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Harnessing heterometallic synergy: from catalysts to copolymers

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Synergy occurs when the combined efforts of different components produce a result that exceeds the sum of their individual contributions, *i.e.* the overall effect is “greater than the sum of its parts”.¹⁻² In a world where sustainability and circular economy are becoming increasingly crucial, harnessing synergy is an attractive method for achieving more with fewer resources.

Mixed-metal (heterometallic) complexes are at the forefront of synergistic catalyst design, and often outperform their homometallic analogues by displaying higher activities and enhanced selectivities.³ This lecture will describe strategies to exploit mixed-metal cooperativity in cyclic ester ring-opening polymerisation, which can enhance the catalytic efficiency by up to 10 times compared to the monometallic analogues.⁴ This concept has been recently expanded from homopolymerisations to the first use of heterometallic “ate” catalysts for the synthesis of poly(ϵ -caprolactone)-*block*-poly(lactic acid) copolymers, where the performance of Mg/Zn and Ca/Zn ProPhenol catalysts are benchmarked against their homobimetallic analogues.⁵

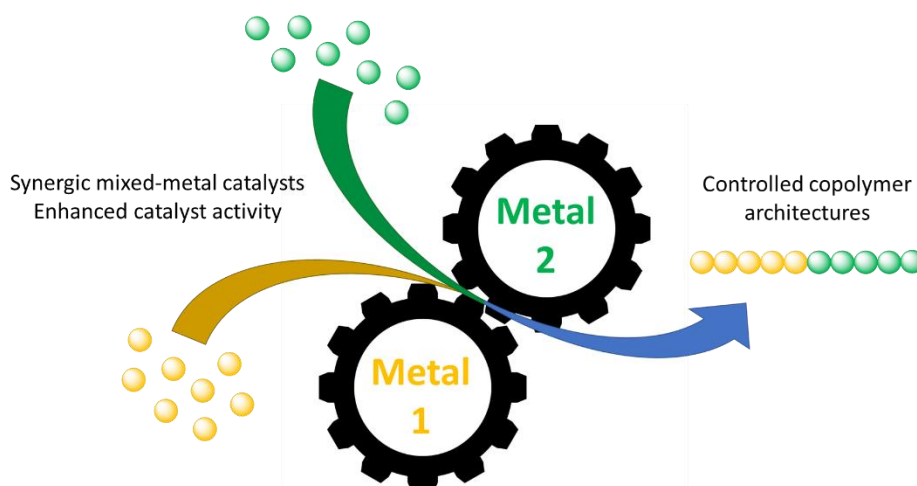


Figure 1. General schematic of multimetallic catalyst systems for copolymer syntheses.

This lecture will demonstrate the powerful potential of heterometallic cooperativity in the synthesis of block copolymers, highlight trade-offs between activity and control, and reveal how the careful choice of the second metal is essential to generate well-defined block copolymer structures.

References

1. P. Buchwalter, J. Rosé, P. Braunstein, *Chem. Rev.* 2015, 115, 28.
2. S. D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* 2019, 119, 8332.
3. W. Gruszka, J. A. Garden, *Nat. Commun.*, 2021, 12, 3252.
4. W. Gruszka, A. Lykkeberg, G. S. Nichol, M. P. Shaver, A. Buchard, J. A. Garden, *Chem. Sci.*, 2020, 11, 11785.
5. M. Abdul Rahman, T. J. Neal, J. A. Garden, *Chem. Commun.*, 2024, 60, 5530.

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.¹⁻⁴ We report the facile and reversible activation of dihydrogen by three-coordinate nacnac magnesium oxide complexes $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2(\mu\text{-O})]$ ($\text{R} = \text{Me, Et, iPr}$ and $\text{Dip} = 2,6\text{-diisopropylphenyl}$) under ambient conditions to yield a bridged hydride/hydroxide complex $[\{(\text{R}^{\text{Dip}}\text{nacnac})\text{Mg}\}_2(\mu\text{-OH})(\mu\text{-H})]$.⁵⁻⁷ This marks the first facile example of dihydrogen activation across a magnesium-oxygen complex.⁵ 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 $\text{R} = \text{iPr}$).⁵ 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.⁵ 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 H^+ and H^- .⁵ The activation of dihydrogen has also been studied via DFT calculations.⁵ NMR spectroscopy and X-ray crystal structures will be presented.⁵

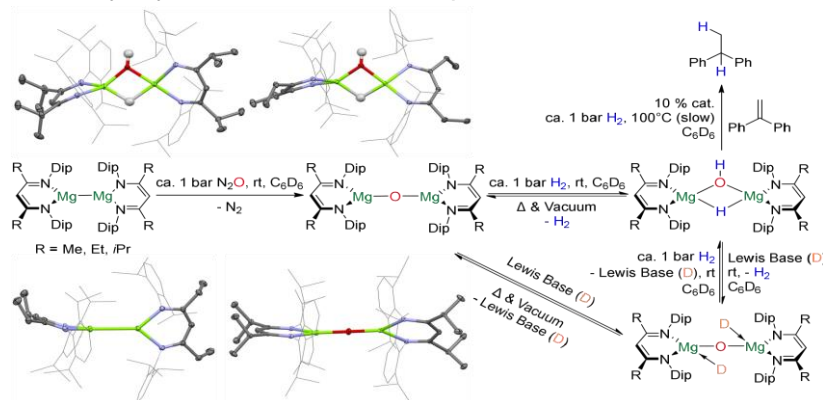


Figure 1. Synthesis of magnesium oxide complexes and reversible hydrogen activation.⁵⁻⁷

References

1. P. J. Brothers, in *Progress in Inorganic Chemistry*, ed. S. J. Lippard, 1981, ch. 1, pp. 1-61.
2. M. A. Stevens and A. L. Colebatch, *Chem. Soc. Rev.*, 2022, **51**, 1881-1898.
3. H. Bauer, M. Alonso, C. Fischer, B. Rosch, H. Elsen and S. Harder, *Angew. Chem. Int. Ed.*, 2018, **57**, 15177-15182.
4. G. J. Kubas, *J. Organomet. Chem.*, 2014, **751**, 33-49.
5. S. Thompson, S. Burnett, R. Ferns, T. V. Mourik, A. McKay, A. Slawin, D. Cordes and A. Stasch, *J. Am. Chem. Soc.*, 2025, DOI: 10.1021/jacs.4c16041.
6. S. Burnett, R. Ferns, D. B. Cordes, A. M. Z. Slawin, T. van Mourik and A. Stasch, *Inorg. Chem.*, 2023, **62**, 16443-16450.
7. R. Lalrempuia, A. Stasch and C. Jones, *Chem. Sci.*, 2013, **4**, 4383-4388.

Alkaline earth electrides: a new weapon in the synthetic arsenal

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Earth abundant and non-toxic alkaline earth (AE) metals promise cheaper and more sustainable alternatives for chemical manufacturing processes, but their lack of redox reactivity prevents their wide application. Since the landmark report of Mg(I) dimers in 2007,¹ this research field has experienced an incredible expansion.² Despite some encouraging progress,³ analogous compounds with calcium, strontium and barium have not been reported to date, often due to the instability of these species in standard ‘wet’ synthetic protocols. Therefore, a new approach is required to finally achieve these prodigious targets and provide a step change to the field of low oxidation state AE chemistry.^{4,5}

In this work we focused on the use of solvent-free mechanochemical methods to attempt the isolation of low oxidation state AE complexes.⁶ Mechanochemical reduction of *tris*-amide and *bis*-amidinate AE(II) precursors did not afford low oxidation state complexes, leading instead to the formation of very rare examples of Room temperature Stable Electrides (RoSEs). Our new AE-RoSEs display remarkable reactivity including C-H activation and C-C coupling chemistry. We also studied in detail the electronic structure of these AE electrides and performed comprehensive characterisation of these systems, using state-of-the-art magnetic measurements and *ab initio* calculations.⁴

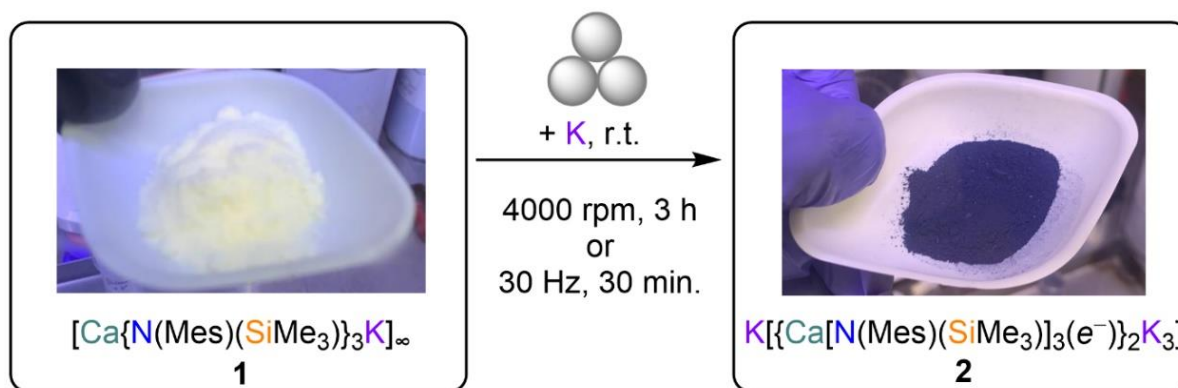


Figure 1. Mechanochemical synthesis of Ca-RoSE.

References

1. S. P. Green, C. Jones, A. Stasch, *Science*, 2007, **318**, 1754–1758.
2. B. Rosch *et al.*, *Nature*, 2021, **592**, 717–721.
3. B. Rösch *et al.*, *Science* 2021, **371**, 1125–1128.
4. A. W. J. Bowles, F. Ortu *et al.*, *Chem. Eur. J.*, 2023, **29**, e202307850.
5. A. W. J. Bowles, Y. Liu, F. Ortu *et al.*, *Inorg. Chem.*, 2024, **63**, 22061–22073.
6. A. W. J. Bowles, F. Ortu *et al.*, *J. Am. Chem. Soc.*, 2024, **146**, 28914–28924.

Diberyllanes and metal beryllyl complexes

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Beryllium and boron are “neighbours” within the second row of the Periodic Table. The properties of the lightest elements, such as these, provide the basis for our models of chemical bonding and reactivity. Nevertheless, the chemistry of beryllium is very poorly understood, chiefly because its toxicity deters most investigators.¹ Indeed, whilst the reactivity of diborane(4) derivatives has been thoroughly developed, that of “diberyllanes” – molecules that feature a Be–Be bond – is almost entirely unknown, with the first examples of such species being reported in 2023.^{2,3}

This talk will describe the chemistry of diberyllanes and their use in the preparation of metal beryllyl (M–BeX) complexes. As a result of beryllium’s very low Pauling electronegativity (1.57), beryllyl groups possess perhaps the most potent σ -donor properties of any ligand class. Thus, beryllyl ligands can stabilise metals in novel valence states. For example, the synthesis and electronic structure of Ni(BeCp)₆ – the first stable hexavalent nickel complex – will be discussed.⁴ Moreover, the divergent reactivities of isostructural metal-beryllyl and -boryl complexes will be explored. In this context, the catalytic C–H beryllation of methane and benzene by manganese- and rhenium-bis(beryllyl) complexes will be detailed.

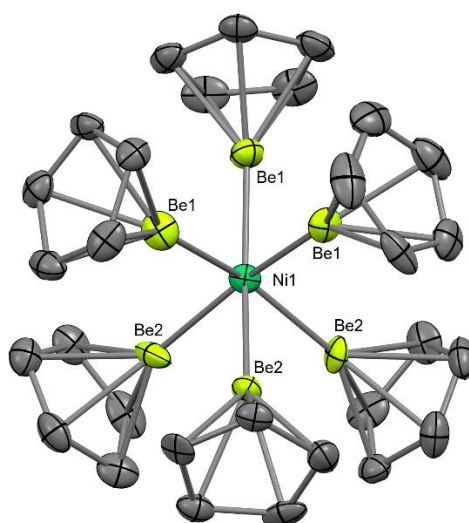


Figure 1: A stable hexavalent nickel complex, Ni(BeCp)₆.

References

1. D. Naglav, M. R. Buchner, G. Bendt, F. Kraus and S. Schulz, *Angew. Chem., Int. Ed.*, 2016, **55**, 10562–10576.
2. J. T. Boronski, A. E. Crumpton, L. L. Wales and S. Aldridge, *Science*, 2023, **380**, 1147–1149.
3. J. T. Boronski, A. E. Crumpton, A. F. Roper and S. Aldridge, *Nat. Chem.*, 2024, **16**, 1295–1300.
4. J. T. Boronski, A. E. Crumpton and S. Aldridge, *J. Am. Chem. Soc.*, 2024, **146**, 35208–35215.

New route to fully unsymmetrical and highly reactive diborenes

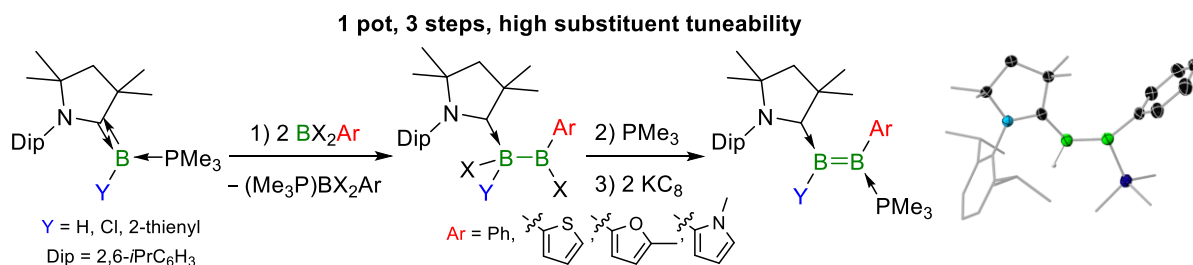
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Since the report of the first neutral Lewis-base (LB)-stabilised diborenes in 2007,¹ these highly reactive diboron analogues of alkenes have generated increasing interest, owing to their high-lying HOMO and small HOMO-LUMO gap, which enables them to undergo facile uncatalysed 1,2-addition and cycloaddition reactions.² The two most prominent synthetic methods, the reductive coupling of (NHC)BRX₂ (NHC = N-heterocyclic carbene, R = anionic substituent, X = halide) and the reduction of [(R'₃P)BRX]₂ diborane precursors, are essentially limited to symmetrical and sterically demanding substitution patterns. Unsymmetrical diborenes may be accessed via the 1,2-addition of polar E–H bonds at diborynes (the diboron analogues of alkynes),³ or by using bespoke ligand systems,⁴ however, these routes do not allow for easy derivatization.

In this study we report a new highly tunable strategy for accessing stable, fully unsymmetrical diborenes from borylenes of the type (CAAC)BY(PMe₃) (CAAC = cyclic alkyl(amino)carbene); Y = H, Cl, 2-thienyl⁵ and BCl₂Ar (Ar = small (hetero)aryl) via a one-pot three-step sequence of oxidative addition, PMe₃ adduct formation, and reduction (see Scheme). The small size of the substituents, added to the lability of the PMe₃ ligand and the high polarisation of the B=B bond, result in a substantial increase in reactivity compared to symmetrical diborenes, while the broad range of derivatives accessible via this route provides unprecedented scope for tuning the electronic properties of these diborenes.



Synthetic route to fully unsymmetrical diborenes via the oxidative addition of haloboranes to borylenes.

References

1. Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2007, **129**, 12412-12413.
2. M. Arrowsmith, H. Braunschweig and T. E. Stennett, *Angew. Chem. Int. Ed.*, 2017, **56**, 96-115.
3. a) T. Brückner, T. E. Stennett, M. Heß and H. Braunschweig, *J. Am. Chem. Soc.*, 2019, **141**, 14898-14903; b) R. Yadav, S. Sinhababu, R. Yadav and S. Kundu, *Dalton Trans.*, 2022, **51**, 2170-2202.
4. a) T. E. Stennett, J. D. Mattock, L. Pentecost, A. Vargas and H. Braunschweig, *Angew. Chem. Int. Ed.* 2018, **57**, 15276-15281; b) W. Lu, Y. Li, R. Ganguly and R. Kinjo, *J. Am. Chem. Soc.*, 2017, **139**, 5047-5050.
5. a) M. Arrowsmith, J. I. Schweizer, M. Heinz, M. Härterich, I. Krummenacher, M. C. Holthausen, H. Braunschweig, *Chem. Sci.*, 2019, **10**, 5095-5103; b) M. Arrowsmith, S. Endres, M. Heinz, V. Nestler, M. C. Holthausen, H. Braunschweig, *Chem. Eur. J.*, 2021, **27**, 17660-17668

Catalytic and selective methane oxidation using main group species

Liam A. Parkin, George J. P. Britovsek, Andrew E. Ashley.

Methane is the most abundant hydrocarbon, and an extremely valuable commodity chemical. However, it is often wasted due to the difficulty in transporting the gas from isolated places (i.e. deep-sea oil rigs). An obvious solution is the upgrading of methane on-site into methanol, an easily transportable liquid product that is of much greater value than the methane alone. However, methane is incredibly difficult to selectively oxidise, as it has very strong C-H bonds and is non-polar.¹ Despite many advancements in the field of selective methane oxidation since the seminal work of Shilov over 50 years ago, there remains no industrially viable process for this transformation.² Systems are plagued by over-oxidation, poor selectivity, low turnover number and frequency, expensive separations, and prohibitively high costs.

We have developed a low cost, main group-based system that can selectively oxidise methane to an easily isolable methyl ester (for example methyl bisulphate, which can be further hydrolysed to form methanol).^{3,4} Oxidation is observed at conditions as low as 1 bar CH₄, and at room temperature, with yields as high as 97% being achieved, an unprecedented result so far in this field. At such low pressures, it is possible to add methane as a low-pressure stream by bubbling through the oxidising solution, hence making the system semi-flow.

Additionally, we have been able to make this system catalytic, by utilising a redox mediator. In doing so we have oxidised methane catalytically using O₂ to a methyl ester which can be hydrolysed to form methanol, as shown in the figure below.

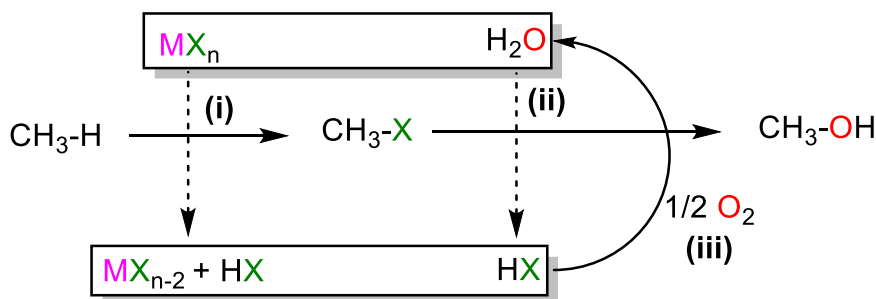


Figure 1: Oxidation of methane using a high valent metal or main group species (for example: M = Pb, Tl; X = CF₃CO₂⁻). (ii) hydrolysis of the formed methyl ester. (iii) Re-oxidation of the reduced metal or main group species using oxygen.⁵

References

- 1 R. H. Crabtree, Chem. Rev., 1995, 95, 987–1007.
- 2 N. F. Gol'dshleger, V. V Es'kova, A. E. Shilov and A. A. Shteinman, Zhurnal Fiz. Khimii (English Transl., 1972, 46, 785–786.
- 3 L. A. Parkin, A. E. Ashley, EPOrg, EP24200554, filed Sep 2024.
- 4 L. A. Parkin, A. E. Ashley, UKIPO, GB2413590, filed Sep 2024.
- 5 B. G. Hashiguchi, M. M. Konnick, S. M. Bischof, S. J. Gustafson, D. Devarajan, N. Gunsalus, D. H. Ess and R. A. Periana, Science, 2014, 343, 1232–1237.

On the Mechanism of Metal-Free Alkene Borylation

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C–H borylation of an sp^2 -carbon is one of the most desired yet arduous chemical transformations.^{1,2} It is an effective way to access useful building blocks for further cross-coupling reactions. For example, taking advantage of boronic ester precursors, the Suzuki–Miyaura coupling ensures that many important pharmaceuticals become available.³ Currently, sp^2 C–H borylation is accessible with platinum-group metal catalysts.^{1,2} However, due to the low earth-abundance of precious metals and meticulous removal of metal traces in the final product, the demand for metal-free borylation is growing.⁴ In fact, metal-free sp^2 C–H borylations are not yet numerous but have already proven to be highly effective.⁵

Herein, we report our efforts in understanding the structure–reactivity relationships and mechanistic details of two different metal-free, main group catalysts (Figure 1), expand the substrate scope and discuss on the limitations of alkene and alkane borylation reactions.^{6,7}

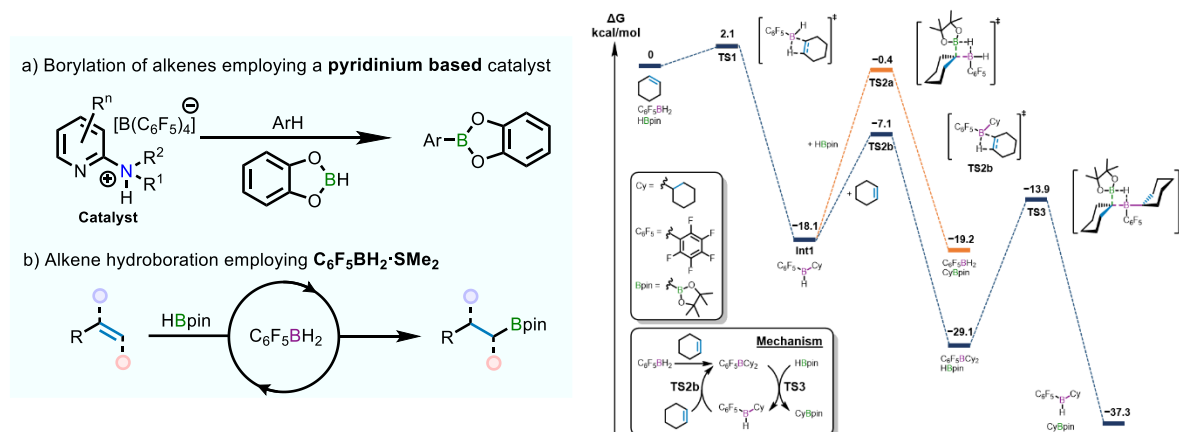


Figure 1. Right: Reaction scheme of a) borylation of alkenes by a pyridinium based catalyst and b) hydroboration of alkenes by $C_6F_5BH_2 \cdot SMe_2$. Left: Calculated reaction mechanism for the hydroboration of cyclohexene.

References

1. T. Dalton, T. Faber and F. Glorius, *ACS Cent. Sci.*, 2021, **7**, 245–261.
2. I. A. I. Mkhaliid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890–931.
3. N. Schneider, D. M. Lowe, R. A. Sayle, M. A. Tarselli and G. A. Landrum, *J. Med. Chem.*, 2016, **59**, 4385–4402.
4. C.-L. Sun and Z.-J. Shi, *Chem. Rev.*, 2014, **114**, 9219–9280.
5. K. Chernichenko, M. Lindqvist, B. Kótai, M. Nieger, K. Sorochkina, I. Pápai and T. Repo, *J. Am. Chem. Soc.*, 2016, **138**, 4860–4868.
6. N. Slesarchuk, E. Ma, J. Miranda-Pizarro, S. Heikkinen, D. Schollmeyer, M. Nieger, P. Vasko and T. Repo, *Dalton Trans.*, 2024, **53**, 9590–9595.
7. N. Slesarchuk, G. Doerksen, P. Vasko and T. Repo, *Manuscript submitted*.

Zinc and Aluminium Catalysed C–H Functionalisation of Heteroarenes

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The selective transformation of C–H bonds into C–M (M = B, Zn, Al, etc.) bonds is essential for modern organic synthesis as it gives access to highly useful reagents (e.g. in cross coupling). Although catalytic C–H borylation for forming aryl-boronate esters has witnessed rapid development in recent years,¹ C–H zincation and aluminatation remain far less explored, and generally rely upon using \geq one equivalent of Brønsted super-bases. In contrast, catalytic C–H zincation/C–H aluminatation is extremely rare with only one approach reported using a Pd-catalyst.²

This talk will present transition-metal free catalytic C–H zincation and C–H aluminatation of heteroarenes using $[(R_3N)H][Anion]$ as a sub-stoichiometric (10 mol%) initiator.³ Key to this approach is coupling an endergonic arene C–H metalation step using a $[(L)M-NR_3]^+$ (M = Zn or Al–Me, L = NacNac) electrophile with a sufficiently exergonic dehydrocoupling step between the formed Brønsted acidic ammonium salt $[(R_3N)H]^+$ and a Zn–H or Al–Me complex. Finally, we will highlight that C–H metalation can be coupled with a σ -bond metathesis step to enable Al/Zn catalysed C–H borylation using the inexpensive and commercially available hydroborane $(H-BBN)_2$ (Figure 1).⁴ Moreover, the Aryl–BBN products can be used in one pot transformations, including a reaction that does not proceed using the analogous pinacol-boronate ester.

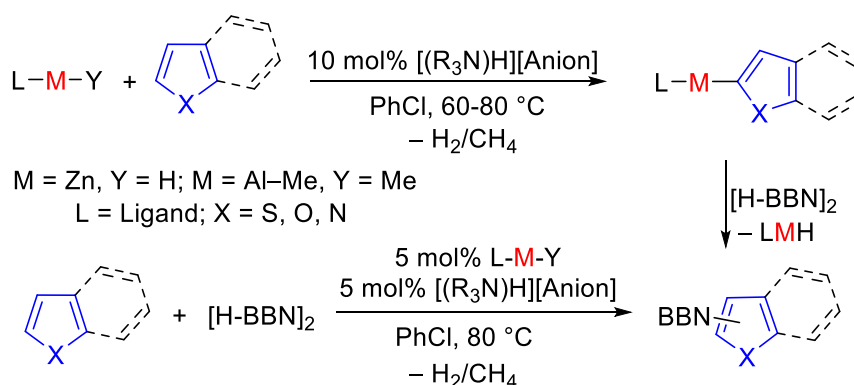


Figure 1. Catalytic C–H functionalisation using Zn/Al catalyst.

References

1. R. Bisht, C. Haldar, M. M. M. Hassan, M. E. Hoque, J. Chaturvedi and B. Chattopadhyay, *Chem. Soc. Rev.*, 2022, **51**, 5042–5100.
2. (a) M. Garçon, N. W. Mun, A. J. P. White and M. R. Crimmin, *Angew. Chem. Int. Ed.*, 2021, **60**, 6145–6153; (b) W. Chen, T. N. Hooper, J. Ng, A. J. P. White and M. R. Crimmin, *Angew. Chem. Int. Ed.*, 2017, **56**, 12687–12691.
3. M. K. Bisai, J. Łosiewicz, L. Sotorrios, G. S. Nichol, A. P. Dominey, M. J. Cowley, S. P. Thomas, S. A. Macgregor and M. J. Ingleson, *Angew. Chem. Int. Ed.*, 2024, **63**, e202404848.
4. M. K. Bisai, J. Łosiewicz, G. S. Nichol, A. P. Dominey, S. P. Thomas, S. A. Macgregor and M. J. Ingleson, *Manuscript submitted*.

A Sterically Accessible Monomeric Stibine Oxide Activates Organotetrel(IV) Halides, Including C–F and Si–F Bonds

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Phosphine oxides and arsine oxides are common laboratory reagents with diverse applications that stem from the chemistry exhibited by these monomeric species. Stibine oxides are, in contrast, generally dimeric or oligomeric species because of the reactivity-quenching self-association of the highly polarized stiboryl ($\text{Sb}=\text{O}/\text{Sb}^+-\text{O}^-$) group. We recently isolated Dipp_3SbO (Dipp = 2,6-diisopropylphenyl), the first example of a kinetically stabilized monomeric stibine oxide, which exists as a bench-stable solid and bears an unperturbed stiboryl group. Herein, we report the isolation of Mes_3SbO (Mes = mesityl), in which the less bulky substituents maintain the monomeric nature of the compound but unlock access to a wider range of reactivity at the unperturbed stiboryl group relative to Dipp_3SbO . Mes_3SbO was found to be a potent Lewis base in the formation of adducts with the main-group Lewis acids PbMe_3Cl and SnMe_3Cl . The accessible Lewis acidity at the Sb atom results in a change in the reactivity with GeMe_3Cl , SiMe_3Cl , and CPh_3Cl . With these species, Mes_3SbO formally adds the E–Cl (E = Ge, Si, C) bond across the unsaturated stiboryl group to form a 5-coordinate stiborane. The biphilicity of Mes_3SbO is sufficiently potent to activate even the C–F and Si–F bonds of $\text{C}(\text{p-MeOPh})_3\text{F}$ and SiEt_3F , respectively. These results mark a significant contribution to an increasingly rich literature on the reactivity of polar, unsaturated main-group motifs. Furthermore, these results highlight the utility of a kinetic stabilization approach to access unusual bonding motifs with unquenched reactivity that can be leveraged for small-molecule activation.

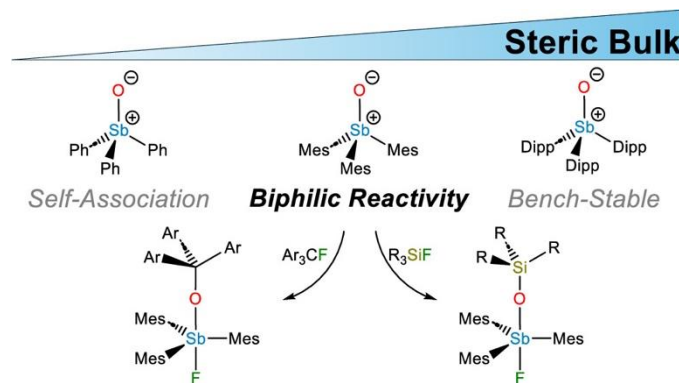


Figure. The stibine oxide Mes_3SbO features intermediate steric protection, enabling access to biphilic activation of C–F and Si–F bonds while preventing self-association of monomers.

References

1. J. S. Wenger and T. C. Johnstone, *J. Am. Chem. Soc.*, 2024, 146, 19350-19359.

Metallomimetic C–F Activation Catalysis by Simple Phosphines

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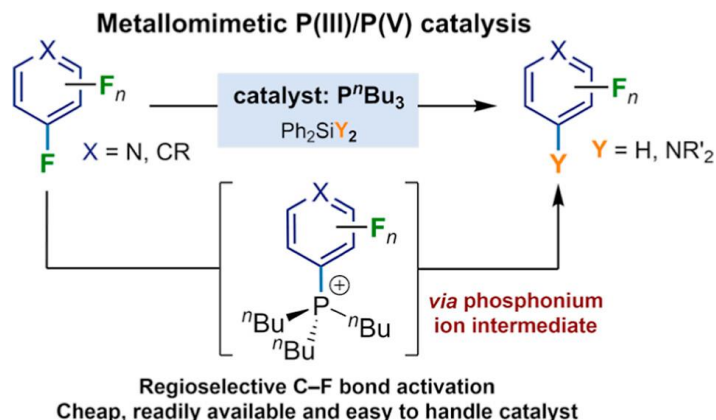
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Fluorine-containing organic molecules are found in a wide range of applications.¹ As such, there is a synthetic requirement to develop efficient and selective methods for the formation of these types of compounds. Furthermore, in recent years there has been considerable interest in the activation and functionalisation of small molecules and strong bonds by main-group-element compounds, mimicking transformations typically promoted by transition metals.²

This work demonstrates that simple, inexpensive and readily available trialkylphosphines are able to hydrodefluorinate and aminodefluorinate polyfluoroaromatics without the need to enforce unusual geometries at phosphorus or use external oxidising/reducing agents.³ Experimental and computational mechanistic studies indicate that catalytic hydrodefluorination reactions are supported by metallomimetic behaviour: phosphines undergo oxidative addition of the fluoroaromatic substrate *via* a Meisenheimer-like transition state, followed by a pseudotransmetallation step with a silane and a final reductive elimination of the product to reform the phosphine catalyst.



Representative scheme of the hydro- and aminodefluorination reaction catalysed by a simple phosphine.

References

1. T. Hiyama, *Organofluorine Compounds*, Springer Berlin, Heidelberg, 1st edn., 2000.
2. C. Weetman and S. Inoue, *ChemCatChem* 2018, **10**, 4213–4228.
3. S. Bonfante, C. Lorber, J. M. Lynam, A. Simonneau and J. M. Slattery, *J. Am. Chem. Soc.*, 2024, **146**, 2005–2014.

Amidinate ligand stabilised low-valent aluminium complexes: syntheses and equilibria

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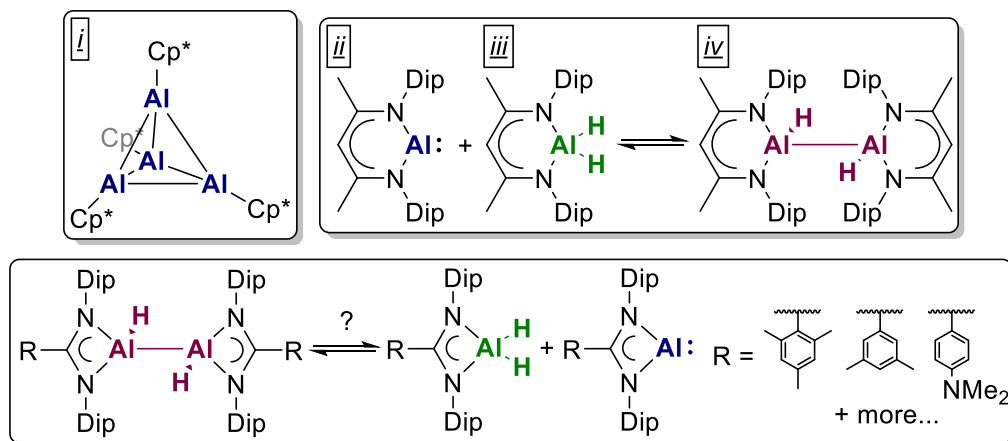
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The requirement for humanity to move away from the use of heavy transition metals is well-trodden ground. As the most abundant metal in the Earth's crust, aluminium represents an attractive alternative but its use in traditionally transition-metal catalysed processes is limited by our meagre understanding of its reactivity. Interest in the synthesis and reactivity of low-oxidation state aluminium compounds has exploded since the seminal first report of the synthesis of a stable aluminium(I) complex¹, the tetrameric [AlCp*]₄ (Cp* = C₅Me₅) (fig., *i*) and the subsequent report from the Roesky group of monomeric beta-diketiminato (BDI) stabilised DipBDIAl(I) (DipBDI = {DipNC(Me)}₂C, Dip = 2,6-diisopropylphenyl) (fig., *ii*).² There has been a growing understanding recently of the crucial role that the dynamic equilibrium between a range of aluminium oxidation states plays in the reactivity of these fascinating species (fig., *ii*, *iii* and *iv*).³

Within the Bakewell group we also have a keen interest in exploring the reactivity of aluminium in low oxidation states. Previously, we have probed the equilibria between Al^I and Al^{III} complexes⁴ and harnessed this equilibrium to synthesise a range of masked dialumenes.⁵

This presentation will detail recent results on the synthesis of a range of new amidinate ligands, their complexation and the subsequent synthesis of a series of low-oxidation state aluminium complexes. Explored will be the effects of altering the ligand steric and electronic contribution on their reduction chemistry, with the details of their formation examined by DFT.



Examples of previously reported low-valent aluminium complexes (above) and amidinate-stabilised low-valent Al equilibria explored in this talk (below).

References

1. Schnöckel et. al.; *Angew. Chem. Int. Ed.*; 1991; **30**; 564-565
2. Roesky et. al.; *Angew. Chem. Int. Ed.*; 2000; **39**; 4274-4276
3. Nikonov et. al.; *J. Am. Chem. Soc.*; 2014; **136**; 9195-9202
4. Bakewell et. al.; *Angew. Chem. Int. Ed.*; 2022; **61**; e2502205901
5. Bakewell et. al.; *Chem Commun.*; 2024; **60**; 12958-12911

Isolation and the reactivity of an acyclic-monomeric aluminyl

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Recently, low valent aluminium compounds, possessing a nucleophilic Al(I) center, isoelectronic to carbene, namely the aluminyl anion ($[R_2Al:]^-M^+$), with comparatively small HOMO-LUMO gaps, showed promising reactivity towards industrially relevant small molecules (e.g., H_2 , CO_2 , N_2O , P_4 , and RN_3 , etc.), leading to the formation of reactive Al-E bonds ($E = H, O, N$).^{1, 2} Typically, these aluminyls are stabilized by N/N, N/C, C/C based di-anionic chelating ligand systems.^{1, 2} Apart from these examples, an acyclic bis amido aluminyl $K_2[Al\{N(Dipp)SiMe_3\}_2]_2$ has been reported, which exists as a dimer in solution as well as in solid state.³ To the best of our knowledge a charge separated monomeric-acyclic aluminyl is still unknown.

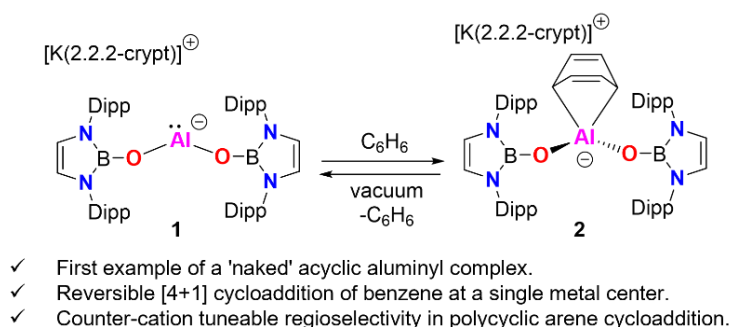


Figure 1: Acyclic aluminyl 1 and its reactivities towards small molecules.

In this talk I will present the first example of a monomeric-acyclic aluminyl $[K(2.2.2\text{-crypt})][Al\{OB(NDipp)CH_2\}_2]$ **1**, stabilized by bis-boryloxy ligands.⁴ Notably compound **1** activate a diverse range of small molecules (e.g., CO , NH_3 , ethylene etc.), including the reversible [4+1] cycloaddition of benzene.

References

1. M. P. Coles and M. J. Evans, *Chem. Commun.*, 2023, **59**, 503-519.
2. J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Angew. Chem. Int. Ed.*, 2021, **60**, 1702-1713.
3. R. A. Jackson, A. J. R. Matthews, P. Vasko, M. F. Mahon, J. Hicks and D. J. Liptrot, *Chem. Commun.*, 2023, **59**, 5277-5280.
4. D. Sarkar, P. Vasko, A. F. Roper, A. E. Crumpton, M. M.D. Roy, C. Bogle, L. P. Griffin and S. Aldridge, *J. Am. Chem. Soc.* 2024, **146**, 11792–11800.

Zinc-Mediated Divergent Transmetalation from a β -diketiminato Calcium Hydride

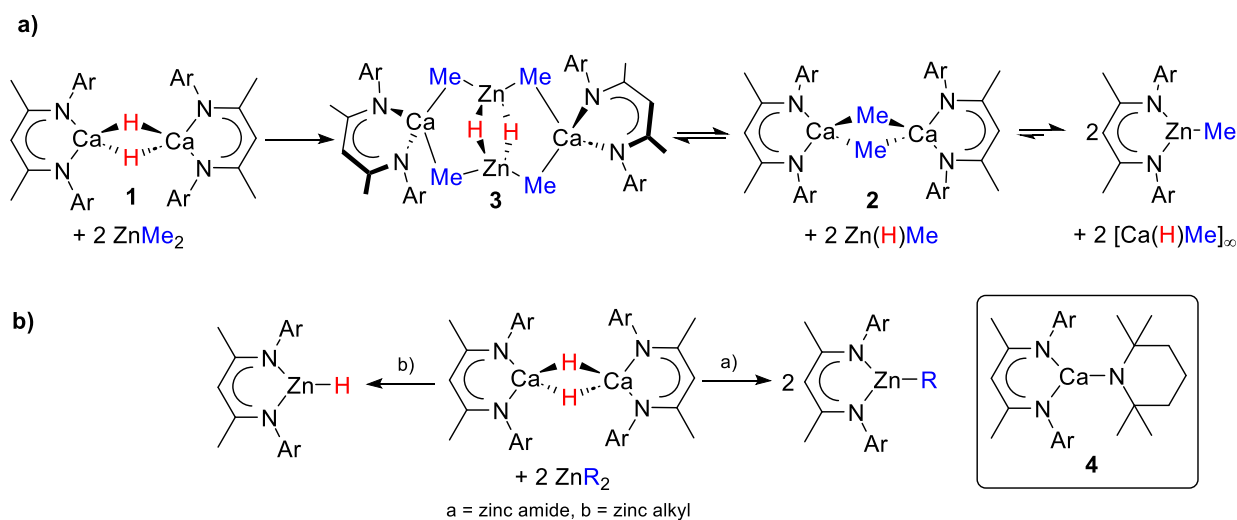
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Transmetalation, the process by which ligands are transferred from one metal to another, is a key reaction step in most catalytic cycles and thus extensively studied. In stark contrast, pre-transmetalation intermediates are less explored, though provide useful insight into the reaction mechanism, which could be exploited for reaction optimisation. With this in mind, the dimeric β -diketiminato calcium hydride (**1**) reacts with dimethyl zinc to ultimately afford a β -diketiminato zinc methyl complex *via* methyl-for-hydride transmetalation (**Scheme 1a**).¹ Under appropriate conditions, the calcium methyl complex (**2**) can be prepared, and the intermediate on this reaction pathway (**3**) can be isolated exclusively, yielding insight into the reaction mechanism, which would typically only be observed *in-silico*.

In an extension of this work (*unpublished*), divergent reactivity has been observed, in which the identity of the zinc reagent dictates the transmetalation product. For example, zinc diamides undergo not only amide-for-hydride exchange but also transmetalation of the β -diketiminato ligand scaffold (**Scheme 1b**), thus ligating and functionalising the zinc centre in a one-pot reaction. Furthermore, the reaction intermediates can be isolated, allowing for the preparation of previously inaccessible organocalcium complexes such as **4**. This work is currently being extended to more exotic zinc reagents, whilst also exploring the reactivity and potential of the isolated intermediates.



Scheme 1. a) reaction pathway between ZnMe_2 and $[(\text{BDI})\text{CaH}]_2$ **b)** Divergent reactivity between ZnR_2 and $[(\text{BDI})\text{CaH}]_2$.

References

1. K. G. Pearce, S. E. Neale, C. L. McMullin, M. F. Mahon and M. S. Hill, Chem Commun., 2024, 60, 7882-7885.

A crystalline nitrogen chain radical anion

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Carbon's ability to form linear molecular chains is unmatched, and central to how our biology and the materials in our world operate. In stark contrast, its neighbour nitrogen heavily disfavours chain formations. In part this is due to the disproportionately strong N≡N triple bond when compared to N–N single and double bonds, making loss of dinitrogen (N₂) gas an enormous enthalpic and entropic driving force from catenated nitrogen.¹ Studying nitrogen chain ions under ambient conditions presents a formidable challenge, and nitrogen chain anions substituted with organic groups are similarly under-investigated.

Almost half a century after the first detection of a compound featuring a {N₄}^{•–} chain in a mass spectrometer, we have shown that a molecule featuring this moiety can be isolated under ambient conditions.^{2,3} Electronically stabilized by aromatic units, crystalline [Ar{N₄}Ar]^{•–} is isolated as a storable solid with multi-week persistence under anaerobic conditions. Spin density calculations accompanied by electron paramagnetic resonance spectroscopy highlight that the unpaired electron is prominently on the {N₄} chain with the terminal nitrogens bearing the most spin density. Reactivity studies reveal that this {N₄} chain can decompose into N1 and N3 units, with reactivity consistent with the generation of a nitrene radical anion.

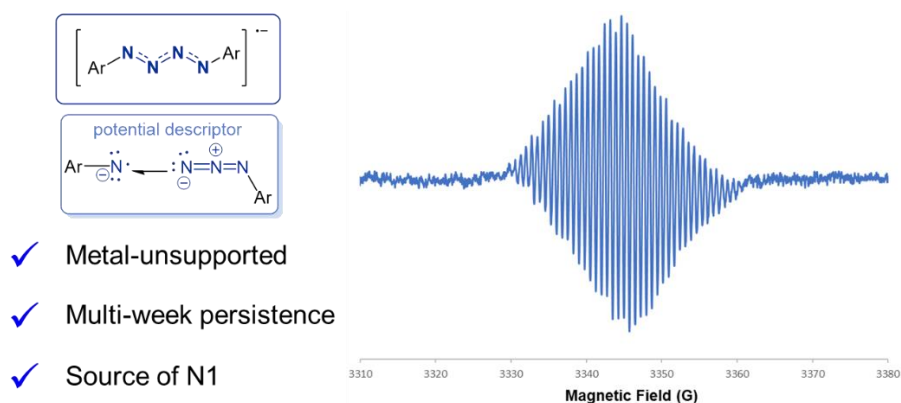


Figure 1: General structure [Ar{N₄}Ar]^{•–} with the potential descriptor that underpins reactivity and continuous wave electron paramagnetic resonance spectrum.

References

1. N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*. Elsevier, Oxford 2012.
2. R. N. McDonald, A. K. Chowdhury, *J Am Chem Soc* 1980, 102(15): 5118-5119.
3. R. Lister-Roberts, D. Galano, B. van IJzendoorn, G. F. S. Whitehead, A. Brookfield, A. M. Bowen, N. Kaltsoyannis, M.Mehta, *submitted*

HF shuttling for the chemical recycling of fluorocarbons

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Fluorocarbons are essential to our way of life, with uses ranging from materials and refrigerants to pharmaceuticals and agrochemicals. However, fluorocarbons are overwhelmingly treated as “single-use”, with little to no recycling. Disposal routes face increasing scrutiny due to emerging research on the pervasiveness of per- and poly-fluorinated substances and the impact of exposure on human health.^{1,2} Methodologies for recycling fluorocarbons are therefore highly attractive.

Hydrofluorination is an essential methodology for the synthesis of fluorocarbons, but typically requires toxic and difficult to handle reagents, such as hydrofluoric acid, Py.HF, Et₃N.HF and DBU.HF, and can suffer from poor selectivity and reactivity.³ There are few methodologies which achieve both hydrofluorination and dehydrofluorination in a single reaction sequence.

In this work, we report BF₃.OEt₂ as a catalyst for shuttling equivalents of HF from fluoroalkanes to alkynes and acid anhydrides, generating difluoroalkanes and acyl fluorides respectively.⁴ Numerous potentially sensitive functional groups including halogens, protected amines, esters and thiophenes are tolerated. Density functional theory calculations have been used to probe the mechanism of the reaction. The system has been leveraged for the dehydrofluorination of both commercial and post-consumer poly(vinylidene difluoride) (PVDF) materials, the second most used fluoropolymer worldwide. Characterisation including IR, XPS, XRD and elemental analysis of the polymer products indicate a high degree of dehydrofluorination, demonstrating HF shuttling's value as a proof-of-concept recycling methodology.⁵

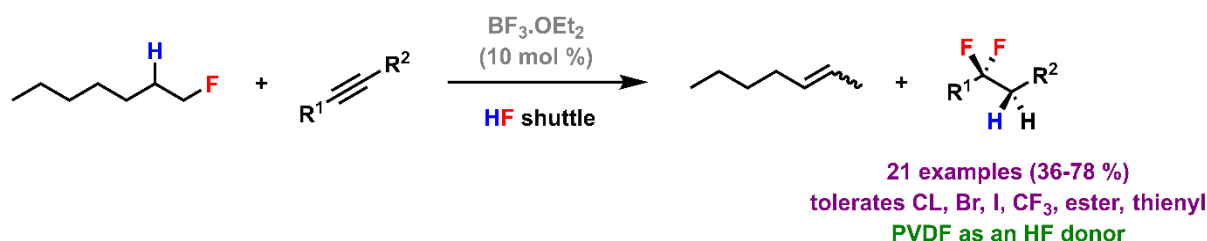


Figure 1: Overview of Lewis acid catalysed HF shuttle between fluoroheptane and alkynes.

References

1. H. Brunn, G. Arnold, W. Körner, G. Rippen, K. G. Steinhäuser, I. Valetin, *Environ. Sci. Euro.*, 2023, **35**, 20
2. Z. Wang, H. C. DeWitt, C. P. Higgins, I. T. Cousins, *Environ. Sci. Technol.*, 2017, **51**, 2508-2518
3. X. Bertrand, L. Chabaud, J. F. Paquin, *Chem. Asian J.*, 2021, **16**, 563-574
4. S. E. S. Farley, D. Mulryan, F. Rekhroukh, A. Phanopolous, M. R. Crimmin, *Angew. Chem. Int. Ed.*, 2024, **63**, e202317550
5. C. Heinekamp, A. G. Buzanich, M. Ahrens, T. Braun, *Chem. Commun.*, 2023, **59**, 11224-11227

Zwitterionic Heavy Main Group Species in Redox Organometallics

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Noble metals such as Pd or Rh are the workhorses of chemical industry due to their ability to engage in substrate coordination and organometallic redox events during catalysis.¹ However, supply and price instability of noble metals pose a tremendous challenge. This has led to a shift towards exploring the realm of main group elements, which have recently shown the potential for emulating the two-electron processes of transition metals.² Within this realm, heavy main group elements present themselves as versatile elements with multiple oxidation states that remain underexplored in the field of redox catalysis.³

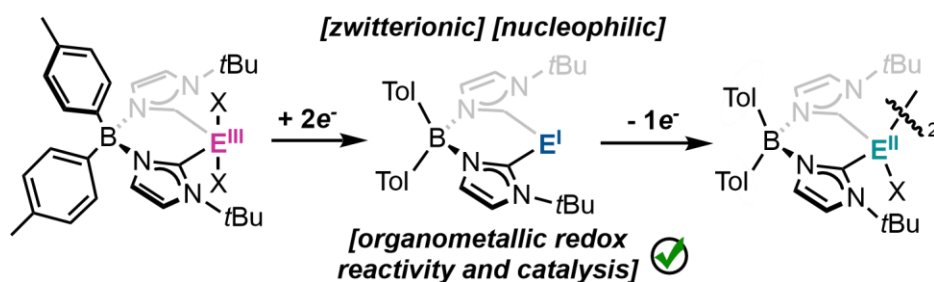


Figure 1. Low-valent zwitterionic main group species bearing bis(NHC)borate ligands.

With the aim of offering a new platform for sustainable redox catalysis as an alternative to noble metals, we introduce a new class of zwitterionic pnictogen compounds stabilized by bis(NHC)borate ligands, enabling the isolation and characterization of Sb and Bi species in oxidation states +1, +2, and +3. Computational studies reveal an electronic structure analogous to tetrylones, with unique electronic properties that underpin their stability and reactivity. We demonstrate Sb(I) species engage in key organometallic transformations, including oxidative addition and reductive elimination. These stoichiometric studies on antimony-mediated fundamental organometallic events laid the foundation for the development of two proof-of-concept catalytic cycles based on the Sb(I)/Sb(III) redox couple, expanding the scope of heavy pnictogen redox catalysis beyond the constraints of conventional *N,C,N*-pincer scaffolds and offering a new approach in main-group catalysis. Additionally, zwitterionic In(II) complexes were isolated and investigated using the same ligand scaffold, revealing promising avenues for the stabilization of elusive In(II) hydride species and highly reactive In(I) analogues. This work highlights the potential of heavier main group elements in redox organometallic chemistry as an alternative to noble metals in synthesis.

References

1. (a) K. Tanaka, *Rhodium catalysis in organic synthesis: Methods and reactions*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2019. (b) J. Tsuji, *Palladium in Organic Synthesis*, Springer, Berlin, 2005.
2. (a) P. P. Power, *Nature*, 2010, **463**, 171-177. (b) R. L. Melen, *Science*, 2019, **363**, 479-484.
3. K. Oberdorf, C. Lichtenberg, *Chem. Commun.*, 2023, **59**, 8043-8058.

Synthesis of a Tin Carbonyl Complex and its Isomerisation to a Carbene-Stabilised Tin Atom

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Transition-metal (TM) carbonyl complexes play a key role in various catalytic processes and their coordination chemistry and reactivity patterns have been well studied. More recently, significant focus has shifted towards low-valent main-group compounds, which have been shown to mimic TM reactivity. Several examples for (non)classical carbonyl complexes of lighter *p*-block elements have been synthesized under ambient conditions.¹ However, only two silicon-based examples for group 14 carbonyl complexes have been reported and heavier congeners have not been achieved thus far.^{2–3}

Our group has previously reported the synthesis of bis(boryl)stannylene **1**,⁴ which has been shown to readily activate E–H (E = N, O, B, Si) bonds, as well as dihydrogen, due to its unique electronic properties.⁵ This can be attributed to the adjacent diazaborolyl substituents, which give rise to a high-lying HOMO and an energetically accessible LUMO. The coordination chemistry of this stannylene, however, has widely been unexplored.

In this work, we report the synthesis of the first tin carbonyl complex (**2**) and its isomerisation to an unprecedented stannavinylidene (**3**), in which a tin atom is stabilized by a single carbene ligand. By adjusting the reaction conditions, stannavinylidene **3** can further react to yield a CO coupling product *via* C–C bond formation. The formation and electronic structures of these novel compounds, as well as the CO homologation mechanism are studied by quantum chemical calculations, which are supported by further coordination and insertion chemistry with an isonitrile derivative. Additionally, single electron reduction of stannylene **1** allows for the isolation of a stable anionic tin-centred radical.

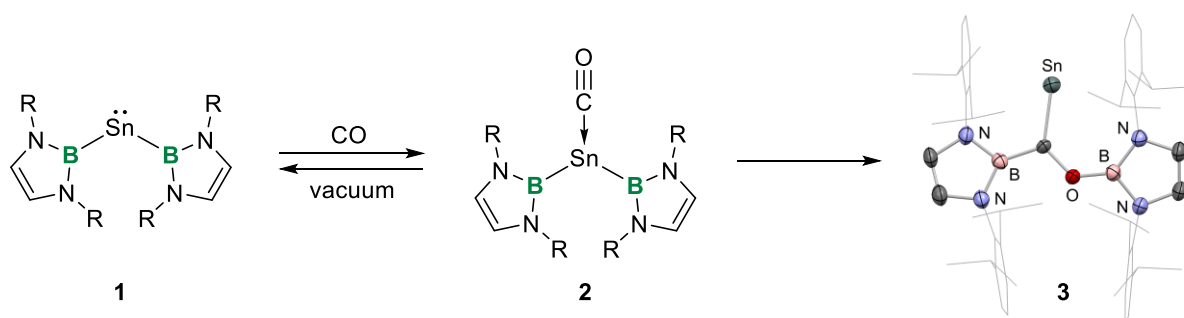


Figure 1. Synthesis of tin carbonyl complex **2** and isomerisation to stannavinylidene **3** (R = 2,6-Diisopropylphenyl).

References

1. S. Fujimori and S. Inoue, *Nat. Commun.*, 2020, **175**, 1–5.
2. C. Ganesamoorthy *et al.*, *Nat. Chem.*, 2020, **12**, 608–614.
3. D. Reiter, R. Holzner, A. Porzelt, P. Frisch and S. Inoue, *Nat. Chem.*, 2020, **12**, 1131–1135.
4. A. V. Protchenko *et al.*, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503.
5. A. V. Protchenko *et al.*, *J. Am. Chem. Soc.*, 2016, **138**, 4555–4564.

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

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

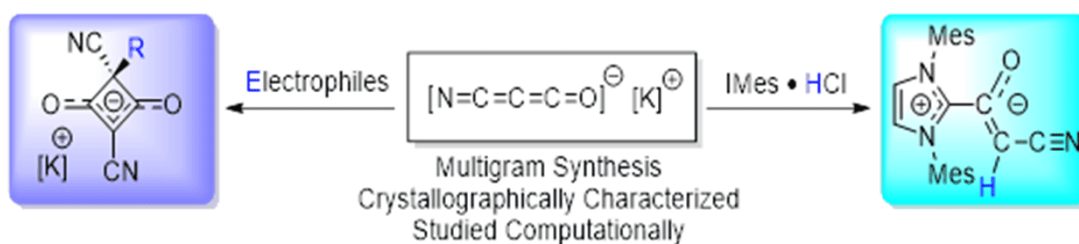


Figure 1: Explored reactivity of [K(18-crown-6)][NCCCO].

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

References

1. B. Ballotta, T. D. Marforio, S. Rampino, E. Martinez-Nunes, V. Barone, M. Melosso, A. Bottoni, L. Dore, *ACS Earth Space Chem.* 2023, **7**, 1172-1180.
2. F. Krischner, V. S. V. S. N. Swamy, K-S. Feichtner, R. J. Ward, V. H. Gessner, *Angew. Chem. Int. Ed.* 2024, e202403766.
3. T. Wang, Z. Guo, L. English, D. Stephan, A. Jupp, M. Xu, *Angew. Chem. Int. Ed.* 2024, e202402728.