



RSC Main Group Chemistry Group Annual Meeting and AGM

1st September 2017

Burlington House, London

**The committee is extremely grateful to our sponsors
for their financial support:**



Annual Meeting of the RSC Main Group Chemistry Interest Group

RSC, Burlington House, London
Friday 1st September 2017

All lectures will be held in the Library

10:00	Registration and coffee Poster mounting for Group A (Posters P1 – P20)
10:30	Welcome from Interest Group Chairman, Prof. Michael Hill, University of Bath
10:35	Prof. Dominic Wright, University of Cambridge <i>PL1- Main Group Macrocycles: Design Concepts and New Host-Guest Chemistry</i>
11:25	Dr James Radcliffe, University of Manchester <i>O1 - Understanding Borocation Activation of N-heterocycles for Reduction Applications</i>
11:45	Dr Marina Uzelac, University of Strathclyde <i>O2 - Trans-metal-trapping Meets FLP Chemistry: Gallium-induced small molecule activation processes</i>
12:05	Buffet lunch and Poster Session A
1.20	Dr Jamie Hicks, University of Oxford <i>O3 - Nucleophilic aluminium: Synthesis, structural and reaction chemistry of an aluminyl anion</i>
1.40	Mr Peter Evans, Newcastle University <i>O4 - Steric influence of phosphorus ligands on the structure of low oxidation state silicon compounds</i>
2.00	Prof. Michael Hill, University of Bath <i>PL2 Nucleophilic Borylation and Alkylation with Heavier Alkaline Earths</i>
2.50	Tea/coffee
3.10	Ms Amy Price, University of Edinburgh <i>O5 - Phosphaborenes: Reagents for the Preparation of P–B/C–C Isosteres</i>
3.30	Ms Wenyi Chen, Imperial College, London <i>O6 - Palladium-Catalysed Transformation of Non-reactive C–F bonds into Reactive C–Al Bonds</i>
3.50	Prof. Warren Piers, University of Calgary <i>PL3 - Standing on the Shoulders of a Giant: New BN Isosteres of Polycyclic Aromatic Hydrocarbons</i>
4.40-5.50pm	Poster session Group B (Posters P21 – P40), drinks and prizes
4.40-5.10pm	Annual General Meeting of Interest Group Members

The conference will end promptly at 5.50pm: we need to clear the building by 6pm.
Thank you in advance for your cooperation.

PLENARY LECTURES

Main Group Macrocycles: Design Concepts and New Host-Guest Chemistry

Dominic S. Wright

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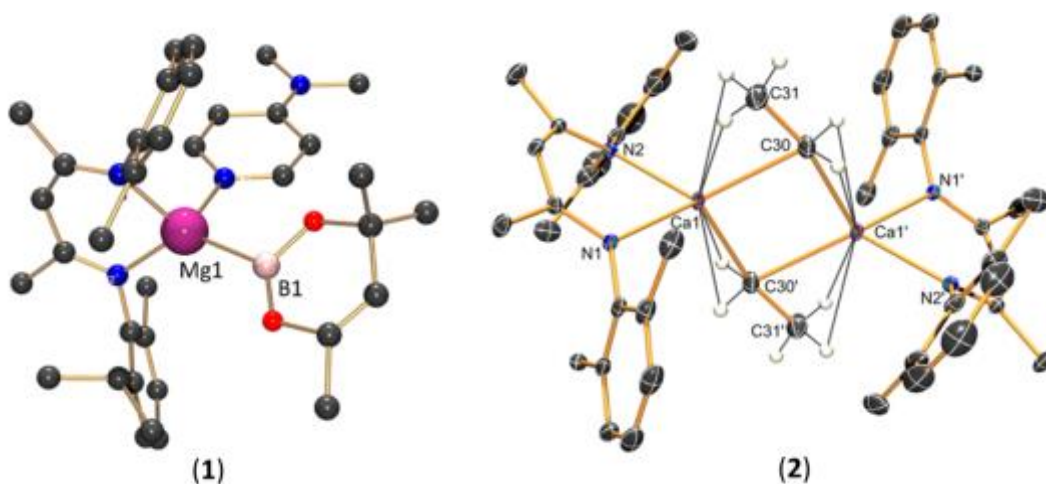
The macrocyclic and macromolecular chemistry of organic species is well established and a central field of research world-wide. Far less well studied are inorganic frameworks of this type. The research we have been involved in has explored the possibility of developing logical approaches to a range of main group macrocycles based on element-N bonds. This has lead to a range of new macrocycles and to the exploration of previously unexplored host-guest chemistry in this area, which can be compared to the behaviour of organic counterparts.

Nucleophilic Borylation and Alkylation with Heavier Alkaline Earths

Michael S. Hill

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Organomagnesium (Grignard) reagents have been one of the workhorses of organic synthesis, allowing the nucleophilic alkylation of a wide range of electrophilic reaction partners, for over 100 years. This talk will describe our recent efforts to develop straightforward routes to magnesium boryls (e.g. **1**) which enable the direct nucleophilic borylation of electrophiles.¹ In addition, the synthesis and reactivity of aliphatic calcium alkyls (e.g. the ethyl derivative, **2**) will be reported. These compounds highlight the advantages and enhancements in reactivity which may be achieved through the development of superficially simple analogues of classical Grignard derivatives derived from magnesium's heavier and more electropositive congeners.



¹ Pécharman, A. F., Colebatch, A. L., Hill, M. S., McMullin, C. L., Mahon, M. F. and Weetman, C., *Nature Communications*, 8, 15022 (2017).

Standing on the Shoulders of a Giant: New BN Isosteres of Polycyclic Aromatic Hydrocarbons

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Substituting “BN” for “CC” in hydrocarbon frameworks has become a fruitful strategy for influencing the photophysical and redox properties of pi conjugated materials. The main focus of the talk will be on recent results from our lab on synthetic methods towards BN indene and indacene derivatives, and the properties and reactivity of these compounds. Prof. Michael Lappert was a pioneer in this area of main group chemistry research, and the first part of the lecture will include personal reflections on how Lappert’s rich legacy of chemistry has influenced research in the Piers group over the years.

INVITED LECTURES

Understanding Borocation Activation of N-heterocycles for Reduction Applications– O

James E. Radcliffe, Jay J. Dunsford, Jessica Cid, Michael J. Ingleson*

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The reduction of *N*-heterocyclic compounds is a vital reaction in the synthesis of many compounds with pharmacological properties. While first reported by Hantzsch in 1882,¹ modern chemistry has developed a number of synthetic routes to reduced *N*-heterocycles.² Unfortunately most of these reduction routes require the use of metals and/or highly reactive starting materials, as well as offering limited selectivity. More recently a series of highly selective metal-free reductions of pyridines mediated by borocations have been published, demonstrating potential for further progress in this important field of chemistry.³

Past work in the Ingleson group has demonstrated the reduction of *N*-Me-acridinium salts as part of a frustrated Lewis pair (FLP) in conjunction with 2,6-lutidine. Their study using acridinium salts as carbon Lewis acids highlights the ability to modulate the Lewis acidity of *N*-heterocyclic compounds through methylation at N, and activating these species towards reduction processes.⁴

HIA, relative to BEt₃ (kcal mol⁻¹)

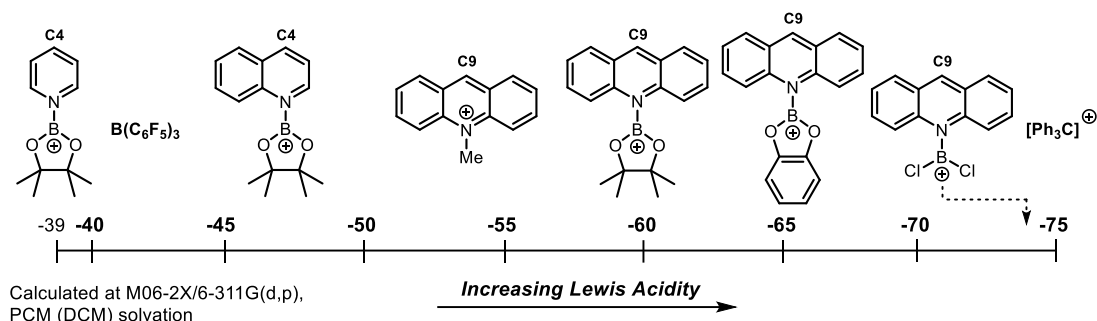


Figure 1: The calculated hydride ion affinities (HIAs) at carbon of a series of *N*-heterocycle-borocation salts, relative to BEt₃.

In this work a series of *N*-heterocycle-borocation salts have been synthesised and their Lewis acidity evaluated by both experimental and computational methods. It has been demonstrated that through the careful choice of both the borane and *N*-heterocycle a wide range of carbon-Lewis acidic species can be formed that are amicable to reduction by hydride abstraction from a variety of hydride donors. Our studies have enabled a better understanding of the factors controlling the borocation mediated reduction of *N*-heterocycles, and current investigations are ongoing to expand the scope of these reactions.

References

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b) E. N. Keyzer, S.S Kang, S. Hanf, D. S. Wright, *Chem. Commun.*, **2017**, Accepted
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Trans-metal-trapping Meets FLP Chemistry: Gallium-induced small molecule activation processes – O2

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Advancing the applications of organogallium complexes for the functionalization of organic substrates, this oral presentation discusses cooperative behaviours observed when pairing tris(alkyl) GaR₃ (R = CH₂SiMe₃) with the utility lithium amide LiTMP^{1,2} or the sterically hindered NHC t^Bu (t^Bu = 1,3-bis(*tert*-butyl)imidazol-2-ylidene).³ Merging two topical areas of Main Group chemistry, namely cooperative bimetallics and FLP activity, the reactivity of these systems is controlled by the steric mismatches between their individual components.⁴ The chemistry developed by this Ga system, highlights stepwise cooperative processes based on either two metal reagents or on a single-metal reagent combined with a special ligand. This study includes unique tandem reactivities for the functionalisation of a range of organic substrates including challenging and pharmaceutically relevant N-heterocyclic molecules and fluoroarenes, enabling their regioselective metallation.

By shedding new light on how these non-cocomplexing partnerships operate and showcasing the potential of Ga reagents to engage in metallation reactions or FLP activations, areas where the use of this metal is scant, this presentation aims to stimulate more interest and activity towards the advancement in organogallium chemistry, bridging the gap in practical utility and knowledge between gallium and its neighbours aluminium and boron.

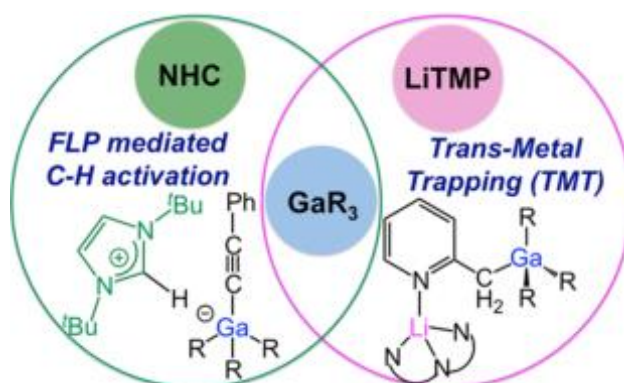


Figure 1. Steric mismatches between GaR₃ with LiTMP or NHCs switch on cooperative effects which enable activation of organic molecules via trans-metal-trapping and FLP approaches respectively.

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Nucleophilic aluminium: Synthesis, structural and reaction chemistry of an aluminyl anion. O

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Aluminium is the most abundant metal in the Earth's crust and is widely exploited in key industrial processes.¹ Being located in group 13 of the Periodic Table it possesses four valence orbitals but only three valence electrons.² Its reactivity is dominated by its electron deficiency and electropositivity: Al^{III} compounds are archetypal electrophiles.² Here we present that anionic Al^I compounds can act as nucleophiles. A dimethylxanthene-stabilized potassium aluminyl compound of the type $[(\text{NON})\text{Al}]\text{K}$ can be synthesized by the potassium graphite reduction of the corresponding (NON)Al species, and shown to be a K⁺ bridged dimer both in the solid state (by X-ray crystallography, Figure 1) and in arene solution (by DOSY NMR). It reacts in an unprecedented 'umpolung' fashion as an aluminium-centred nucleophile in the formation of Al-E covalent bonds (E = H, C or metals).

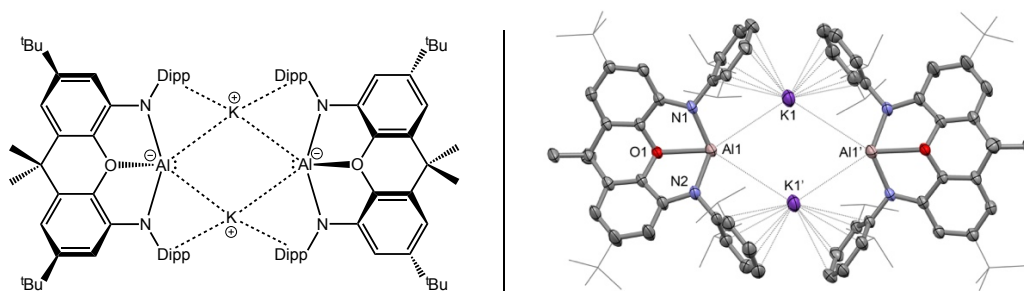


Figure 1. Diagrammatic representation (left) and solid state structure (right) of $[(\text{NON})\text{Al}]\text{K}_2$, an aluminyl anion.

References

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Steric influence of phosphorus ligands on the structure of low oxidation state silicon compounds – O

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The low oxidation state chemistry of the group 14 elements is dominated by the use of amido ligands, mainly *N*-heterocyclic ligands, to stabilise carbenes and their heavier analogues (tetrylenes). There are fewer examples of systems containing phosphide ligands, which can be largely attributed to the high energy of planarization of phosphorus. Therefore, phosphorus centres in these systems typically adopt a trigonal pyramidal geometry that cannot efficiently donate the phosphorus lone pairs into the vacant orbitals of the low oxidation state centres.

Recent advances in ligand design have led to the isolation of the first carbene¹, germylene² [GeR₂] and stannylene³ [SnR₂] stabilised by efficient pπ-pπ interactions from a planar phosphorus centre. Our aim was to use this knowledge to synthesise a diphospha-silylene [(R₂P)₂Si] stabilised by pπ-pπ interactions.

Initial attempts yielded the unique tetraphosphadisilene⁴ [(Mes)₂P]₂Si₂ **1** and the phosphasilene (Dipp)₂PSi(Dipp)P(Dipp) **2** [Mes = 2,4,6-Me₃C₆H₂, Dipp = 2,6-ⁱPr₂C₆H₃]. Compound **1** is the first example of a fully heteroatom-substituted disilene, which contains 4 trigonal pyramidal phosphorus centres and a large *trans*-bending angle of 40.6°. The more sterically demanding ligand (Dipp)₂P was employed in an attempt to prevent dimerization. However, this resulted in the isolation of **2** that we suggest forms by a 1,2-aryl migration from an initial diphosphasilylene {(Dipp)₂P}Si.

The stark difference in the structures of **1** and **2**, achieved only by altering the steric demands on the phosphide ligand from (Mes)₂P to (Dipp)₂P, highlights the reactivity of the low oxidation state Si centre and its affinity for higher coordination.

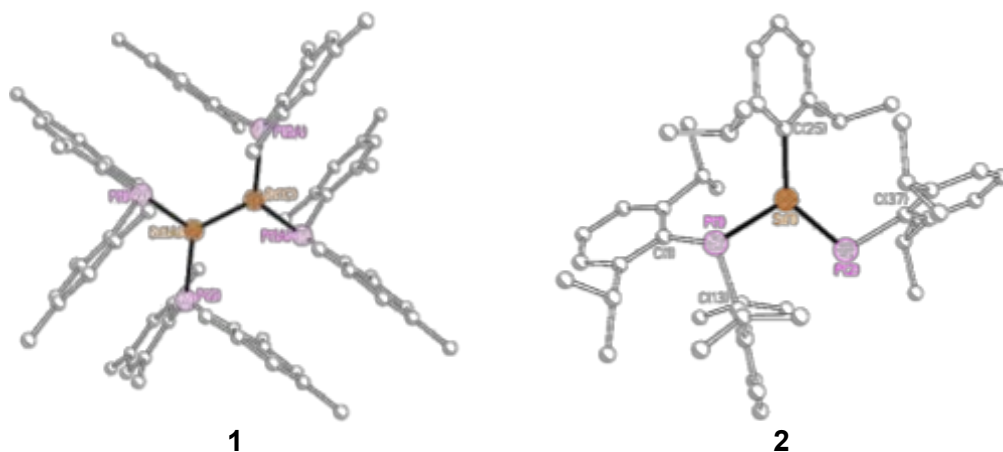


Fig. 1: Crystal structures of **1** and **2** with hydrogen atoms omitted for clarity

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Phosphaborenes: Reagents for the Preparation of P–B/C–C Isosteres - O

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The preparation of unsaturated molecules, where C=C units are formally replaced by isoelectronic nitrogen-boron or phosphorus-boron units, results in compounds with altered electronic properties and reactivities. Whilst the chemistry of unsaturated B/N compounds is relatively well developed, the same cannot be said of the analogous B/P systems, which is largely due to a lack of synthetic methods for their preparation. A handful of P/B containing benzene analogues and Lewis acid or base stabilised phosphaborenes (RP=B(L)R') make up a large proportion of the literature on the subject.¹⁻²

We report a facile solution-phase method for the thermal generation of a transient phosphaborene, Mes*P=BNR₂, **1**, which reacts regioselectively with terminal acetylenes to form cyclobutene analogues such as **2**.³ The 1,2-phosphaborete, **2**, undergoes ring opening reactions with Lewis acids or bases to generate the 1,4-bora-phospha-butadienes **3a** and **b**, which exhibit similar orbital conjugation through their backbones to that found in butadiene. The cyclobutene analogue **2** also undergoes ring-strain promoted insertion reactions with carbon monoxide to form the five-membered ring system **4**.

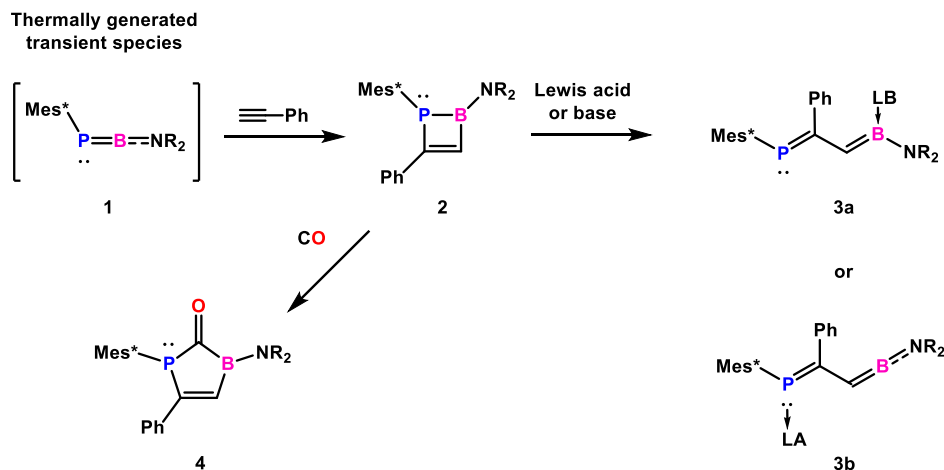


Figure 1: Scheme for the preparation of P-B/C-C isosteres from a thermally generated boraphosphene. (Mes* = 2,4,5-tri-*tert*-butylbenzene, NR₂ = 2,2,6,6-tetramethylpiperidine, LA = Lewis acid, LB = Lewis Base)

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Palladium-Catalysed Transformation of Non-reactive C–F bonds into Reactive C–Al Bonds

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Fluorinated organics constitute at least 20% of all pharmaceuticals and agrochemicals.¹ One strategy to access these molecules is by the use of commercially available and inexpensive perfluoroarenes. C–F bonds of perfluoroarenes can be activated and then transformed into other desired bonds. Much work has focused on a C–F to C–H bond transformation of these substrates; a reaction termed hydrodefluorination (HDF). As the newly formed C–H bond is typically not reactive the synthetic use of HDF is arguably limited. Recently, we and others have become interested in the catalytic transformation of C–F bonds into more reactive chemical bonds, such as C–B, C–Mg and C–Al bonds.^{2–8}

Through the discovery of an active trace metal impurity, we now reported [Pd(PCy₃)₂] as an effective and selective catalyst for C–F alumination, whereby the inert C–F bonds are transformed into reactive C–Al bonds. The catalyst both suppresses the formation of HDF products and operates at 1 mol % loading or less (Figure 1). The yields and regiochemistry of the products were confirmed by protic workup and spectroscopic analysis. Initial control reactions show that the catalyst mixture is capable of activating C–H bonds of fluoroarenes, which indicates that the reaction may proceed by sequential HDF and C–H alumination of the substrates.

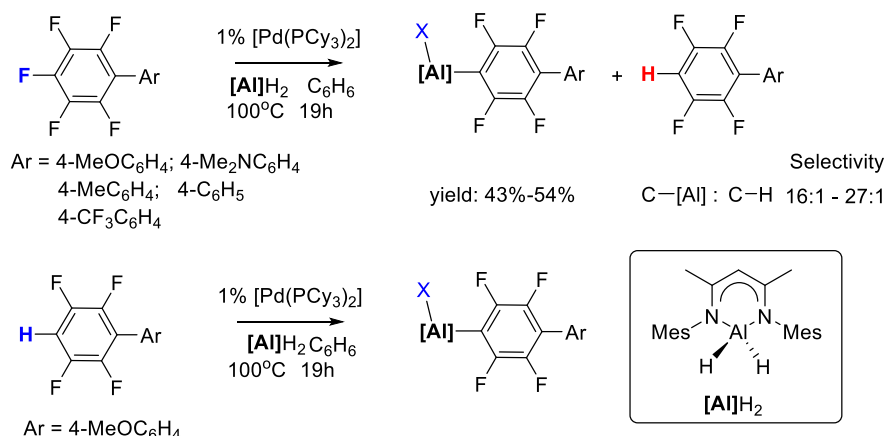


Figure 1. Pd-catalysed alumination of C–F and C–H bonds of fluoroarenes

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