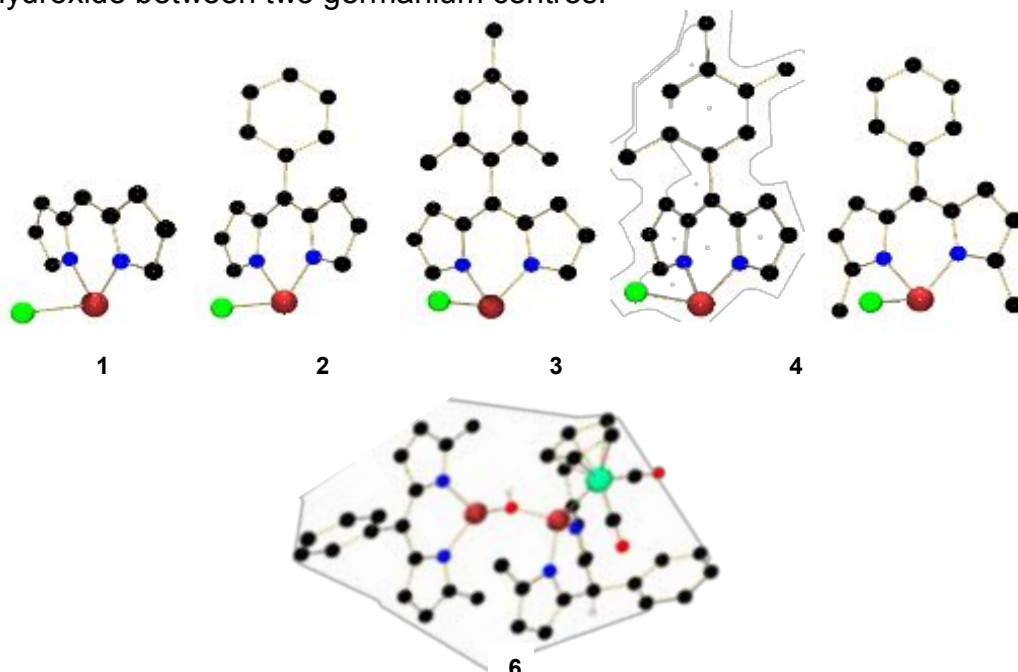
Synthesis, Reactivity, and High Pressure Studies of Germanium Analogues of BODIPY_P

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Since their discovery in 1968, boron dipyrromethene dyes (also known as BODIPY) have been of much interest to the scientific community due to their fluorescent properties. Substitutions on the *alpha*, *beta*, and/or *meso* position of the dipyrryn scaffold allows changes in their fluorescent, electrochemical and physical properties [1]. In the last 25 years main group analogues of BODIPY have been investigated, with only two examples of dipyrryns bearing group 14 metal centres having been synthesised in the last 8 years [2,3].

The lack of group 14 dipyrryns in the literature has promoted an interest in the synthesis of novel germanium analogues of BODIPY (**1-5**). High pressure crystallographic studies have been performed on **3** which shows a phase change of the solid state structure from P2₁/c to P-1 at pressures above 35.85 kbar. Reactivity of these germanium complexes *via* salt metathesis reactions have also been explored, reactions of **5** with KFp led to the formation of **6**, where introduction of a water molecule to the complex resulted in a bridging hydroxide between two germanium centres.



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Halogen Bonding Interactions in BODIPY Crystals

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Difluoroborondipyrin (BODIPY) compounds have been investigated for over 40 years as highly stable dyes with useful fluorescence and electrochemical properties.¹ The BODIPY framework can be readily functionalised, incorporating halogen atoms, for investigation in applications such as solar cell technology, sensors, and photodynamic therapy (PDT).² However, none of these studies have focused on understanding the effect of the halogen atoms on the solid state structure of BODIPY, studying weak intermolecular interactions such as halogen bonding. Halogen bonding is the non-covalent interaction that can occur between an electrophilic region of a halogen in a molecule and a nucleophilic region of another molecule (**Fig. 1**),^{3,4} and may have implications for the solid state and photophysical properties of BODIPY.

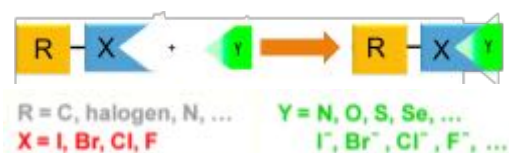


Fig. 1 Schematic representation of halogen bonding.

In order to study the halogen bonding effects in BODIPY compounds, we have crystallographically characterised bromo-BODIPY (**1**), and iodo-BODIPY (**2** and **3**) compounds (**Fig 2**). In the solid state **1** exhibits polymorphism, and shows two different types of halogen-halogen bonding. The solid state structure of iodo-BODIPY **3** exhibits short halogen-oxygen bonding interactions.

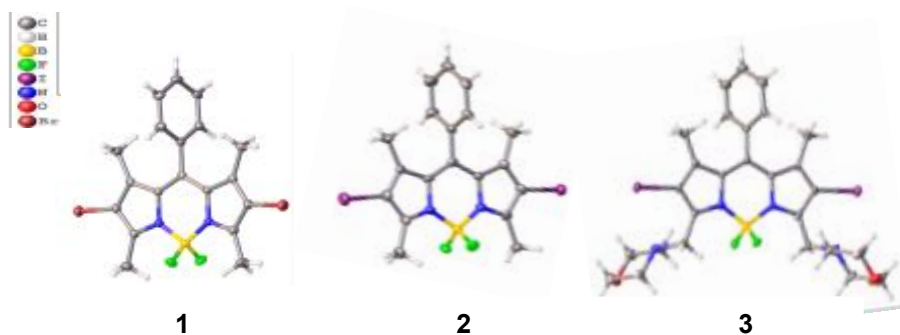


Fig. 2 Solid state structures of halogenated BODIPY compounds **1-3**.

References

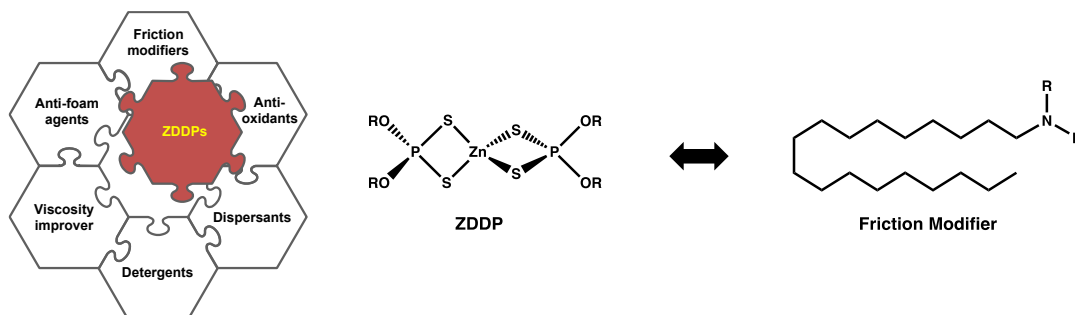
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Organophosphorus Additive Interactions in Engine Lubricant Formulations – P

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Zinc dialkyl(aryl) dithiophosphates (ZDDPs), $\text{Zn}\{\text{S}_2\text{P}(\text{OR})_2\}$, are the most successful lubricant additives ever developed. They offer not only antioxidant, but also long-lasting anti-wear and extreme pressure properties. However, in modern crankcase engine lubricants, ZDDPs are used alongside a myriad of other additives, thereby creating the potential for both synergistic and/or antagonistic interactions in solution.¹ The understanding and consequences of any such interactions however, is an area that is significantly under-developed, and thus hinders the development of next-generation engine lubricant systems.

The convergence of emission and fuel economy demands alongside tighter legislation,² in particular, highlights the pressing need for a more fundamental understanding of additive-additive interactions in order to enable the design and develop new lubricant package formulations which meet the contradictory future demands of engine lubricants. Here, we expose the complex nature and impact of solution-phase interactions of ZDDPs with various amine-functional friction modifiers of commercial interest, or suitable model amine alternatives where applicable. Complexation occurs *via* amine coordination to zinc of ZDDP and is accompanied by a significant change in coordination behavior of the associated dithiophosphate ligands.

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Selective Reduction of CO₂ with Heterobimetallic Gold---Copper Hydride Complexes

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In recent years, there has been increasing interest in monomeric and dimeric coinage metal hydride complexes. Little is known, however, about heterobimetallic compounds of coinage metals containing M–H–M interactions (M = Cu, Ag, Au).^{1,2} Here we present the synthesis and characterisation of the first examples of heterobimetallic hydrides of the coinage metals along with their application as catalysts for the reduction of carbon dioxide with a borane. We recently documented the synthesis of a series of σ -complexes of copper in which M–H and E–H (M = Al, Zn, Mg, Ca, E = B) σ -bonds reversibly coordinate to a copper(I) fragment.³ Heterobimetallic Au–H–Cu complexes have been similarly prepared by reaction of a bent {CuL₂} fragment with [(IPr)AuH] (L₂ = [{ArNC(CR₃)₂CH}]₂; Ar = Mes, C₆F₅, R = F, Me; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).



Scheme 1. Synthesis of Au–H–Cu heterobimetallics **1-3•Au**.

Complexes **1-2•Au** are an effective catalyst for the reduction of CO₂ with HBPin (HBPin = pinacolborane).^{4,5} A heterobimetallic effect is observed. The Au–H–Cu bimetallic catalyses the reaction of CO₂ and HBPin to form HO₂CBpin with vastly improved conversions and selectivity compared to the single-site monometallic complexes [(IPr)AuH] and **1-2•tol** [{CuL₂}(η^2 -toluene)].

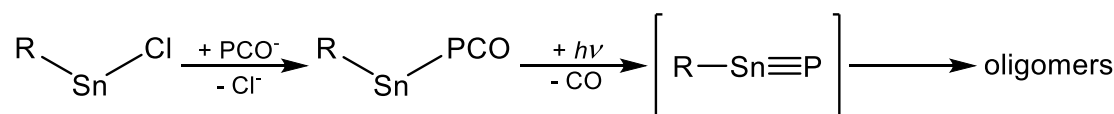
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Towards the Sn≡P Triple Bond – O

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The quest for multiple bonds between heavier main group elements has been pursued for decades.^[1] While alkynes, molecules with a C≡C triple bond, are stable species, their heavier congeners require steric and electronic stabilisation in order to enable their isolation. Thus, disilynes (2004), digermynes (2002), distannynes (2002) and diplumbynes (2000) have all been synthesised using this strategy.^[2] The bonding situation changes dramatically on descending group 14, and the bond order decreases substantially. These heavy alkyne analogues show remarkable reactivity in the activation of small molecules.^[3] To date, and in contrast to terminal transition metal phosphides, stable heteroatomic main group species exhibiting a triple bond to phosphorus are unknown.



After synthesising 2-arsaethynolate salts and demonstrating their use in cycloaddition and As⁻ transfer reactions,^[4] we decided to employ several stannylene-phosphaketenes and -arsaketenes as precursors for a phosphastannynes and arsastannynes, respectively. Bulky chlorostannynes were converted to stannylene-phosphaketenes and -arsaketenes by metathesis reaction with [Na(dioxane)_{2.5}]PCO and [Na(dioxane)_{2.5}]AsCO. Upon thermal or photolytical decarbonylation, intermediate R–Sn≡P and R–Sn≡As species are formed which subsequently tetramerise in case of terphenyl substituents. The utilisation of various amido substituents allowed the formation of corresponding trimers, dimers and monomers.

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Exploring routes to *hypercloso* metallacarboranes via ligand manipulation – P

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Wade's rules allow the structure of main group and transition metal cluster compounds to be predicted based on the number of vertices (n) and Skeletal Electron Pairs (SEPs) they possess. The aim of this project is to synthesise metallacarboranes that have fewer than the $(n+1)$ SEPs required to form a *closo* structure. Species with only (n) SEPs are referred to as *hypercloso* compounds, of which very few have been reported to date.

Previous work within the group has demonstrated that members of this class of compound can be synthesised via insertion of one-vertex one-electron transition metal fragments into anionic *closo* metallacarboranes.¹ An alternative route to *hypercloso* metallacarboranes would be to first insert a one-vertex two-electron metal fragment (isolobal with {BH}) containing at least one labile ligand and to then abstract a ligand from the metal, converting this vertex to a one-vertex zero-electron fragment, and thus the structure from *closo* to *hypercloso*.

Recent work has involved first synthesising *closo* species containing the one-vertex two-electron fragments {Ru(PPh₃)₂Cl} or {Mo(CO)₃I} followed by the subsequent abstraction of a halide (a representative example is given in figure 1) with the aim of generating *hypercloso* species containing the one-vertex zero-electron fragments {Ru(PPh₃)₂} or {Mo(CO)₃}. This poster will discuss the unanticipated consequences of such ligand abstraction.

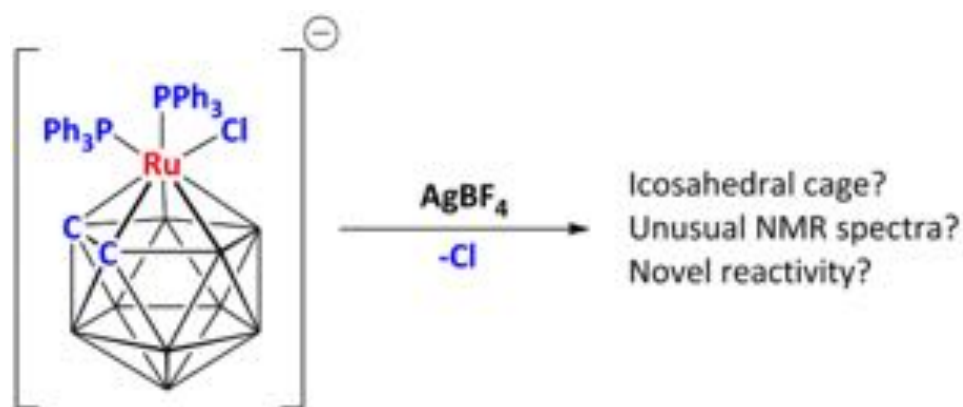


Figure 1 Proposed synthesis of a *hypercloso* 12-vertex metallacarborane containing the one-vertex zero-electron fragment {Ru(PPh₃)₂}.

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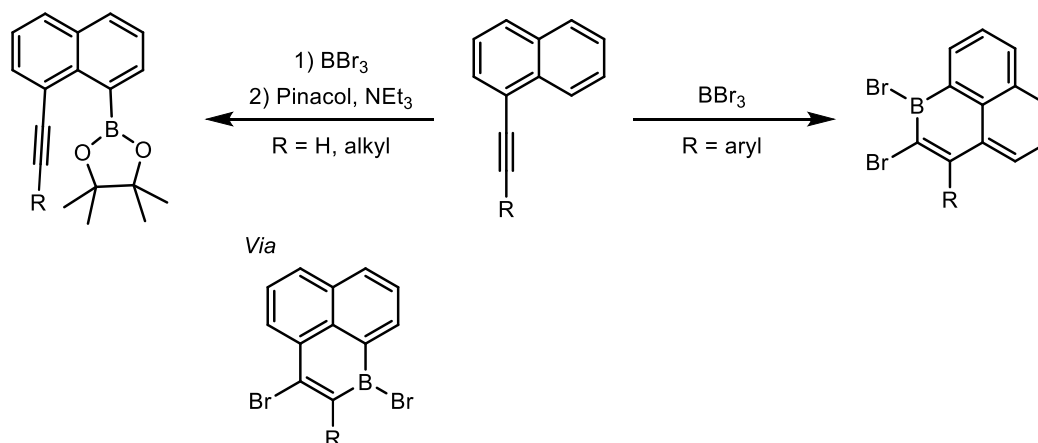
Alkyne Directed C–H Borylation and Borylative Cyclisation – P

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The elemento-boration of alkynes by boron electrophiles, particularly hydroboration, has been used as a powerful tool to form vinylboranes for decades. Recently, the scope of elemento-boration has increased due to the need for non-toxic, inexpensive routes to vinyl and aryl boronic acid derivatives.¹ Notable developments include aminoboration,² oxoboration,³ *trans*-hydroboration of alkynes,⁴ and 1,1-carboboration reactions.⁵

In contrast to hydroboration, relatively few novel haloboration reactions have been reported, despite this generating a useful ambipolar synthon. 1,2-haloboration was first reported by Lappert *et al.* in 1964,⁶ and typically involves the *syn*-1,2-addition of a B–X bond across an alkyne. We now report that 1-ethynylnaphthalene reagents undergo a range of novel transformations with BBr₃. These include alkyne directed C–H borylation of terminal and alkyl ethynylnaphthalenes *via* 1,3-dibromoboraphenalene, and borylative cyclization and rearrangement sequences of aryl ethynylnaphthalenes to yield 1,2-bromoboraphenalenes.



Scheme 1 Reactivity of ethynylnaphthalenes with BBr₃

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M–H Bond Activation By A Ruthenium *Bis*(Dinitrogen) Complex

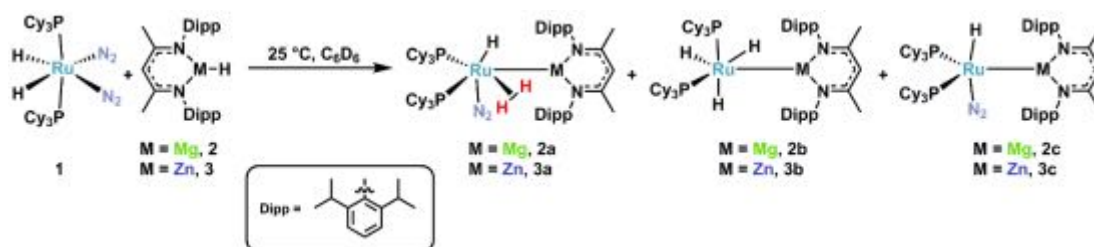
S. Lau^a, A. J. P. White^a, I. Casely^b and M. Crimmin^a

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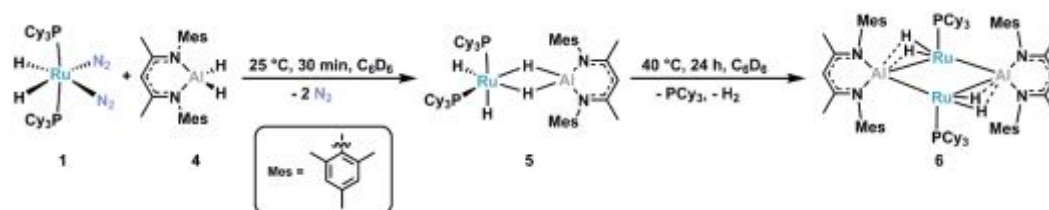
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Formation of σ -complexes from the reaction of E–H fragments (where E = H, B, Si and Ge) with transition metal (TM) centres have been postulated as reactive intermediates in a number of important catalytic transformations including hydrogenation, hydrosilylation and dehydrocoupling reactions^[1–5]. However expansion of main group element to include Al, Mg, and Zn have been, so far, underdeveloped.



Here we present a series of new heterobimetallic complexes formed from the reaction of a ruthenium *bis*(dinitrogen) complex (1) with different main group hydrides supported by bulky β -diketiminato ligands (M = Al, Mg, Zn).



DFT calculations, supported by solution and solid state data, are currently underway to understand the degree of activation of the M–H bonds across the Ru centre in these heterobimetallic complexes.

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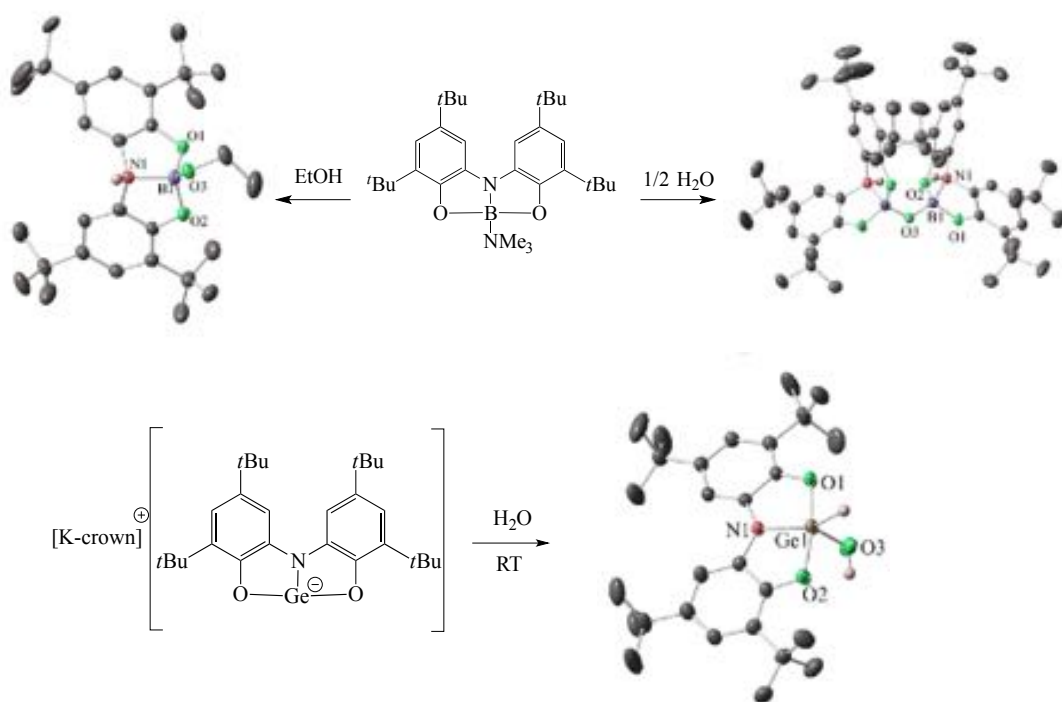
Constrained Geometry Main Group Complexes for Small Molecule Activation

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Precious metal compounds capable of reversible redox process in the activation of small (e.g. H₂, CO₂, NH₃) have been thoroughly investigated over the past decades. However, these metals are rare, expensive and often toxic, therefore creating significant interest in abundant main-group alternatives. Accordingly, recent studies have highlighted a number of main-group systems that are capable of activating small molecules.^{1–3}

A variety of novel species bearing a geometrically constrained N,N-bis(3,5-di-tert-butyl-2-phenolate)amide pincer ligand (ONO)^{3–}. The boron compound, B(ONO)NMe₃, show frustrated Lewis pair (FLP) type reactivity towards water and ethanol. The anionic germanium species, [Ge(ONO)][–], can activate water via oxidative addition, as shown in the picture below.



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Low valent germanium cations for small molecule activation

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In recent years, a range of main group systems have demonstrated the capability for oxidative addition of small molecules.¹ However, subsequent further reactivity, including reductive elimination, is much rarer.² Research from our group and others has probed the consequences of incorporating a net positive charge in carbene-type systems. Germylenes of the type $[R(L)Ge]^+$, for example, show a greater propensity for oxidative addition, disincentivised aggregation of $Ge=E$ bonds,³ and in one case reversible E-H bond activation.⁴

Herein, novel low-coordinate germanium cations are described, featuring an N-heterocyclic carbene and a strong anionic donor. Oxidative addition of a range of E-H bonds has been demonstrated, with evidence for onward reactivity. Furthermore, novel two-centre addition reactivity has been observed across sterically unprotected $Ge=N$ and $Ge=C$ moieties.

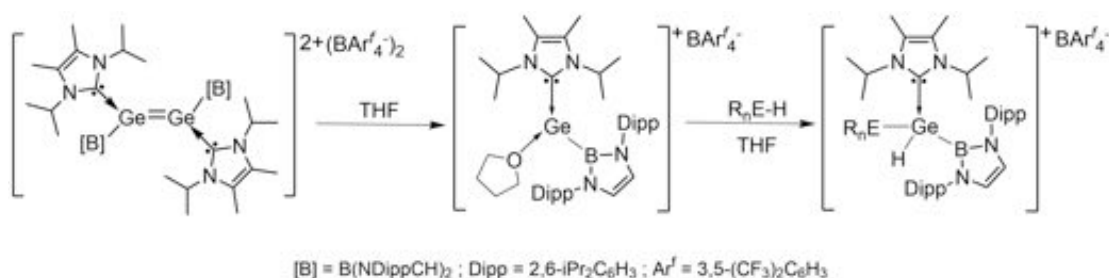


Figure 1 Reactivity of a boryl substituted germanium cation

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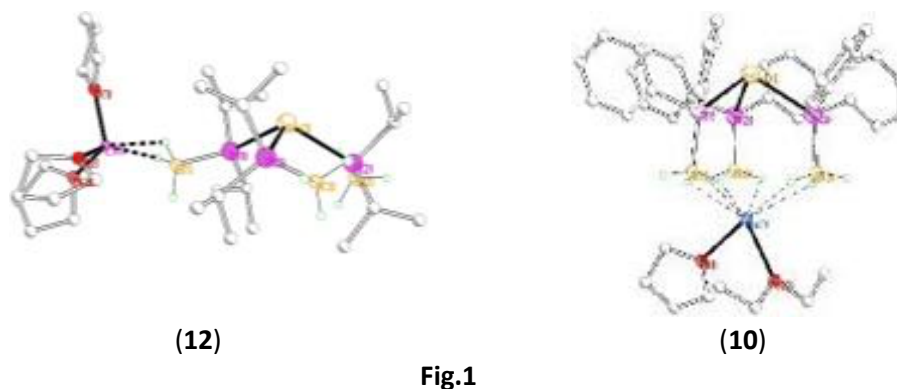
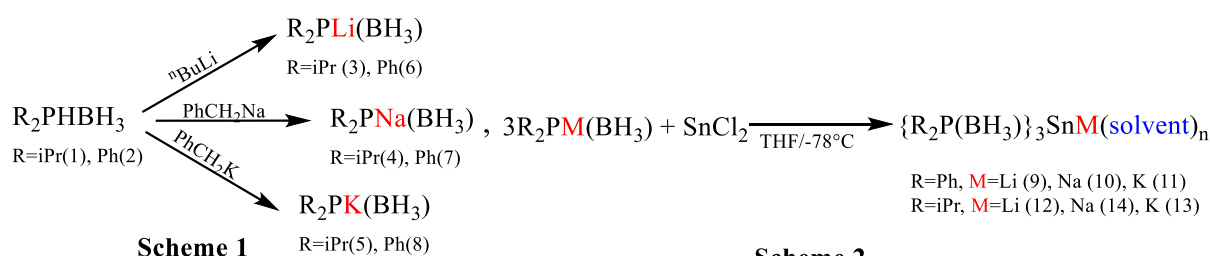
Phosphido-borane Complexes of Tin(II)

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Phosphido-borane ligands, $R_2P(BH_3)^-$, are isoelectronic analogues of trialkylsilyl ligands, R_3Si^- . However, in spite of the ease of synthesis of phosphido-borane ligands, their coordination chemistry is largely unexplored and is limited to a small number of alkali metal derivatives and a handful of p-block and transition metal species.¹

We report the synthesis of a series of tris(phosphido-borane)tin(II) compounds, which have been proposed as intermediates in the synthesis of an unsupported hydridic stannate(II) compound, but not previously isolated.² In this work we report the effect of the alkali metal counterion on the solid-state structures of tris(phosphido-borane)tin(II) complexes. The phosphine-boranes R_2PHBH_3 {R = *i*Pr (**1**), Ph (**2**)} were utilised as ligands after *in situ* preparation of their Li, Na, and K derivatives (**3-8**, Scheme 1). In addition, compounds **9-13** (Scheme 2) were characterized by X-ray crystallography (Fig. 1) and multinuclear NMR spectroscopy.



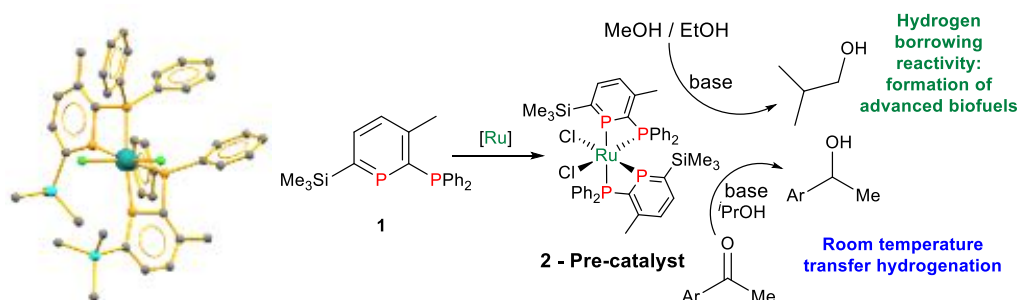
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Coordination Chemistry and Catalysis with Phosphinophosphinine Ligands (O)

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Märkl's landmark 1966 synthesis of 2,4,6-triphenylphosphinine¹ represented an important advance in fundamental inorganic chemistry and has led to much interest in unusual "low-coordinate" phosphorus ligands.² DFT calculations have shown that phosphinine (the P-analogue of pyridine) is a strongly π -accepting ligand,³ however, we are also interested in the donor properties of the sp^2 -hybridized phosphorus lone pair that should decrease the directional preference of the ligand. We sought to exploit this property by incorporating an *ortho*-phosphine moiety, creating a tuneable, small bite-angle ligand that is more likely to form chelating complexes and thus offer improvements in catalysis. Using the 1,3,2-diazaphosphinine methodology reported by Le Floch and Mathey,⁴ air-stable proligand **1** was prepared in good yields on a multi-gram scale.. Reaction of **1** with 0.5 equivalents of *cis*-[Ru(dmsO)₄Cl₂], gave complex **2**, and X-ray crystallography demonstrated the first structural evidence of chelating κ^2 coordination of an *ortho*-phosphinophosphinine.⁵ Complex **2** was investigated as a pre-catalyst for the transfer-hydrogenation of acetophenones, and gave excellent results at room temperature with high conversions observed within one hour for several substrates. In collaboration with researchers at the University of Bristol who have reported new and significant developments in the "Guerbet-type" upgrading of ethanol to the biofuels *n*-isobutanol,⁶ complex **2** was tested in the catalytic synthesis of isobutanol from ethanol and methanol. This reaction, which proceeds by two consecutive "hydrogen borrowing" steps, gave a 50% yield of isobutanol in 96% selectivity and highlights the untapped potential for the use of phosphinophosphinine complexes in catalysis.



Scheme 1. Catalysis with the first chelating phosphinophosphinine complex

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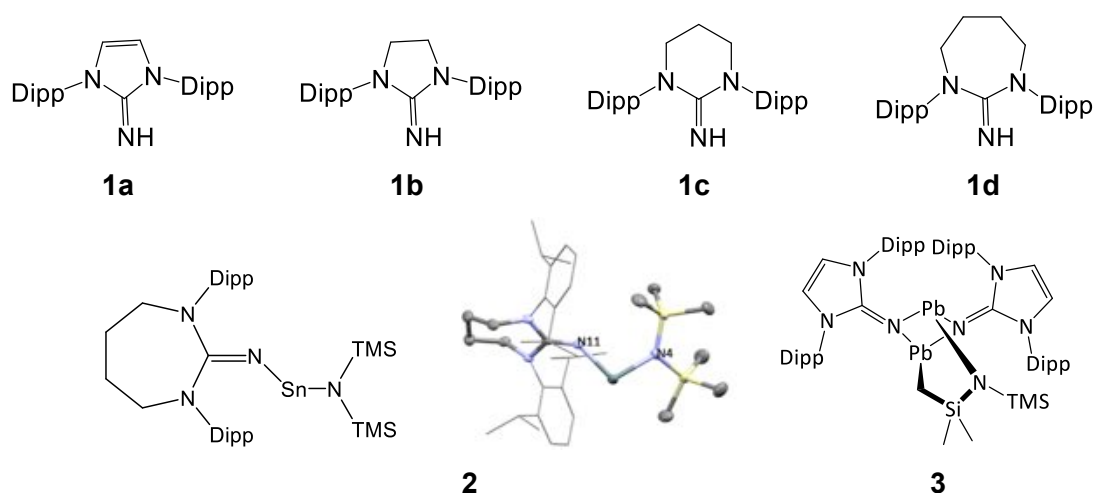
Coordination chemistry of the heavier Main Group elements with bulky anionic guanidinato ligands - P

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Ligands of the guanidinato family have been pioneered by Tamm, Inoue and Rivard, and proved to be highly effective at stabilising novel *p*-, *d*- and *f*-block metal systems.¹⁻³ As an extension to this work we have synthesized two further additions to the guanidinato ligand family, 6-DippNH (**1c**) and 7-DippNH (**1d**), *i.e.* ring expanded analogues of the previously reported systems IDippNH (**1a**)¹ and 5-DippNH (**1b**).⁴ The syntheses of **1c** and **1d** require approaches: access to **1d** proceeds via the free carbene, while **1c** can be synthesized through the silver-carbene complex. These protio-ligands have been structurally characterized and the dependence of their σ - and π - donor properties on heterocycle ring size have been probed by DFT calculations. In general, the ring expanded versions are predicted to be even stronger donors than their 5-membered counterparts.

To probe these computational hypotheses, we have investigated the coordination chemistry of the heavier group 14 elements (Sn, Pb) with guanidinato ligands. These have yielded a range of unsymmetrical and symmetrical tetrelene compounds including the heteroleptic stannylene complexes (*n*-DippN){(Me₃Si)₂N}Sn (where *n* = 5, 6, and 7). These compounds have been characterised by multinuclear NMR spectroscopy and in the case of the 7-DippN system (**2**) by X-ray crystallography. In the case of Pb chemistry, analogous compounds are found to be somewhat more labile, with the intermediate (IDippN){(Me₃Si)₂N}Pb, being readily converted into plumbylenoid **3** at room temperature. This conversion serves as a rare example of C-H activation by a bimetallic group 14 system.



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Small Molecule Activation Using Metal(II)-Pincer Complexes -P

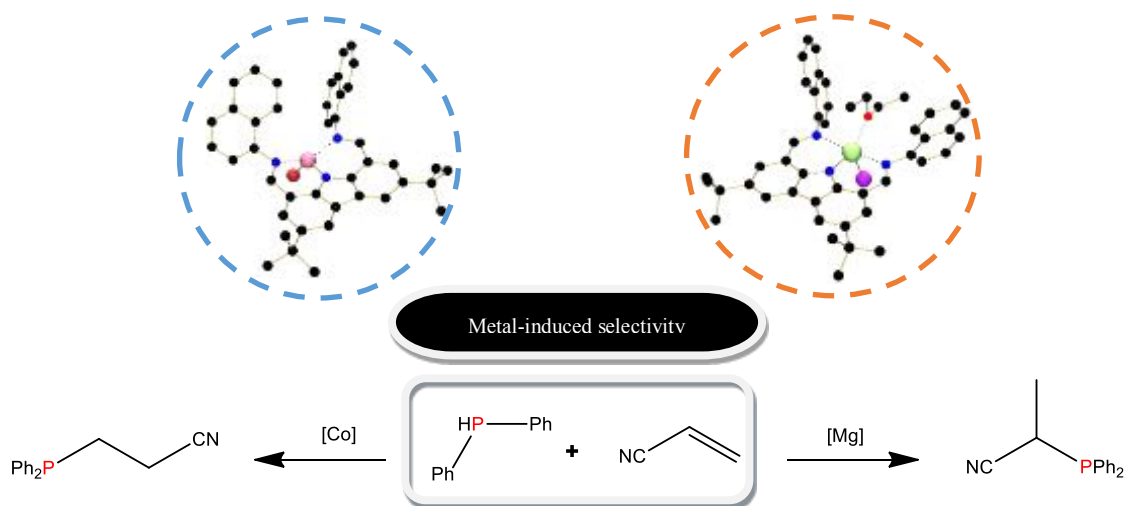
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The use of sterically demanding ligands is a key component in the challenging task of stabilising coordinatively unsaturated complexes. For this purpose, *N*-based pincer 1,8-bis(imino)-carbazol-9-yl species have shown to be a very versatile class of ligands, offering a robust and well-defined framework.¹ This kind of ligand and the ease of modification of the supporting flanking groups, offers a strong σ -donor functionality, essential for the study of the coordination chemistry of the s, p and d-block elements.^{2,3} As such, the synthesis of a new symmetric 1,8-bis(imino) substituted carbazole is presented, relying on naphthyl groups as sterically bulky substituents.

The corresponding Group 1 salts, have shown to be active in the catalytic dehydrogenation of amine-borane adducts.⁴ While in parallel, their isolation has enabled the synthesis of a wide range of metal(II) based species by means of a metathetical pathway. Following this methodology, the formation of heteroleptic Group 2, first-row transition-metal, Group 12 and Group 14 species has been accomplished.

Most noticeably, analogous heteroleptic [Co] and [Mg] complexes have shown to facilitate the hydrophosphination of unsaturated substrates with differing activity and selectivity. The contrasting substitution pattern seems to be directly linked to dissimilar environments around the metal centre, an area of research we are currently exploring.



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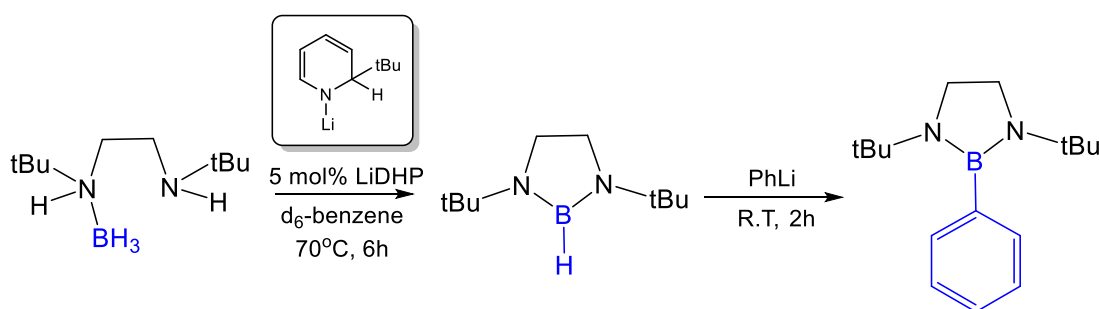
Advancing Alkali-Metal-Mediated Catalysis: Catalytic Applications in Dehydrogenative Cyclisation and Hydroboration_P

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This presentation summarises the development of the catalytic applications of Group 1 dihydropyridines. Firstly, the reported lithium dihydropyridine (LiDHP, 1-Li-2-tBu-NC₅H₅) proved a valuable precursor to act as a metal hydride transport vessel.¹ The first catalytic role of LiDHPs was established in the dehydrogenative cyclisation of diamine boranes.² It was found that the LiDHP catalyst could compete with a ruthenium catalyst³ to prepare 1,3,2-borolidines. A three-step mechanism has been suggested, (deprotonation, β -hydride elimination and intramolecular hydrogen loss) supported by crystallographically characterised intermediates and extensive NMR studies. The borolidines were further functionalised to synthetically useful phenylborane derivatives. LiDHP was next subjected to a catalytic screening for hydroboration of carbonyls.⁴ This also proved successful for preparing boronate esters, from a range of aldehydes and ketones with pinacolborane. The reaction was thought to proceed via a hydrometallation followed by a metathesis step.



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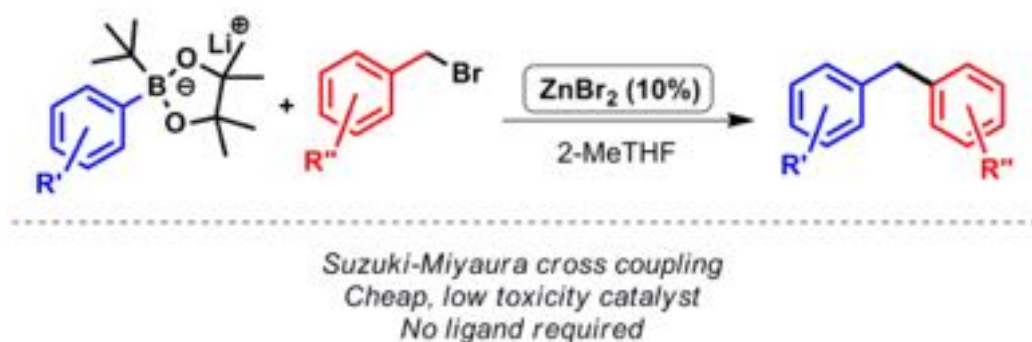
Zinc catalysed Suzuki-Miyaura Csp² – Csp³ cross coupling – P

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The Suzuki-Miyaura cross coupling reaction, forming a new C-C bond by coupling an organoboron nucleophile with an electrophile, is a very powerful and versatile synthetic reaction.¹ Since its discovery in the 1970s this reaction has become increasingly important – including in industrial applications, particularly pharmaceuticals synthesis. This is despite the fact that the most common catalysts are based on expensive and toxic palladium or toxic nickel compounds.² Replacement of Ni or Pd with low toxicity, inexpensive metals with less supply chain risk would be highly attractive, and significant progress has been achieved using Fe catalysts.³ Zinc is also cheap and has low toxicity, however it is most commonly utilised in cross coupling reactions as a stoichiometric coupling partner requiring transition metal catalysis (Pd catalysed Negishi coupling).⁴ While there are recent examples of transition metal catalyst free zinc mediated coupling of organoboron reagents with benzyl bromides⁵ and direct coupling of aryl zinc reagents with alkyl bromides⁶, these reactions use stoichiometric zinc.

Recently, however, we have shown the capability of zinc salts to effectively catalyse the coupling of aryl-borate reagents with benzyl halides, with high selectivity for hetero-coupling and high yields. This poster will introduce the scope and initial mechanistic work into this reaction, which to the best of our knowledge represents the first example of a zinc catalysed Suzuki-Miyaura cross coupling protocol.



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Tetraalkoxysilanes as (overlooked) reagents for direct amidation – O

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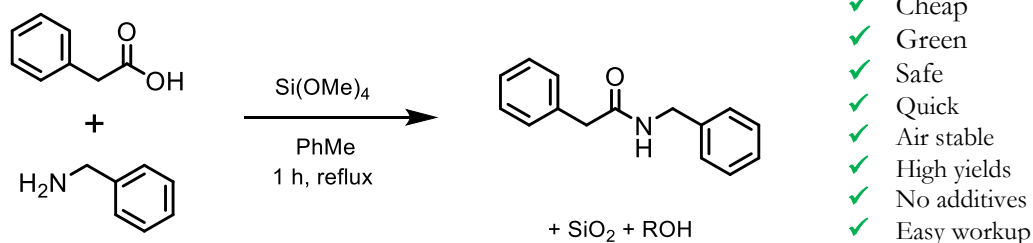
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Amides are widespread in the modern world: from natural products to synthetic materials, the amide group is a vitally important functionality. For synthesizing amides the ‘direct’ reaction of a carboxylic acid with an amine is the most obvious and flexible approach. This is a thermodynamically favourable process, but because a salt is formed on mixing the reagents the substrate scope is limited to those which can survive the high temperatures (>160 °C) required to dehydrate the salt.

To circumvent this restriction the carboxylic acid is typically activated by forming a reactive intermediate prior to reaction with an amine. Although this reduces the temperatures required, it also involves an extra synthetic step. This leads to wastefulness (poor atom economy), it introduces the possibility of undesirable side reactions and it often involves toxic materials such as SOCl₂. Thus the ACS Green Chemistry Institute Pharmaceutical Roundtable recently selected amide formation as the most important industrial reaction for which better reagents are required.¹



The work presented today will showcase our recent results using main group alkoxides such as TMOS (tetramethylorthosilicate) as reagents for the direct formation of amides. The reactions are high-yielding and quick, no additives or specialized equipment is required and the workup is straightforward (no chromatography!), affording a wide range of amides in high purity.²

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Synthesis of a new sterically hindered phosphane (P)

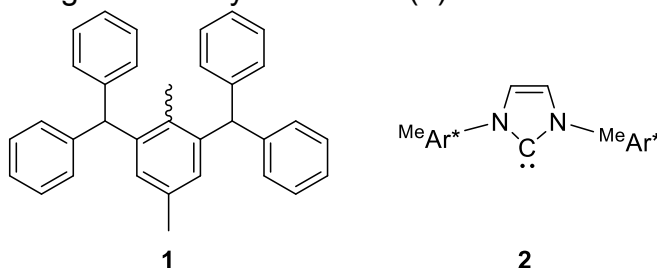
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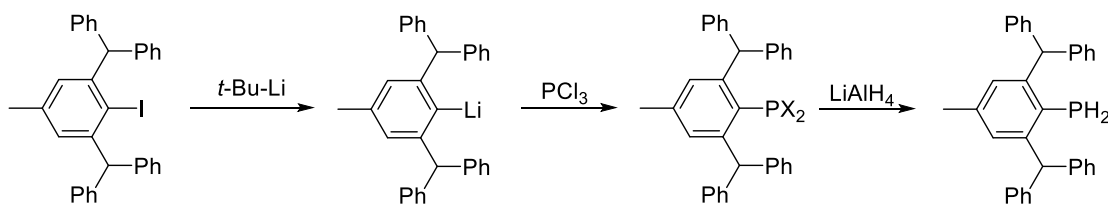
Sterical hindrance is vital for the isolation of low valent phosphorus compounds, as dimerization or oligomerization is often thermodynamically favoured over the formation of a monomeric species.^[1] In phosphorus chemistry, Mes* and Ter substituents are frequently utilised, but the stabilisation provided was not sufficient for the long-standing goal of obtaining the diazonium analogous [R-PP]⁺ cation.^[2]

A recent example of a sterically demanding group is ^{Me}Ar* (**1**). Established in 2010, Guillaume Berthon-Gelloz used ^{Me}Ar*-NH₂ to synthesize a highly sterically demanding N-heterocyclic carbene (**2**).^[3]



Our project is aimed at introducing the ^{Me}Ar* moiety into phosphorus chemistry.

Because the amine ^{Me}Ar*-NH₂ is readily available, it was chosen as a starting material. Subsequently, a diazotation was performed and the diazonium salt was converted to the chloride, bromide and iodide derivatives ^{Me}Ar*-X (X=Cl, Br, I) could be obtained, isolated and fully characterized. Lithiation and reaction with phosphorus trichloride yielded ^{Me}Ar*-PX₂ (X=I, Cl). Hydrogenation with LiAlH₄ resulted in the desired phosphane.



Current studies are focused on the reactivity of this phosphane and its coordination chemistry.

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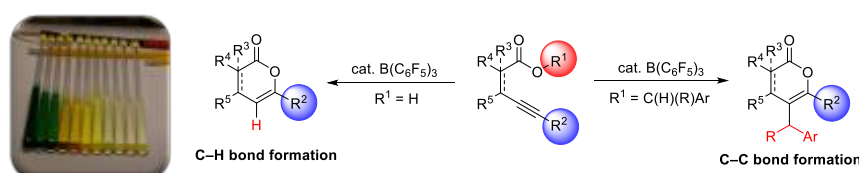
B(C₆F₅)₃: Stoichiometric and Catalytic C-C and C-H Bond Formation via Cationic Intermediates. O

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Functionalised heterocycles are key components in many natural products and synthetic pharmaceuticals. Therefore Lewis-Acid catalysed addition of hetero-atoms across unsaturated carbon-carbon bonds has been the target of several studies, in order to create biologically active compounds such as highly functionalised oxazoles.^{1–3}



Scheme 1: B(C₆F₅)₃ catalysed cyclization of alkynyl acids and esters⁴

Fluorinated triarylboranes have proven to be powerful catalysts in many catalytic reactions, such as cyclisations, hydrosilylations and hydroborations.^{3,5,6} The scope of the BCF-catalysed carbo-oxycarbonylation with various alkynyl acids and esters was examined, and results showed the products to be unsaturated 6-membered heterocyclic species, and that the reactions can be achieved both stoichiometrically and catalytically in mild conditions.⁴

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A Zwitterionic Disilene

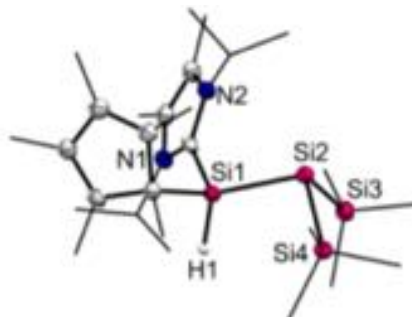
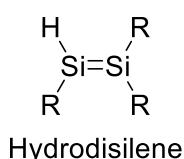
Unique Synthesis and Divergent Reactivity - P

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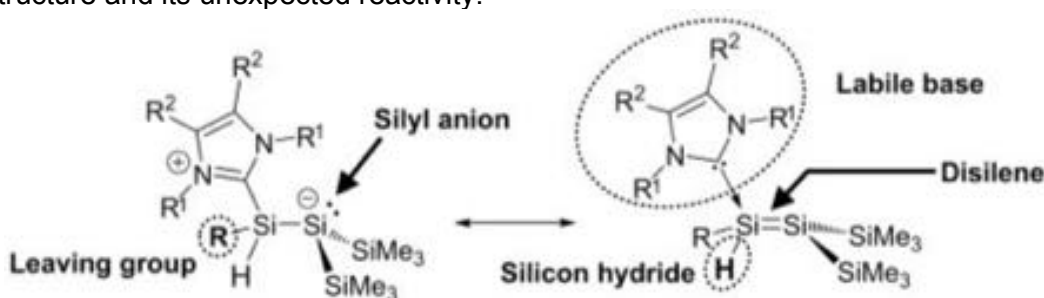
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Compounds with multiple bonds to carbon are essential to all areas of chemistry as reactive precursors and as functional products. Multiple bonding between heavier p-block elements has received considerable attention, but such compounds are almost always stabilised by large, unreactive and sterically protecting substituents. Functionalised disilenes ($R_2Si=SiRX$), for example, are still rare.¹ Therefore, methods to prepare such compounds with reactive functionality are of high interest.

Hydrosilanes (R_3Si-H) are highly reactive and versatile reagents in organic and organometallic chemistry, making them an attractive silicon feedstock.² In contrast, only a handful of hydrosilenes have been isolated.^{1,3,4} Equally, base-stabilised disilenes, which can act as a source of reactive, non-sterically protected disilene, are uncommon and their reactivity remains largely unexplored.⁵



Here we present a hydrosilene with multiple reactive sites and related compounds. The presence of a lone pair on Si2 is evidenced by ^{29}Si NMR, structural features and DFT calculations. We present further details on its novel, safe and simple synthesis, structure and its unexpected reactivity.



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Synthesis of sustainable polymers catalysed by a hemi-labile aluminium complex– O

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In 2014 311 megatonnes of plastics were produced worldwide.¹ The wide variety of properties exhibited by different polymers make them extremely useful and therefore widespread throughout many different industrial sectors. Unfortunately many plastics are unsustainable. The majority of polymers are derived from fossil fuel sources, a finite resource and most plastics are extremely environmentally persistent. Two alternative processes which yield biodegradable polyesters are the ring-opening polymerisation (ROP) of ϵ -caprolactone and the ring-opening co-polymerisation (ROCOP) of epoxides and anhydrides (figure 1a,b).^{2,3}

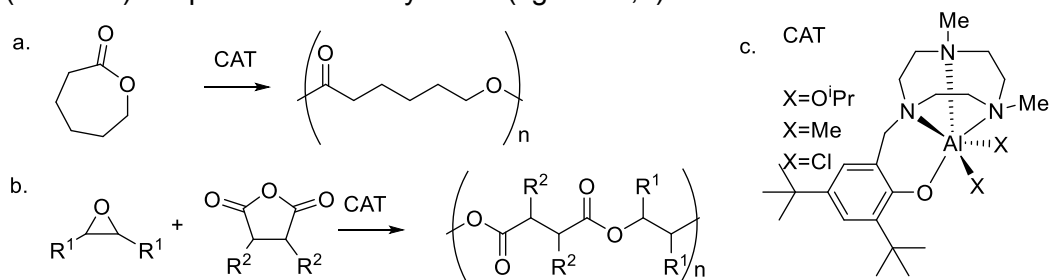


Figure 1 a. ROP of ϵ -caprolactone b. ROCOP of epoxides and anhydrides c. Catalyst

The catalytic ROP of ϵ -caprolactone and ROCOP of epoxides and anhydrides have been studied. The catalyst used in these polymerisations is an aluminium complex ligated by the pendent-arm macrocycle, hydroxy-di-*t*Bu-benzyl-TACN (L) (figure 1c), which shows unusual hemi-labile binding of the ligand to the aluminium metal centre;⁴ the ligand has been reported to coordinate via a κ^2 or a κ^4 mode and the equilibrium between the two states has been investigated.

$\text{Al}(\text{L})(\text{O}^i\text{Pr})_2$ and $\text{Al}(\text{L})(\text{Me})_2$ were investigated as catalysts for the ROP of ϵ -caprolactone. The polymers produced were of high molecular weight (Mw) and narrow polydispersity (PDI). The reaction mechanism was probed using DFT and the effect of catalyst structure on the energetics of reaction pathway was investigated.

$\text{Al}(\text{L})\text{Cl}_2$ was employed as a catalyst in the ROCOP of a number of different epoxides and anhydrides. This reaction has been the subject of a great deal of interest over recent years because of the potential to easily vary the properties of the polymer by a judicious choice of monomers. Polymers with excellent selectivities and good Mw were synthesised. Of particular note are the polyesters synthesised from limonene oxide with good selectivities and in a solvent free manner making the process very sustainable.

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Reactivity of a dimethylxanthene based frustrated Lewis pair towards boranes – P

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The combination of a Lewis acid and a Lewis base, either as separate molecules or constrained into a single entity, is called a frustrated Lewis pair, FLP. Recently, these compounds have been shown to exhibit remarkable reactivity, for example, in the capture and activation of small molecules and as “metal-free” catalysts in hydrogenation reactions.¹ To facilitate this behaviour, it is imperative that the donor ($R_3P:$) and acceptor (BR'_3) sites of the FLP do not form a coordinative bond, but are able to polarize the target chemical bond to the point of heterolytic cleavage (Figure 1a). However, the drawbacks of using FLPs as catalysts have been the requirement for high catalyst loadings and low turnover numbers. To this end, our group developed an FLP based on a dimethylxanthine backbone (compound **1**, figure 1b), which can reversibly activate H_2 and perform catalytic dehydrocoupling of amine-boranes in ambient conditions.² In view of these results, we were interested in extending our study to the hydroboration of alkynes. In this contribution, we will show the reactivity of **1** towards selected boranes, pinacolborane (HBpin) and catecholborane (HBcat), which results in a migration of the $B(C_6F_5)_2$ group (Figure 1b). In addition, the FLP catalyzed hydroboration reactions of some terminal and internal alkynes is discussed.

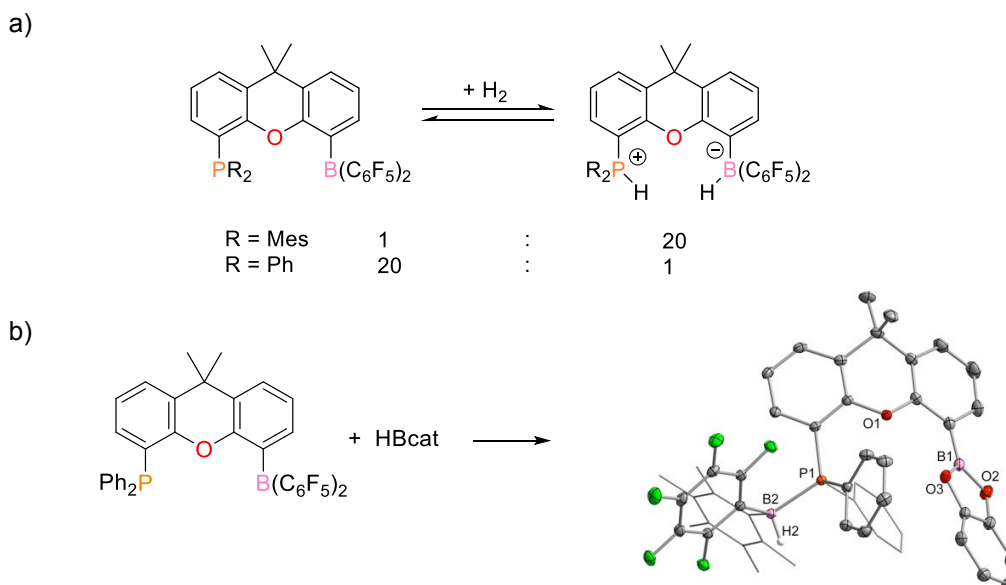


Figure 1. a) Example of reversible binding of H_2 by an FLP; b) Reaction of FLP **1** with catecholborane.

References

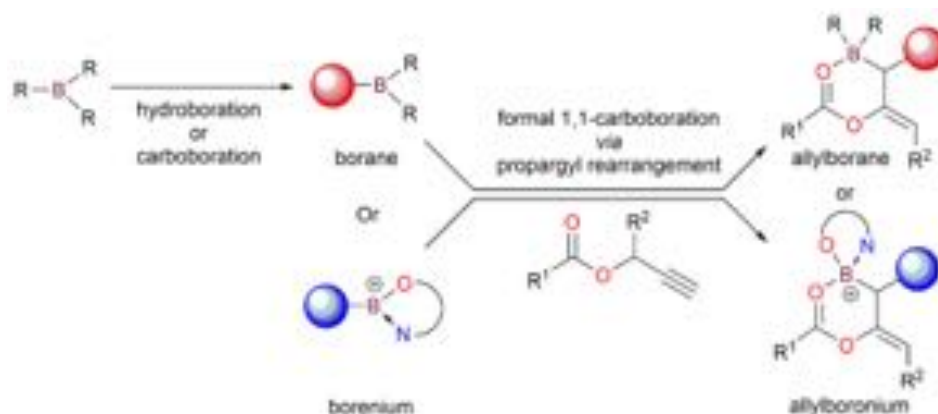
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The Softer Side to Boron: Taming Hard Lewis Acids for Soft Centred Chemistry – O

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The advent of frustrated Lewis pairs (FLPs) a decade ago has been a major advance in main group chemistry with regards to the properties and reactivity, particularly in metal-free catalysis.¹ This concept has been expanded to intramolecular cyclisations promoted through the activation of unsaturated carbon–carbon frameworks by π -Lewis acids² with our work focusing on a tethered Lewis basic carbonyl functional group.³ Whilst this type of activation is commonplace in transition metal chemistry through the use of coinage metals such as gold and palladium, the shift in focus to alternative more abundant main group sources to compliment this already established field is long overdue.



In this work, the activation of π -bonds in alkynyl esters using traditionally hard Lewis acids was investigated.⁴ The activation of the alkynyl functionality in propargyl systems results in the 1,2-trans-oxyboration to produce a wide variety of heterocyclic synthetically useful compounds. Interestingly, the use of borocations were also useful in the selective 'R-group' transfer garnering functionalised allylboron reagents, additionally the products of a 1,1-carboboration reaction were used in a highly effective method to invoke further cyclisations and addition reactions to yield a plethora of densely functionalised dioxaboronines.

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Using Heavier Group 15 Cyanate Analogues for the Synthesis of New Nickel Pnictogen Complexes (P)

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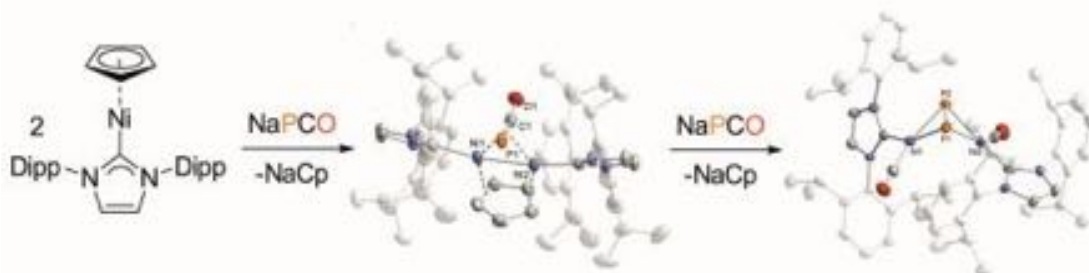
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Despite still being regarded as rare, the chemistry of nickel compounds in the +1 oxidation state has undergone significant development over the last decades.^[1] At the same time, the reactivity of the heavier group 15 cyanate analogue 2-phosphaethynolate PCO^- has also rapidly evolved due to the stability and facile preparation of its sodium salt NaPCO .^[2] This small anion has been shown to undergo salt metathesis reactions with metal halides which leads to a variety of unprecedented phosphorus-containing complexes.^[3]

Nickel(I)-complexes of the type $\text{CpNi}(\text{NHC})$ ($\text{NHC} = \text{IMes}, \text{IDipp}$) undergo salt metathesis reactions with the heavier group 15 cyanate analogues NaPCO and NaAsCO , giving rise to $[\text{NiE}(\text{CO})(\text{NHC})]_2$ complexes ($\text{E} = \text{P}, \text{As}$) with $\mu, \eta^{2:2}\text{-E}_2$. Intermediates in these reactions such as phosphinidene complexes and phosphaketenes were isolated and characterised. Moreover, the new $[\text{NiP}(\text{CO})(\text{NHC})]_2$ complexes release white phosphorus (P_4) upon reaction with CO .



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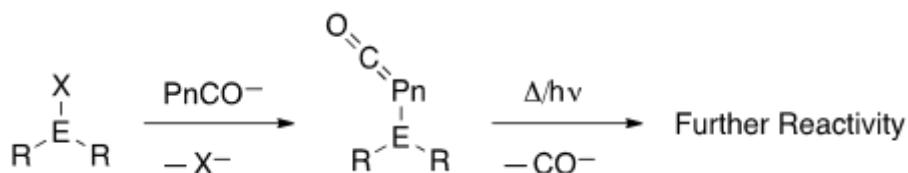
Synthesis and Reactivity of Novel Molecules and Solids Derived from Heavier Group 15 Cyanate Analogues P

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Metal pnictides are a varied family of solids that adopt a wealth of structures and stoichiometries.¹ Amongst their many applications they have been employed as fumigants, pesticides, flares and, perhaps most notably, as semiconductors.² The diversity of their physical and chemical properties makes such compounds interesting for a range of technological applications. However, while many such species can be readily synthesised using a variety of methods, these often come at a high energetic cost. Moreover, our ability to access well defined nanoscale materials is still significantly limited by existing technological methods.

We are interested in solution-phase metathesis reactions between the heavier group 15 cyanate analogues and a variety of metal salts with the aim of developing a novel bottom-up approach to metal phosphaketenes. These species, upon spontaneous, thermal, or photolytic decarbonylation, can be employed as precursors to novel molecules and materials. Recently, metathesis reactions have provided pathways to a number of group 14 and 15 phosphaketene compounds (silyl to plumbyl,³ germylenyl,⁴ and phosphanyl).⁵ However, no group 13 phosphaketenes have yet been identified.



E = B, Al, Ga, In; Pn = P, As; R = Aryl, OR, NR₂

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Pyridine-based pincer complexes as a platform for forming well-defined cobalt fluoride species - P

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Transition-metal fluoride compounds, display some fascinating properties due, in part, to the unique structural and bonding characteristics imparted by the fluoride ligand. From an electronic point of view, fluoride is the best π -donor hence leading to an increase in electron density at the metal centre. On the other hand, from a steric point of view, the limited steric hindrance imposed by the fluoride ligand can lead to high coordination numbers or a more accessible metal centre. As a result, high selectivity and high reactivity and might be expected.^[1] More specifically, late transition metal fluoride complexes are of interest because they are potentially useful in a multitude of catalytic applications, including olefin polymerization and C-F bond activation and indeed the term “*fluoride effect*” has been coined.^[2-4]

Herein, we report the synthesis and characterization of a range of novel cobalt complexes bearing NNO- and NNN-pincer ligands and use these as a platform to introduce fluoride (**Fig. 1**). Two approaches will be explored, namely, i) chloride-fluoride ligand exchange using a cobalt chloride pincer complex in combination with a suitable fluoride agent, ii) via B-F abstraction from BF_4 counter ion in a pre-disposed cobalt complex.^[5]

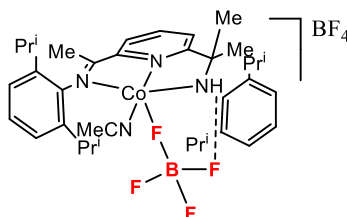


Figure. 1 An example of a cobalt-fluoride pincer complex synthesized in this study.

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Synthesis of bio-degradable co-polymers using aluminium constrained-geometry catalysts – P

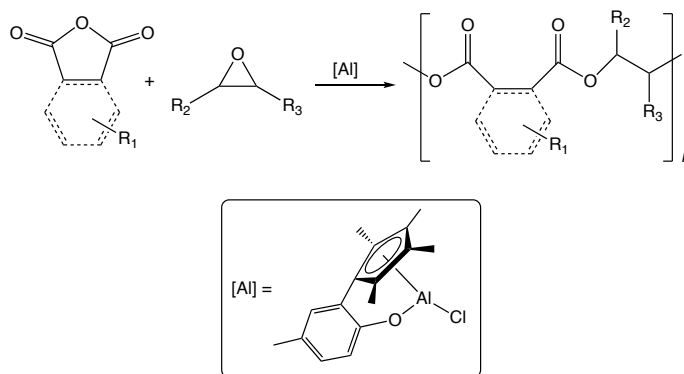
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Synthetic polymers find widespread use in almost every aspect of life, from the packaging of commodity products to high-performance materials in aeroplanes; the use of polymers has revolutionised society and has been instrumental in many of the products that we now take for granted. Although they are ubiquitous, only 5% of synthetic polymers are bio-degradable; those which are non-biodegradable result in severe pollution and damage to the natural environment.

Whilst polyesters such as poly(lactic acid) and poly(ϵ -caprolactone) have become important in tackling the need for biodegradable polymers,¹ the development of co-polymers derived from CO₂/epoxide or anhydride/epoxide combinations is quickly gaining momentum;² anhydride/epoxide based polymers in particular could offer an effectively limitless number of derivatives for tailor-made polymers. Since these polymers all contain ester linkages, they are all, in principle, more biodegradable than their poly(olefin) counterparts.



Scheme 1

We have been investigating the use of aluminium constrained-geometry catalysts³ for the co-polymerisation of anhydrides and epoxides (Scheme 1). Aluminium is in plentiful supply, being the 3rd most abundant element in the Earth's crust, and is therefore inexpensive, making it ideal for next-generation catalysts. Preliminary catalytic data suggest a good level of control over the alternating microstructure.

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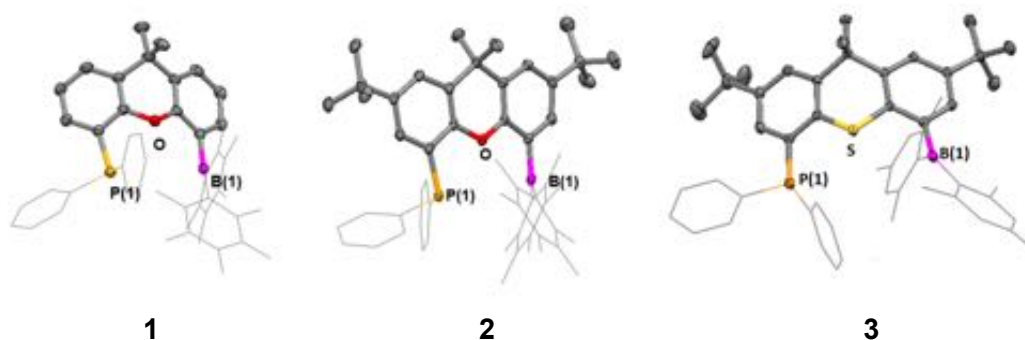
Developing the scope of intramolecular frustrated phosphine-borane Lewis pairs based on a dimethylxanthene backbone

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Frustrated Lewis pair (FLP) chemistry is of enormous current interest because it provides a versatile “metal free” way of carrying out bond activation and ultimately catalysis. The key design features of frustrated Lewis pairs (FLPs) are strong Lewis acid and Lewis base components (usually a tertiary phosphine, PR_3 , and a borane BR'_3) which can be separate molecular entities or be combined in one species, where the R and R' groups are too bulky to allow them to come together via coordinate bond formation ($\text{R}_3\text{P} \rightarrow \text{BR}'_3$).¹

In recent work we have developed single component frustrated Lewis pairs (FLPs) based on a dimethylxanthene backbone that possess a $\text{P} \cdots \text{B}$ separation (4.2–4.5 Å) preorganized for the facile uptake of H_2 .² Moreover, by varying the cumulative Lewis acid/base strength of phosphine and borane components, a system can be designed which cleaves H_2 to give an equilibrium mixture of free FLP and zwitterionic FLP- H_2 in solution at room temperature.³ Based on the success of the dimethylxanthene FLPs in their metal free catalytic behaviour, new preorganised intramolecular FLPs by with different P—B separations have been synthesized (e.g. **1** - **3**) and their reactivity tested in a range of catalytic processes. These include related thioxanthene systems (e.g. **3**) which possess wider binding cavities, and systems such as **1** and **2** in which the P-bound or backbone substituents can be varied.



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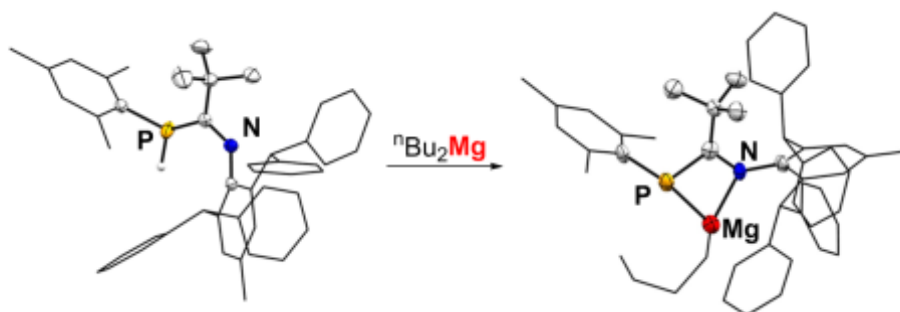
A Monomeric, Three-Coordinate Alkyl Magnesium Complex Featuring a Super Bulky Phosphaamidinate – P

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Bidentate ligands based on nitrogen are well used across many types of chemistry. β -diketimate (NacNac) magnesium derivative of the type LMg^nBu have found applications in catalysis¹ and can undergo interesting molecular transformations.² With a shorter carbon backbone, amidinate complexes of magnesium are stereo-selective catalysts for ring-opening polymerization,³ however readily undergo ligand redistribution to L_2Mg type species due to the Schlenk equilibrium, a major deactivation pathway in catalysis.⁴

Phosphaamidines, in comparison with amidines, are relatively undeveloped. Their synthetic accessibility was greatly improved by the recent report of the reaction of a primary phosphine with a carbonitrilium salt to form an easily deprotonated pro-ligand.⁵ Using this method we report new examples of phosphaamidines with increased steric bulk around the nitrogen substituent, including a penta-phenyl derivative (scheme 1).



Scheme 1 Formation of a monomeric three coordinate magnesium complex by deprotonation of a phosphaamidinate

Complexation of these ligands with magnesium allows various solvent-free *mono*- and *bis*-ligated species to be isolated with the general formulae LMg^nBu and L_2Mg , respectively. Of the former, a monomeric, three-coordinate magnesium centre has been isolated.

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