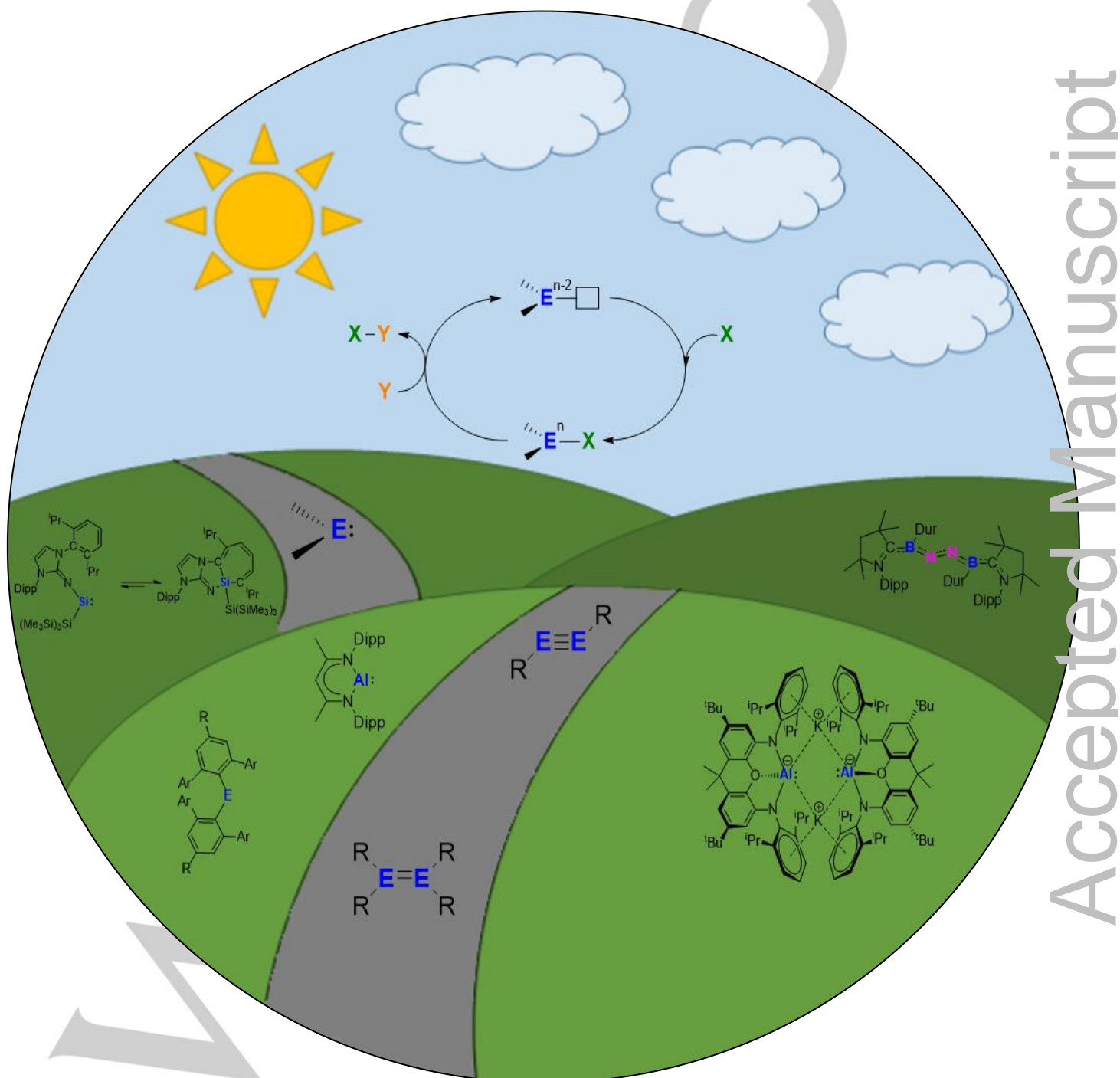WILEY-VCH

MINIREVIEW

The Road Travelled: After Main-group Elements as Transition Metals

Catherine Weetman and Shigeyoshi Inoue*

Dedicated to Professor Philip Power on the occasion of his 65th birthday

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CONCEPT

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Abstract: Since the latter quarter of the twentieth century, main group chemistry has undergone significant advances. Power's timely review in 2010 highlighted the inherent differences between the lighter and heavier main group elements, and that the heavier analogues resemble transition metals as shown by their reactivity towards small molecules. In this concept article, we present an overview of the last 10 years since Power's seminal review, and the progress made for catalytic application. This examines the use of low-oxidation state and/or low-coordinate group 13 and 14 complexes towards small molecule activation (oxidative addition step in a redox based cycle) and how ligand design plays a crucial role in influencing subsequent reactivity. The challenge in these redox based catalytic cycles still centres on the main group complexes' ability to undergo reductive elimination, however considerable progress in this field has been reported *via* reversible oxidative addition reactions. Within the last 5 years the first examples of well-defined low valent main group catalysts have begun to emerge, representing a bright future ahead for main group chemistry.

Introduction

It has been nearly 10 years since Phil Power wrote *'Main-Group Elements as Transition Metals'* which surveyed the similarities between molecular compounds containing heavier main group elements and transition metals.[1] Prior to this, it was thought that the heavier main group elements drew more resemblance to their lighter congeners. However, driven by simple desire and curiosity to synthesise main group complexes several key compounds were isolated in the latter quarter of the 20th century that challenged this view and re-wrote the rule books. Of particular importance in the development of main group chemistry was the isolation of Lappert's Stannylene[2] and West's disilene[3], followed shortly after by the isolation of P=P[4] and Si=C[5] containing complexes by Yoshifuji and Brook within the same year, respectively. These compounds broke the so called 'Double-bond rule' with the key to their isolation being the use of steric bulk in the supporting ligands. This use of kinetic stabilisation has provided access to a plethora of low valent, low-oxidation state systems and have been the subject of numerous reviews.[6] Comparisons between main group elements and transition metals were drawn when main group species were found to undergo reactivity towards small molecules at ambient

conditions. This was rationalised due to main group species possessing donor/acceptor frontier orbitals which are separated by modest energy gaps, thus drawing comparisons to open-shell transition metal species.

In the last 10 years since the landmark review, main group chemistry has continued to flourish. Frustrated Lewis Pair (FLP) chemistry has been widely established since the pioneering work of Stephan.[7] Many more donor/acceptor combinations of main-group elements have been isolated (as predicted by Power[1]) and have led to a variety of new reactions through new mechanistic pathways.[8] For example, the use of phosphonium cations have been shown to catalyse a range of reactions,[9] whilst a very recent example has shown group 15's lightest element, nitrogen, is also capable of FLP type reactivity due to the Lewis acidic nitrenium cation.[10] This rapid ascent of FLP chemistry has even made transition metal chemists take note. Combinations of Lewis acidic transition metals with Lewis basic main group elements have become established,[11] examples of the inverse case[12] are also starting to emerge along with metal-only FLP systems.[13] FLP catalysts are progressing towards industrial use and have been widely reviewed.[14]

Another topic discussed in *'Main-Group Elements as Transition Metals'* was the development of main group diradicaloids (or biradicaloids). This field has continued to develop with biradicaloids derived from cyclobutanediyl attracting the most attention over the last 20 years.[15] Power and co-workers showed that addition of diazenes or arylnitrosyl to the triple bonded-digermyne species results in the formation of stable diradicaloids.[16] Sekiguchi and co-workers succeeded in isolating the first silicon based four-membered heterocyclic biradicaloid from reaction of disilyne.[17] Further advances in this field have stemmed from Schulz and co-workers on the isolation of the first group 15 cyclic biradicaloids of the type $[E(\mu-NR)]_2$ (where E = P, As)[18] and their utilisation for the activation of small molecules.[19]

Other recent advances in main group chemistry have focussed on attempts to tame highly air- and moisture-sensitive reagents or the development of alternate reagents so that main group elements can be used in synthesis for more economically viable methods. For example, Hevia and co-workers have shown it is possible to use the widely implemented organolithium reagents in deeply eutectic solvents – a new class of solvent which are environmentally benign.[20] Whilst Cummins' recent report in *Science* highlights the use of a bis(trichlorosilyl)phosphide anion as an alternative to P_4 for the synthesis of organophosphorus containing compounds.[21] In somewhat related work, new synthetic routes for the isolation of the versatile PCO- anion[22] have been developed and subsequent extension to the heavier AsCO- species.[23] Also research within this field has been recently expanded to include synthetic

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methodologies for the P and As containing chalcogen analogues by Goicoechea and co-workers.[24]

Not to be forgotten is the progress made in *s*-block chemistry, since the successful isolation of a dimeric Mg(I) compound supported by a β-diketiminate ligand by Jones in 2007,[25] *s*-block chemistry has been firmly put back on the table. This dimeric Mg(I) compound has been found to be a soluble, selective reducing agent with applications in both organic[26] and inorganic[27] synthesis. Further development of group 2 chemistry was centred around their application in homogeneous catalysis for the reduction of organic substrates and small molecules.[28] Of particular interest in this field are the recent reports by Hill and co-workers in which calcium mediates nucleophilic alkylation at benzene[29] and the development of an easy access to a nucleophilic boron centre *via* a β-diketiminate Mg complex.[30]

Another remarkable recent achievement in group 2 chemistry, was the successful isolation and structural characterisation of dimethylcalcium, [CaMe$_2$]$_n$. Upon reaction with a bulky proligand in a donor solvent (to prevent Schlenk equilibria) allowed for the isolation of a monomeric complex containing the first examples of terminal Ca-CH$_3$ bonds.[31] Further highlights in *s*-block chemistry have focussed on the development of the synergistic properties between group 1 and 2 metals, which have shown unique properties through formation of new bimetallic species. In particular, the ability to direct the metalation of arenes including the previously unobtainable *ortho*-metalation.[32] Advances in this field arising from the utilisation of two metal centres will surely lead to many exciting future developments and the ability to target many challenging transformations.

In terms of catalysis, main group chemistry is making considerable progress towards catalytic application and in mimicking the behaviour of transition metals. This is highly advantageous as efforts towards using more environmentally benign and abundant metals are becoming paramount. Catalytic cycles for transition metals are typically based upon redox processes, owing to their ease in which they can change their oxidation state. In the case of redox inactive *s*-block and lanthanide metals (Ln^{3+}) catalytic cycles have been developed around σ-bond metathesis and insertion reactions.[28a, 33] For *p*-block metals a range of oxidation states are available, however the ability to stabilise low-oxidation states requires steric bulk of the supporting ligand. Upon oxidative addition, these reactive low-valent species tend to form very stable products[34] thus rendering the reductive elimination step highly challenging and inhibiting turnover. Despite this challenge, significant progress is being made in this field and will be discussed herein.

Along with the need to move away from precious metals typically used in industrial catalysis, the drive towards utilisation of small molecules such as H$_2$, CO, CO$_2$, and NH$_3$ for use as synthons for value added products is of current interest for future applications. It is, therefore, of utmost importance to combine these small molecules into catalytic cycles using main group elements as the catalysts. This may be best achieved through use of redox based-catalytic cycle, akin to transition metal-based catalysis. In order to achieve this, several key challenges must be met (Scheme 1): (1) synthesis of stable low-oxidation state main group complexes with an open coordination site; (2) activation of small molecules; (3) elimination of a functionalised product; (4) regeneration of the active catalyst.
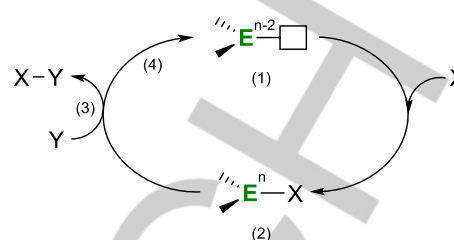
Scheme 1. Generic catalytic cycle for the catalytic functionalisation of small molecules. E = main group element; n = oxidation state; X = small molecule; Y = reagent (eg. silane, borane, etc.).

Progress in the synthesis of low valent compounds has led to many unique and exciting structures that many thought may have been impossible, for example multiply bonded heavier main group compounds.[6a, 6b] These species have subsequently shown that main group elements can act as transition metals for the activation of small molecules and cleavage of strong σ-bonds.[35] The first example of which was reported by Power and co-workers where Ar^{Trip}Ge≡GeAr^{Trip} (**1**) (Ar^{Trip} = 2,6-Trip$_2$-C$_6$H$_3$, Trip = 2,4,6-tri-*iso*-propyl$_3$-C$_6$H$_2$) was found to split dihydrogen under ambient conditions.[36] Computational studies revealed this was possible through synergistic interaction of its frontier orbitals with H$_2$, which is analogous reactivity to that observed for transition metals. The synergic electron donation from the π-HOMO orbital of Ar^{Trip}GeGeAr^{Trip} into the σ*-orbital of H$_2$ weakens the H-H bond, enabling oxidative addition to occur. Despite analogous reactivity, the orbitals involved are different between main group and transition metal species and are highlighted in Figure 1. Small molecule activation with singlet state tetrylenes, in which the main group element possesses a lone pair of electrons and a vacant *p*-orbital, has also been shown to be possible with similar reactivity to transition metals and multiply bonded main group species.
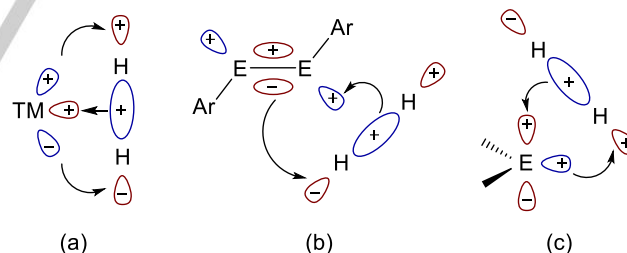
Figure 1. Frontier orbital interaction of dihydrogen with (a) transition metals, (b) main group multiple bonds, and (c) singlet main group species eg. carbenes, tetrylenes.

Main group chemistry has grown considerably in the last 10 years and has been subject to a number of recent reviews. '*Oxidative Addition and Reductive Elimination at Main Group Metal Centres*' by Chu and Nikonov[35a] is a comprehensive review also showcasing the progress made in this field during the last 10 years. Whilst Hadlington, Driess and Jones have also recently reviewed '*Low-valent group 14 element hydride chemistry: towards catalysis*'.[37] Therefore, this concept article aims to present an up-to-date overview since Power's seminal review. The main discussion focusses on the key reactivity highlights from

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group 13 and 14 low-oxidation state and/or low-coordinate complexes and the subtle ligand/electronic effects that enable small molecule activation to occur and how catalytic turnover may be achieved.

Activation of small molecules with Group 13 complexes

As mentioned previously, the activation and utilisation of small molecules is of keen synthetic interest. Many examples of H_2, CO, CO_2, and NH_3 have been shown, and will be discussed herein, yet activation of N_2 with main group elements remained elusive until recently. Transition metals have been shown to bind N_2 which results in weakening or cleavage of the strong N≡N triple bond. This is made possible through π-backbonding from the transition metal d-orbitals into the antibonding π-orbital of N_2 (Figure 2a). With the lack of accessible d-orbitals in main group elements this was thought to impede their ability to bind and subsequently weaken the NN bond. Braunschweig and co-workers showed that reduction of $[(CAAC)DurBBr_2]$ (**2**) (Dur = 2,3,5,6-tetramethylphenyl; CAAC = 1-(2,6-di-iso-propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene) in a nitrogen atmosphere resulted in reduction of N_2 under ambient conditions to yield $[(CAAC)DurB]_2(\mu\text{-}N_2)$ (**3**) as the minor product, with C-H activation product (**3a**) as the major species (Scheme 2).[38] Prior to this report the only other main group example of N_2 activation at room temperature utilised elemental lithium,[39] other examples require the use of strongly Lewis acidic species generated in the gas phase or use of matrix isolation conditions.[40]
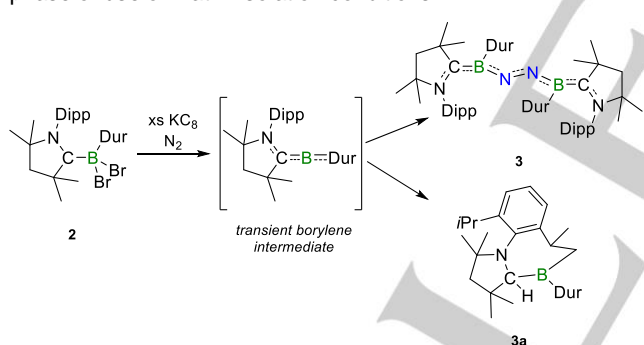
Scheme 2. Activation of dinitrogen under ambient conditions *via* a transient borylene intermediate.

The reaction is thought to be possible through the formation of a transient borylene as the intermediate. The borylene fragment is implicated in the X-ray crystallographic structure, the central B-N-N-B core is non-linear, unlike transition metal complexes in which nearly linear arrangements are commonly observed.[41] The N-N bond length [1.248(4) Å] is closer to that of a double bond rather than a single bond, and the short B-C^{CAAC} bond lengths [1.528(5) and 1.541(4) Å] indicate delocalisation of the lone pairs of the B atoms across the molecule. This indicates that the lone pair on the monovalent boron atom is involved in π-backdonation and that the N_2 acts as a Lewis σ-donor and π-acceptor, mimicking transition metals (Figure 2). Base-stabilised borylenes

have previously shown strong π-donating ability. Bertrand and co-workers reported CO fixation with a borylene-like complex[42] and Braunschweig and co-workers reported the photolytic decarbonylation and donor exchange reactions at monovalent boron centres.[43]
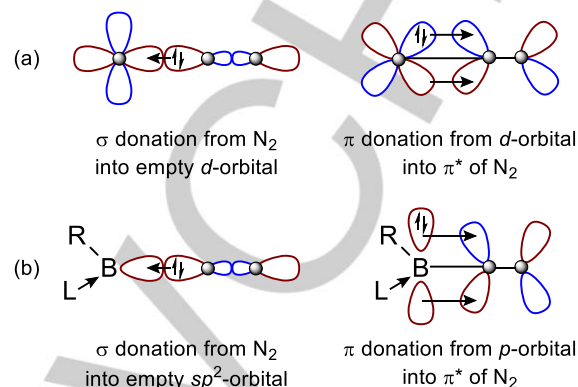

Figure 2. Binding of N_2 to (a) transition metals and (b) monovalent boron centres

Computational calculations (Density Functional Theory (DFT) along with the determination of Wiberg Bond Indices (WBI)) are both in agreement with the crystallographic structure and consistent with B-N and N-N multiple bonding. Kohn-Sham orbital analysis also was in agreement with the HOMO-1 which consists of contributions from the N-N π*, B p-orbital and C-N^{CAAC} π* further supporting the delocalisation of electrons from B p-orbital across the central core. Addition of further equivalents of KC_8 resulted in the isolation of a dipotassium complex $\{[(CAAC)DurB]_2(\mu^2\text{-}N_2K_2)\}$, this species undergoes further reactivity with distilled water to yield the reduced dinitrogen complex $\{[(CAAC)DurB]_2(\mu^2\text{-}N_2H_2)\}$. This pivotal report by Braunschweig and co-workers will lead the way for many new areas of nitrogen activation and related small molecule activation. Other exemplary work in the field of boron chemistry has also come from the Braunschweig group with the development of borene and borylene chemistry and subsequent reactivity towards small molecules which has been recently reviewed.[44]

Aluminium chemistry has experienced a renaissance over the last 10-20 years, due to the ability to tame and isolate reactive Al(I) species. Use of the sterically demanding Cp* ligand (Cp* = pentamethylcyclopentadienyl) provided access to the widely studied [Cp*Al]₄ tetramer,[45] which upon heating readily dissociates into its monomeric form. An alternate route to obtain Al(I) species, utilised the bidentate β-diketiminate ligand to yield a 2-coordinate Al(I) complex (**4**).[46] Reactivity studies of both of these compounds towards small molecules have been extensively investigated, and they largely undergo oxidative addition reactions with substrates.[47] This was highlighted recently, by Nikonov and co-workers in which they reported the use of **4** for the oxidative addition of a range of H-X σ-bonds (X = H, Si, B, Al, C, N, P, O).[48] Interestingly, the reaction of **4** with dihydrogen results in the formation of compound **4a**. When the related oxidative addition of **4a** to **4** was studied this was found to be in equilibrium with compound **5** (Scheme 3). Upon mild heating (50 °C) compound **5** undergoes disproportionation back to the

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starting materials, indicating the potential for reductive elimination in these systems.
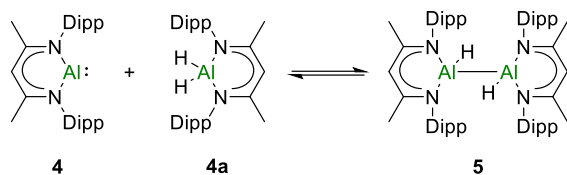
Scheme 3. Reversible activation of Al-H bonds.

Another remarkable achievement from the use of compound **4** was recently reported by Crimmin and co-workers,[49] they showed it was possible to break strong sp^2 and sp^3 C-F bonds through either oxidative addition at the Al centre or *via* formation of a metallocyclopropane intermediate which subsequently undergoes α- or β-fluoride elimination.

As depicted in Figure 1, one mode of small molecule activation is through the use of multiple bonds. The field of aluminium multiple bonds[50] is one that is currently gaining much attention due to the recent isolation of the first dialumene.[51] Through a simple two step synthetic route, the dialumene (**6**) can be obtained in good yields (53 %). This complex is stable due to the presence of the external electron donor, the NHC ligand I^{i}Pr$_2$Me$_2$ (I^{i}Pr$_2$Me$_2$ = 1,3-di-*iso*-propyl-4,5-dimethyl-imidazol-2-ylidene), and through the use of the sterically demanding di-*tert*-butyl(methyl)silyl group (^{t}Bu$_2$MeSi) which provides kinetic stabilisation. This combination forces the *s*- and the *p*- valence electrons of the aluminium centre to hybridise and form a homonuclear double-bond.

Previous attempts to isolate Al-Al double bonds have resulted in formal [4+2] cycloaddition products, in which the incipient dialumene reacted with the aromatic solvent or acetylenes to produce masked dialumenes.[52] Therefore, experimental evidence for the double bonding nature of compound **6** centred upon its reactivity with ethylene and phenyl acetylene with the aim of forming the analogous masked species. This reactivity proceeded as expected (Scheme 4), upon reaction of **6** with ethylene formal [2+2] addition occurred to yield dialuminacyclobutane (**7**). Reaction with phenyl acetylene also formed the cycloaddition product (**8**) along with concomitant formation of a C-H insertion product to yield compound **9**, thus confirming the presence of a double bond in **6**.
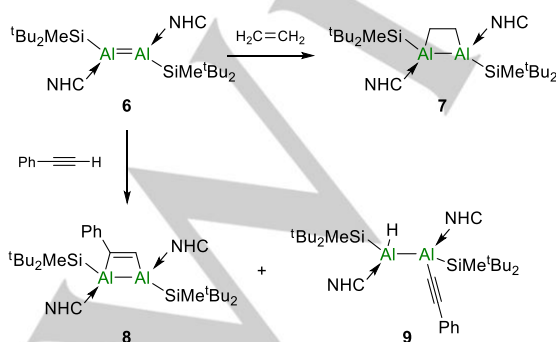
Scheme 4. Reactivity of dialumene (**6**) with unsaturated substrates.

So far, the chemistry of aluminium has been dictated by its Lewis acidity and therefore electrophilicity of the metal centre. Very recently, Aldridge and Goicoechea flipped this long standing reactivity through the isolation of a nucleophilic Al(I) centre, namely an aluminyl (**10**).[53] Compound **10** was isolated through use of sterically demanding and σ-electron-withdrawing arylamido substituents in combination with a flexible chelating dimethylxanthine backbone. It is also of note that a nucleophilic indyl anion has also been recently reported.[54] This recent interest in the ability to isolate previously unobtainable group 13 nucleophiles represent exciting future prospects in main group chemistry.
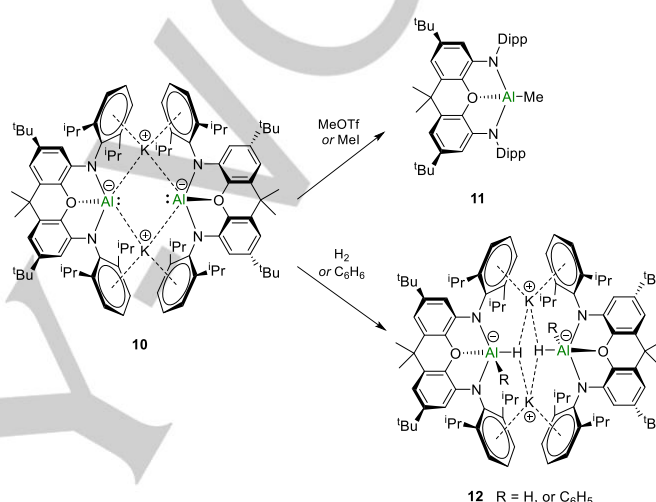

Scheme 5. Reactivity of aluminyl (**10**) showing formation of Al-C (**11**) and Al-H bonds (**12**).

DFT calculations also revealed the high nucleophilic character of Al centre in **10**, based on a higher contribution of the Al 3*p* to the lone pair (24% in **10** vs 10% for compound **4**). This was also proven experimentally (Scheme 5), reaction with methyliodide or methyl triflate resulted in the formation of aluminium-carbon bonds (**11**). Compound **10** was found to be stable at room temperature for several days, however heating a benzene solution of **11** resulted in a formal oxidative cleavage of a benzene C-H bond at the Al centre, forming [K{Ph(H)Al(NON)}$_2$ (**12**, NON = 4,5-bis(2,6-di-*iso*-propylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) . This is the first example of oxidative addition of benzene at a well-defined main group metal centre, thus showing the potential of this system towards small molecule activation and catalysis. This previously inaccessible nucleophilic Al centered reactivity will surely lead to many exciting and novel applications in the near future.

The first reports of gallium activation of small molecules were reported by Power and co-workers, utilising a digallane species of the type Ar^{Dipp}Ga=GaAr^{Dipp} (**13**) (Ar^{Dipp} = 2,6-Dipp$_2$-C$_6$H$_3$, or 2,6-Dipp$_2$-4-SiMe$_3$-C$_6$H$_2$; Dipp = 2,6-di-*iso*-propyl$_3$-C$_6$H$_3$). Compound **13** was found to react readily with H$_2$ and NH$_3$ to yield compounds **14** and **15,** respectively (Scheme 6).[55] In solution the digallane (**13**) partly dissociates into its monomeric Ga(I) form, however computational studies revealed a high activation barrier (50 kcal mol^{-1}) for the reaction of Ga(I) and H$_2$ thus making this

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open-shell mechanism unlikely.[56] Compound **13**, therefore, was found to undergo the addition of one equivalent of H_2 to yield a 1,2-dihydride intermediate, which subsequently reacted with a further equivalent of H_2 resulting in the cleavage of the Ga-Ga bond and formation of $Ar^{Dipp}GaH_2$ which dimerises to yield compound **14**.
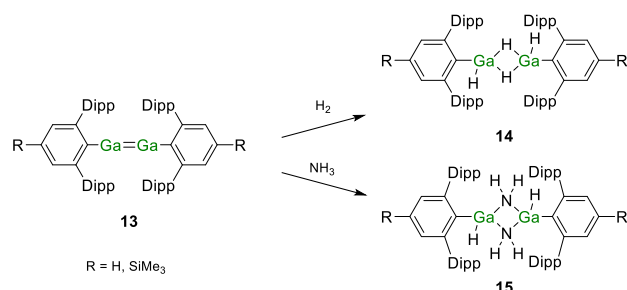
Scheme 6. Activation of H_2 and NH_3 with digallane (**13**).

It has since been shown that small molecule activation with open-shell Ga(I) centres is also possible, use of the β-diketiminate supported Ga(I) species with H_2 or diethylamine resulted in oxidative addition to yield a gallium hydride or a gallium hydrido amido complex, respectively.[57] Use of a zwitterionic N-heterocyclic Ga(III) centre has also shown to be active towards small molecules.[58]
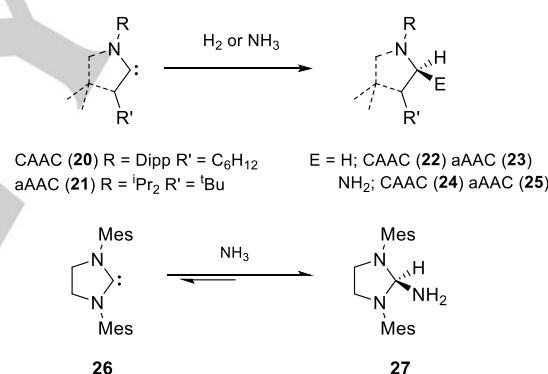
In comparison to the established chemistry of low-oxidation state Al and Ga, much less is known about the heaviest group 13 congeners. In terms of multiple bonded compounds, lowering of the π-σ* energy gap upon descending the group results in increased lone pair character and therefore weakening of the M-M bonding. This is also the case with heavier group 14 congeners, and often results in dissociation to the monomers in solution. Despite this challenge, there are a few examples of In and Tl multiple bonded compounds which utilise the terphenyl ligand system in order to aid the stability of the dimetallene compounds, $Ar^{Dipp}MMAr^{Dipp}$ (M = In (**16**),[59] Tl (**17**)[60]). Small molecule reactivity of these $Ar^{Dipp}MMAr^{Dipp}$ compounds is limited to a few examples. Formation of metal chalcogenides is possible for indene (**16**) through reaction with N_2O and sulphur to yield the chalcogenide-bridged dimers, $[Ar^{Dipp}InE]_2$ (E = O (**18**); S (**19**)) (Scheme 7).[61] However, no characterisable products were identified with analogous dithallene compound (**17**).
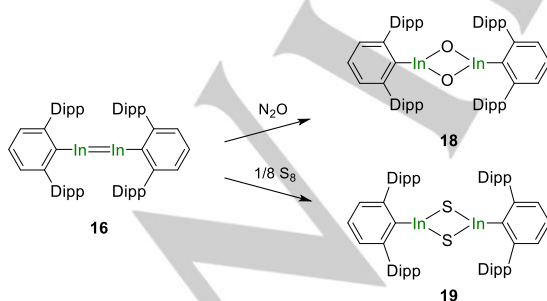
Scheme 7. Small molecule activation with diindene (**16**).

Activation of small molecules with Group 14 complexes

The use of carbenes is now ubiquitous in modern day transition metal and main group chemistry,[62] the ability to finely tune the steric and electronic demands has led to a wealth of new complexes and subsequent reactivity. Carbenes can be considered to be 'transition-metal like' as they possess a lone pair in a non-bonding orbital and vacant orbital.[8a] The ability to fine tune the nature of the carbene has an effect on the σ-donating properties of the lone pair of the carbene carbon and consequently can be the difference between the ability to cleave dihydrogen or not. For example, NHCs do not react with H_2 but reaction of CAACs (**20**) or acyclic alkyl amino carbenes (aAACs, **21**) afford the oxidative addition products (**22 and 23**, respectively) (Scheme 8a). Compounds **20** and **21** were also found to react with NH_3 in the same manner to yield products **24** and **25**.[8a] This discrepancy is attributed to their differences in the singlet-triplet energy gap (46 kcal mol^{-1} CAACs vs 68 kcal mol^{-1} NHCs). Oxidative addition reaction of NH_3 with the saturated NHC (**26**) (*N,N'*-dimesityl-4,5-dihydroimidazol-2-ylidene) was found to be reversible (Scheme 8b).[63] This is an important step towards catalysis as dynamic N-H activation will allow for transfer and/or release of the activated/functionalised product in catalytic turnover (Scheme 1, steps 3 and 4).

CAAC (**20**) R = Dipp R' = C_6H_{12} E = H; CAAC (**22**) aAAC (**23**)
aAAC (**21**) R = $^iPr_2$ R' = ^tBu NH_2; CAAC (**24**) aAAC (**25**)

26   **27**

Scheme 8. (a) Reactivity of CAACs and aAACs towards H_2 and NH_3. (b) Reversible addition of NH_3 to NHC (**26**).

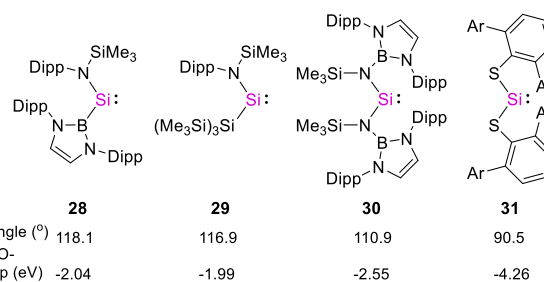|	**28**	**29**	**30**	**31**
X-Si-X Angle (°)	118.1	116.9	110.9	90.5
HOMO-LUMO gap (eV)	-2.04	-1.99	-2.55	-4.26

Figure 3. Selected acyclic silylenes with comparisons of bite angles and HOMO-LUMO energy gaps.

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Low-valent chemistry of Si(II) compounds has expanded rapidly over recent years, leading to a plethora of stable cyclic and acyclic silylenes.[47e, 64] Acyclic silylenes (Figure 3, **28**[65] and **29**[66]) have shown it is possible to split dihydrogen to form the corresponding silanes, however not all acyclic silylenes are capable of this reactivity (**30**[67] and **31**[68]). The bite angle of the two-coordinate silicon centre was found to influence the HOMO-LUMO gap and thus the ability to activate dihydrogen.[69] Whilst compounds **30** and **31** were unreactive towards H2, they were found to readily react with NH3 to yield the expected oxidative addition product. Interestingly, compound **31** was found to reversibly react with ethylene under ambient conditions.[70] This is a key step towards catalysis as the reductive elimination back to Si(II) compounds is challenging.

Further progress in this area has been reported by our group, in which a formal Si(IV) compound is converted back to Si(II) through use of a masked silylene, namely 'silepin' (**33**) (Scheme 9a).[71] Compound (**33**) was obtained through intramolecular insertion of the *in situ* generated iminosilylsilylene (**32**) into the C=C bond of the supporting Dipp group of the N-heterocyclic Imino (NHI) ligand.[71] Experimental and computational studies revealed that the equilibrium between **32** and **33** was thermally accessible, and subsequent reactivity studies with small molecules showed reactivity akin to silylenes through facile activation of H2, CO2, and ethylene. Interestingly, reaction of **33** with N2O resulted in the clean formation of the first acyclic silanone (**37**) which also underwent further reactivity with small molecules to yield compounds **38** and **39** (Scheme 9b).[72]

reactivity towards small molecule activation remains scarce in comparison, although a few examples have shown NH3 activation.[74] The first reported H2 activation by a multiply bonded Si compound was accounted by our group in 2017.[75] Use of a bulky NHI ligand, with tBu substituents rather than aryl, prevents formation of the silepin and yields a *trans*-bent disilene compound (**40**) with a twisted double bond. This compound contains the longest Si=Si double bond to date (2.3124(7) Å), typical Si=Si 2.14-2.29 Å, and is therefore best described as a very weak double donor-acceptor bond. These unique properties enabled the facile activation of H2 to yield the corresponding disilane (**41**) in an exclusively racemic (RR/SS) configuration indicating a stereospecific *trans*-hydrogenation (Scheme 10). A further recent report of the reactivity of **37** has shown successful small molecule activation with N2O (**42**), CO2 (**43**, **44**), O2 (**45**), and NH3 (**46**).[76] Interestingly, the reaction with CO2 leads to the selective formation of a CO2 adduct when carried out at -78 °C but at room temperature a mixture of products is formed. Compound **43** was identified as one of these species after addition of CO2 to compound **42** and comparison of NMR data.
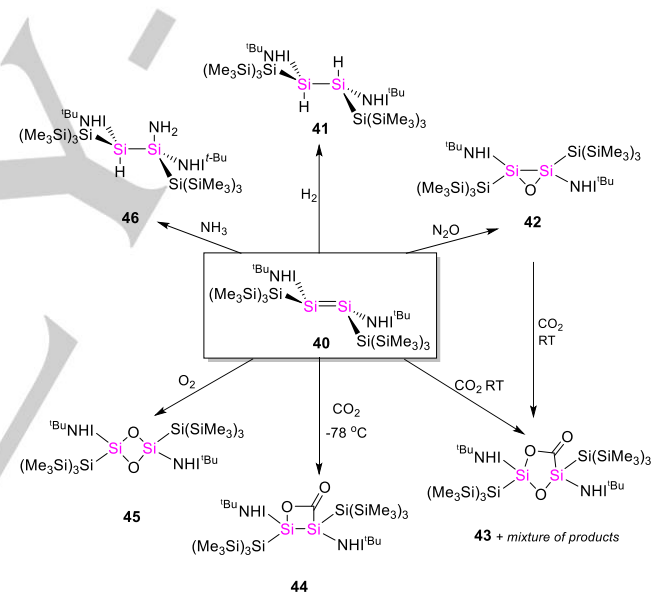
Scheme 10. Activation of small molecules with disilene (**40**)

As previously mentioned, the first example of small molecule activation with a main group element was through use of a Ge-Ge triple bond (**1**).[36] Since this seminal report, germanium small molecule activation has expanded rapidly through use of both multiply-bonded and mono-nuclear complexes. Remarkably, Jones and co-workers reported the use of a bulky amido-digermyne, L†GeGeL† (L† = −N(Ar†)(SiiPr3), Ar† = C6H2{C(H)Ph2}2iPr-2,6,4) single bonded compound (**47**) which activates H2 in the solid state at room temperature, and also in solution as low as -10 °C (Scheme 11).[77] Interestingly, activation of H2 results in an asymmetric monohydrogenation product L†Ge-Ge(H2)L† (**48**), and addition of further equivalents of H2, or heating up to 100 °C, does not result in further addition. Computational studies revealed the reaction initially proceeds through the formation of bridged hydride species, LGe(μ-H)Ge(H)L, which
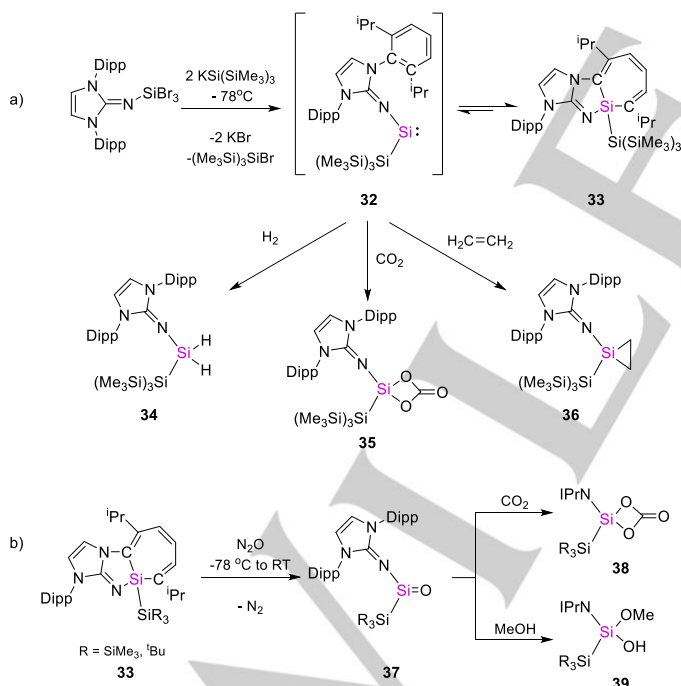
Scheme 9. a) Synthesis of a masked silylene (**33**) and subsequent small molecule activation. b) Synthesis of silanone (**37**) and subsequent small molecule activation

Since the discovery of West's disilene, several multiply bonded silicon complexes have been reported.[73] However,

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rearranges to the more thermally stable compound **48**. Subsequent reports of compound **47** towards small molecules have shown it is possible to reduce CO_2 to CO through formation of a bis-germylene oxide.[78]
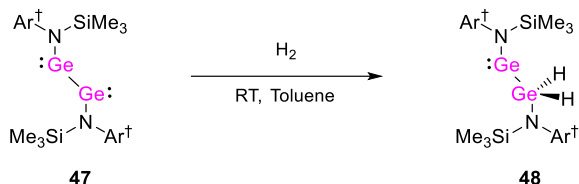
**Scheme 11**. Activation of H_2 with a bulky amido-digermane (**47**).

Other examples of Ge small molecule activation have focused on the use of two-coordinate germylenes. Power and co-workers reported the use of $Ge(Ar^R)_2$ (**49**, **50**) for the activation of H_2 (Scheme 12).[79] Differences in the steric bulk of the supporting aryl group provided different products, use of mesityl substituents (**49**, Ar = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) provided a dihydride (**51**) whereas use of the bulkier Dipp substituted germylene (**50**, Ar = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) resulted in formation of the trihydride (**52**) with concomitant elimination of HAr^{Dipp}. Computational studies revealed the initial stages of the mechanism to be the same (Figure 1c), however the increased steric bulk of **50** introduces sufficient strain so that elimination of HAr^{Dipp} is energetically preferred. Power and co-workers showed that these compounds (**49**, **50**) are also capable of activating NH_3 to yield the expected oxidative addition products.[79]
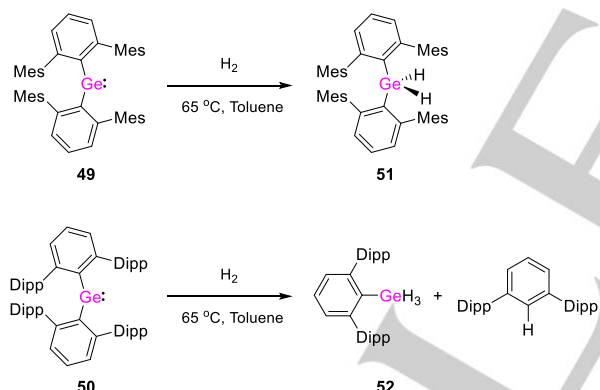
Scheme 12. Activation of H_2 with Germylenes (**49** and **50**).

Extension of small molecule reactivity to Sn complexes has largely focussed on analogous Ge complexes. Despite the use of the same ligand frameworks, reactivity differs due to the decreased π-σ* gap in multiple-bonded species.[80] This is exemplified in the reaction of Ar^{Dipp}SnSnAr^{Dipp} (**53**).[81] In the case of the seminal Ar^{Dipp}GeGeAr^{Dipp} compound (**1**) multiple H_2 additions are observed, whereas Ar^{Dipp}SnSnAr^{Dipp} results in sole formation of a hydride bridged dimer (**54**). Calculations revealed that this reaction proceeds *via* formation of Ar^{Dipp}Sn(H)-Sn(H)Ar^{Dipp} which promptly dissociates into the monomeric Ar^{Dipp}SnH which then dimerises to yield compound **54** (Scheme 13).[81] Jones and co-workers also reported the comparison of the reactivity towards H_2 with the Sn analogue to the bulky amido-

digermyne compound **47**. This also resulted in the H-bridged dimer rather than the asymmetric monohydrogenation complex.[82]
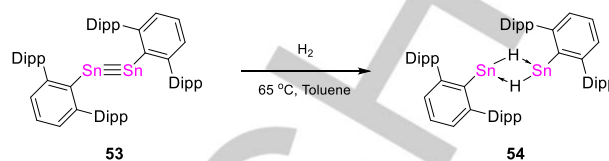
Scheme 13. Activation of H_2 with distannyne (**53**).

Power and co-workers reported the use of stannylenes **55** and **56** (analogous to Ge compounds **49** and **50**) for H_2 activation, whereas only reaction with the bulky Ar^{Dipp} (**56**) was successful owing to its wider bite angle (114.7(2)° (**55**) vs 117.6(8)° (**56**)) in line with analogous silylene chemistry.[83] Further comparative studies, between Ar$_2$E (E = Ge, Sn and Pb) homologues examined the electron-donating and -withdrawing properties of the supporting terphenyl ligands and their subsequent influence on reactivity. This was achieved through synthesis of various Ar$_2$E compounds and comparison of their structural and spectroscopic properties, along with computational studies (Figure 4).[84]

It was found that use of electron poor ligands results in increased *s*-character of the lone pair, through a higher contribution of *p*-orbitals from the tetrel atom in the E-Ar σ-bond. This leads to larger HOMO-LUMO gaps and narrow Ar-E-Ar bite angles and these compounds are, therefore, not expected to activate small molecules such as H_2 and NH_3. The opposite holds true for electron rich ligands, with the wider bite angles and narrower HOMO-LUMO gap resulting in small molecule activation (**55** vs **56**).[84] Recent further study by Power and co-workers for heavier tetrylenes (Ge, Sn, Pb) revealed that the narrower Ar−E−Ar angles are observed for the bulkier substituents, rather than expected wider angles, due to interligand attractive London dispersion forces between the two terphenyl groups.[85]
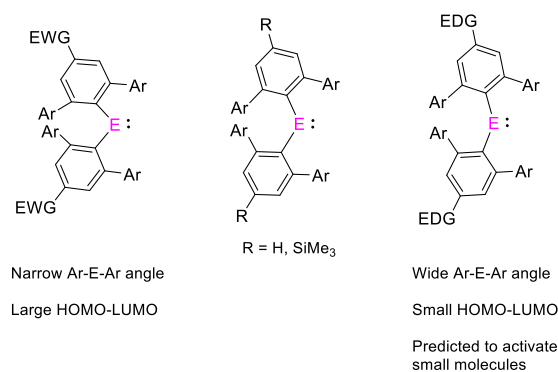

Figure 4. Influence of ligand substituents on Ar$_2$E systems.

Aldridge and co-workers also reported a systematic study of a range of germylenes (ArGeR) towards E-H bond activations.[86] Varying the R substituent across a range of σ- and π-electronic properties, as well as steric bulk, revealed that the Ar-Ge-R bond widens with the use of sterically demanding/electropositive substituents and subsequently leads to smaller HOMO-LUMO gaps. This is in agreement with that depicted in Figure 4. The

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reactivity of these complexes were assessed with regards to E-H bond activations and again those with the narrowest HOMO-LUMO gaps were found to be the most reactive.

Next step: Catalysis

Considerable progress in main group chemistry has occurred over the last 10 years. Understanding of the key features required for small molecule activation, particularly in terms of ligand design, has placed this field in good standing for targeting catalytic turnover. Assembling catalytic cycles based on traditional transition metal redox processes seems likely based on the current strength in oxidative addition reactions of small molecules to low-valent main group centres. However, as noted in the previous sections reductive elimination back to the low-valent main group centre is highly challenging due to the typically reducing conditions required for their synthesis in the first place. Alternatively catalytic cycles based upon non-redox processes, as shown to be successful for s- and f-block catalysts, can also be targeted by main group complexes.

Reductive Elimination

Recent developments, which may allow for the incorporation of reductive elimination steps in catalytic cycles, have centred on the use of reductive elimination steps as a means for the isolation of low-valent main group species. Thus, circumventing the need for harsh reducing conditions typically employed. Fischer and co-workers reported the reductive elimination of Cp*H from Cp*AlH$_2$ to yield the reactive [Cp*Al]$_4$ species.[87] Further study by Cowley and co-workers reported the effect of coordinated ligands on the promotion of this reductive elimination step and found that increasing coordination number and electron density at the Al(III) centre inhibits reductive elimination.[88] In related work, Braunschweig and co-workers showed that Lewis bases were capable of mediating the Al(II) to Al(I)/Al(III) disproportionation.[89] Prior to this, Weseman and co-workers had reported the use of an external base (NHC, pyridine or amine derivatives) for the reductive elimination of hydrogen from arylstannanes (RSnH$_3$), as a novel route to access stannylenes (RSnH).[90] Use of an additional base is commonly employed in organocatalysis to enable efficient turnover, therefore this may provide a route to enable turnover in main group catalytic systems.
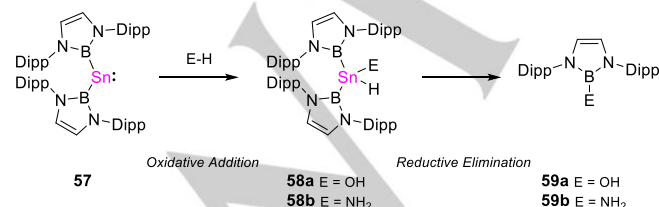
Scheme 14. Stoichiometric oxidative addition and subsequent reductive elimination with a bis(boryl)stannylene (57).

Stoichiometric oxidative addition of small molecules and subsequent reductive elimination has been achieved by Aldridge

and co-workers, through the use of a bis(boryl)stannylene (57, Scheme 14). The boryl (BX$_2$) ligands were chosen due to their strongly σ-donating nature, which is then thought to reduce the HOMO-LUMO gap thus making small molecule activation more facile. This was indeed found to be the case, as H$_2$ activation proceeded steadily at room temperature to yield the corresponding dihydride. Extension to H$_2$O and NH$_3$ also yielded the expected oxidation addition products (58a and 58b, respectively). Interestingly, upon heating or storage at room temperature over increased periods of time reductive elimination was observed to occur to yield the O- or N-borylation products (Scheme 14, 59a and 59b, respectively) and tin metal.[91]

Reversible bond activations

One method to overcome the challenging reductive elimination step is through the reversible substrate binding, a key feature in transition metal catalysis and in FLP chemistry, as this will enable subsequent transfer and/or elimination of the functionalised product. Whilst this reversibility has been shown in some cases with small molecules, extension to H-E (E = B, Si, P etc) bond activation provides potential for hydroelementation catalysis and isolation of value added products. Within this field, Baceiredo and Kato reported reversible silylene insertion reactions[92] into Si-H and P-H σ-bonds at room temperature (Scheme 15a).[93] The silylene (60) and the H-E activation product (61) are in equilibrium, with the position of the equilibrium determined by the temperature, steric bulk of the silylene and bulkiness of the substrate. Reaction of a stannylsilylene (62) with phenylsilane resulted in substituent exchange to yield a mixture of disilanes through a readily reversible oxidative addition/reductive elimination pathway (Scheme 15b).[93]
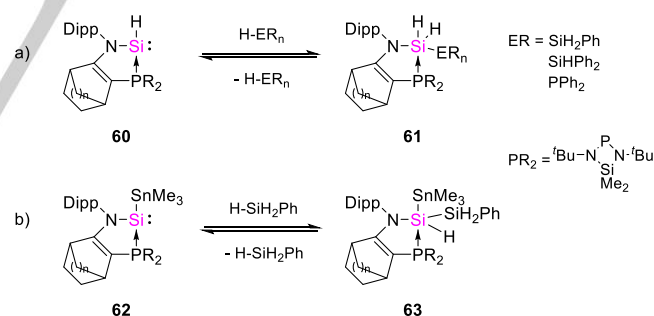
Scheme 15. (a) Reversible silylene (60) insertion into H-X bonds, (b) substituent exchange between 62 and phenylsilane.

Power and co-workers reported the reactivity of Germylene, Stannylene, and Plumbylene terphenyl complexes towards group 13 metal trialkyls.[94] In most cases insertion of the tetrylene into the M-C bond was observed, however in the case of stannylene and trialkylgallium this reaction was found to be reversible under ambient conditions. Extension of this work towards other reversible M-C insertions was found to be successful with dimethylzinc and stannylene.[95] Currently examples of reversible tetrylene reactions are limited to a handful of reports,[70, 92, 96] thus showing great potential for this class of compounds towards

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catalysis, particularly Power's recent example of reversible elimination of H_2 from a stannylene.[97]

Tobita and co-workers showed that reversible E-H insertion reactions were possible using a cationic metallogermylene [Cp*(CO)$_3$WGe(IDipp)][BArF$_4$] (**64**) (IDipp = 1,3-bis(2,6-di-*iso*-propylphenyl)-imidazol-2-ylidene, ArF = 3,5-(CF$_3$)$_2$C$_6$H$_3$). Complex **64** was found to react with H_2 irreversibly at 60 °C, however addition of ethyldimethylsilane at room temperature for 6 h gave [Cp*(CO)$_3$WGeH(SiMe$_2$Et)(IDipp)][BArF$_4$] (**65**), through insertion of **64** into the Si−H bond. Heating compound **65** to 60 °C resulted in reformation of **64** through reductive elimination (Scheme 15). The same was also found for the reaction with HBpin to yield the analogous B-H insertion product **66**. The high reactivity of **64**, in comparison to its neutral counterpart [Cp*(CO)$_3$WGeCl(IDipp)], has a smaller HOMO-LUMO gap and higher electrophilicity due to the overall positive charge of the complex.[98]
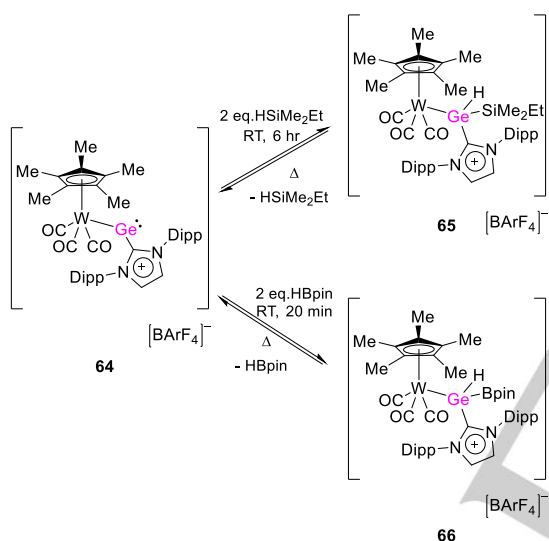

Scheme 16. Reversible insertion of H-E bonds with a cationic metallogermylene (**64**).

Redox-catalysis

As mentioned, redox cycles are based upon an initial oxidative addition step followed by reductive elimination to yield the desired product, whilst regenerating the active catalyst (Figure 1). Reversible binding of substrates also aids this turnover, as it helps to stabilise reactive intermediates whilst allowing for dissociation to reveal active sites. This key reversible feature is exemplified in a recent example by Sasamori and co-workers for the catalytic formation of C-C bonds.[99] Use of 4 mol % ^{Tbb}GeGe^{Tbb} (**67**) (Tbb = 4-^{t}Bu-2,6-[CH-(SiMe$_3$)$_2$]-C$_6$H$_2$) at 60 °C catalysed the trimerisation of a range of phenylacetylenes. Previously, the group had shown high reactivity towards C-C multiple bonds due to the low-lying LUMO, the in-plane π* orbital and the simultaneous σ-/π-donation and back π-donation from/towards the C-C multiple bond which agrees well with the frontier orbitals of the Ge≡Ge triple bond.[100] Mechanistic studies revealed that **67** acts as a precatalyst and **68** (Scheme 17) is the resting active catalyst, which is in likely equilibrium with a

germole-germylene species (**69**) at elevated temperatures. This ability to switch between Ge^{II} (germylene) and Ge^{IV} (germole) species stabilises the redox process during the cyclotrimerisation enabling turnover.
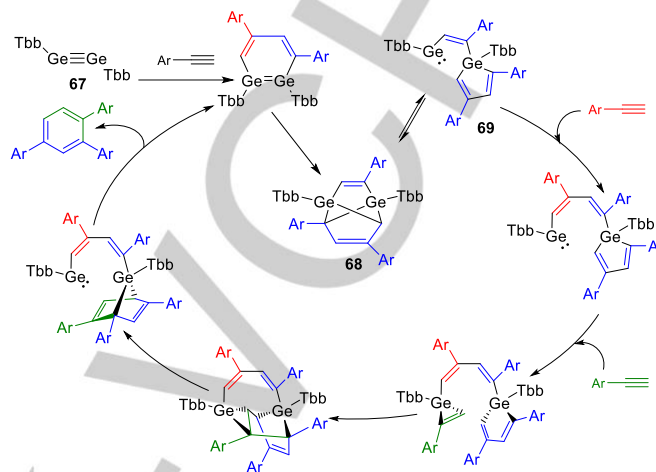
Scheme 17. Proposed mechanism for the digermyne catalysed cyclotrimerisation of phenylacetylenes

This example by Sasamori and co-workers represents an exciting area for main-group multiply bonded compounds and their use as catalysts. The ability of compound **68** to undergo reversible addition to **69** is the key step in this cycle and shows how crucial this can be for enabling catalytic turnover in redox based processes.

Non-Redox based catalysis

Considerable progress has been made towards redox based catalytic cycles, the activation of H-E bonds (typically oxidative addition step) has now been relatively well studied over the last 10 years (*see previous sections*). These studies have revealed feasible routes to low-coordinate main group hydrides which allows for access to non-redox based catalytic cycles.[37] Cycles based upon σ-bond metathesis and insertion reactions have previously been used as an entry point into the formation of alkaline earth or lanthanide hydride catalysis.[28a, 33a] In 2014, Jones and co-workers reported the use of two-coordinate L†GeH (**70**) and L†SnO^{t}Bu (**71**) bulky amido complexes for the catalytic hydroboration of carbonyl compounds (Scheme 18).[101] Turnover was found to be possible using as little as 0.05 mol% of **70** or **71** at room temperature for aldehydes, whereas increased loadings up to 2.5% were required for the reduction of ketones. N-heterocyclic ylide-like germylene complex has also been shown to effectively catalyse the hydroboration of carbonyl containing compounds.[102]

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Since this report, main group mediated-hydroboration reactions have gained attention over recent years and several catalytic transformations have been reported. Notable examples are the use of a β-diketiminate supported Ga hydride for the catalytic hydroboration of CO_2,[58] use of Ge, Sn, Pb Lewis pairs for the hydroboration of aldehydes and ketones[103] and the use of commercially available aluminium hydride reagents for the hydroboration of alkynes.[104]
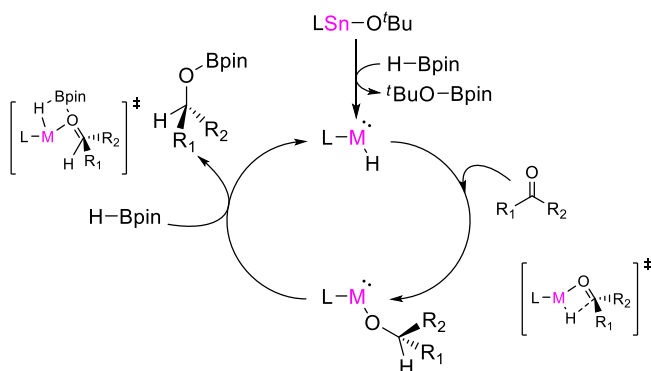
Scheme 18. Hydroboration of carbonyls with a well-defined low-valent main group hydride (M = Ge (**70**), Sn (**71**)).

Surprisingly, Harder and co-workers recently showed that $LiAlH_4$ was able to hydrogenate imines under 1 bar of hydrogen.[105] This atom efficient reduction route relies upon the cooperation of the Li and Al centres as comparable catalytic reactions with LiH, AlH_3 and $NaAlH_4$ did not proceed as efficiently. In a somewhat related work, Mulvey and co-workers also highlighted this synergistic effect of the two distinct metal centres, Li and Al, in their recent study towards hydroboration catalysis.[106] Comparisons between the neutral Al complexes and the bimetallic 'ate' complexes revealed higher activities for the 'ate' complexes. This was attributed to the greater polarisation of key intermediates induced by the heterobimetallic speices. Interestingly, use of the neutral $^{i}Bu_2Al$(TMP) (TMP =2,2,6,6-tetramethylpiperidinates) was found to efficiently undergo hydroboration reactions, even though it is devoid of a Al-H bond. It was found that this acts as a masked hydride as it undergoes a β-hydride transfer process for the reduction of benzophenone, indicating new potential catalytic pathways.[106a]

Catalytic cycles based upon σ-bond metathesis/insertion reactions circumvents the requirement of the reductive elimination step, thus providing an alternative route for main group complexes in catalysis. Use of H-E type reagents (E = B, N, Si, P etc) are well suited to cycles of this type as the formation of element-element bonds is driven by the concomitant release of hydrogen (Scheme 19). This catalytic cycle allows for both homo- and hetero-dehydrocoupling reactions depending on the choice of H-E.[107] Amine-borane dehydrocoupling is the most established reactivity of this type as its high hydrogen content by mass (ca. 20% for H_3NBH_3) makes it an ideal candidate for hydrogen storage applications. Also, of interest is the formation of boron-nitrides. Hexagonal boron-nitrides are isoelectronic with graphite and are therefore of keen interest to the materials industry.[108]

$$E = NR_2, PR_2, OR, SR$$
$$E' = SiR_3, BR_2$$
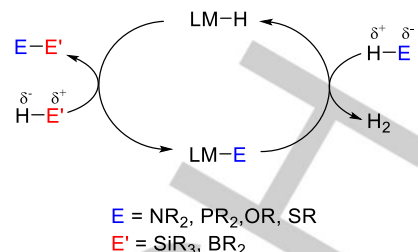
Scheme 19. Generic dehydrocoupling cycle based upon σ-bond metathesis and insertion reactions.

Dehydrocoupling of amine-boranes has been well studied with alkaline earth metals, with mechanistic studies revealing higher activity for the smaller electropositive group 2 metal ions and β-hydride elimination being a key step in the catalytic cycle.[28a] In line with transition metal chemistry, β-hydride elimination is also more favourable for 'hard' metal centres and therefore use of the highly Lewis acidic group 13 metal centres should also provide facile turnover. Indeed, this is the case with Al^{3+} and Ga^{3+} providing efficient turnover under ambient conditions for amine-borane dehydrocoupling.[107] Mechanistic studies revealed analogous mechanisms to those reported for group 2 systems, with Ga found to be more active. However, the lifetime of Ga catalyst was shorter owing to its redox instability, as precipitation of Ga metal was observed to occur during the reaction.[109] Rivard and co-workers have also shown the metal-free dehydrogenation catalysis to be possible through use of N-heterocyclic iminoborane catalysts.[110]

Extension of dehydrocoupling chemistry for the synthesis of Si-E bonds is highly desirable due to their widespread applications. Lewis acid-mediated catalysis has so far been successful in this field with $B(C_6F_5)_3$ and $F-P(C_6F_5)_3$ providing efficient turnover for a series of Si-E (E = O, N, S) bond forming reactions. The key to these systems is that the steric bulk around the B or P centre is sufficiently crowded enabling reversible complexation of the substrates, akin to frustrated Lewis pair chemistry.[111]

Routes to inorganic polymers such as polygermanes and polystannanes are sought due to their unique conducting properties. This can be achieved through dehydrocoupling routes from use of E-H substrates,[112] which occurs much more readily compared to their lighter congeners due to the weaker E-H bonds (E = Ge, Sn, As), however the resulting E-E or E-E' bonds are weaker. This, therefore, requires the use of milder catalysts that are selective for E-H bonds. Currently, most catalysts for formation of p-block polymers are based on transition metals, however, developments in this field are adding to the increasing knowledge base in the formation of main group element-element bonds and p-block coordination chemistry.

Another alternate non-redox based catalytic cycle for bond forming reactions has been shown by Shao et al.[113] Inspired by Mascarelli's early work on phenyl cations[114] and Siegel and co-workers silylium mediated intramolecular Friedel-Crafts reaction of aryl fluorides, in which a phenyl cation was implicated as an intermediate.[115] They proposed that β-silylated aryl fluorides would be well-suited as a phenyl cation precursor due to a decrease in the barrier for fluoride abstraction and enhancing the

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nucleophilicity of the arene ring. This was indeed the case and a wide range of β-silylated aryl fluorides were shown to be excellent reagents for the arylation of unactivated sp^3 and sp^2 C-H bonds, including methane (Scheme 20).
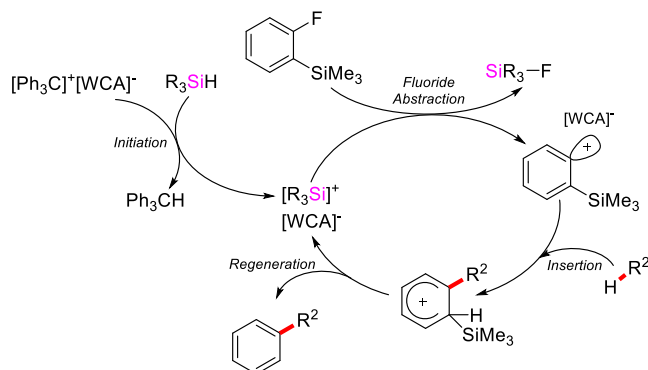
Scheme 20. Proposed catalytic cycle for arylation of hydrocarbons.

Conclusions and Outlook

Since Power's seminal review main group chemistry has continued to flourish. Advances in main group chemistry have led to an increased understanding in the vital importance of ligand design for the stabilisation of low-coordinate and/or low-oxidation state species. Use of β-diketiminate, terphenyl, NHC/NHI and boryl amido derived ligand scaffolds have become widely implemented and have led to many successful small molecule activation reactions. Through careful ligand design, isolation of previously unobtainable species has been made possible (diboryne, dialumene, aluminyl, acyclic silylene etc) and the differences in electronic and steric demands have been crucial to understanding how they may or may not react towards small molecules (Figure 4). For example, modification of the substituents in carbenes, from NHCs to CAACs, influences the σ-donating properties of the carbene lone pair and thus differences in reactivity towards H$_2$ are observed (Scheme 8). Also, ligand design directly influences the bite angle in the two-coordinate tetrylenes, which in turn influences their reactivity towards small molecules (Figure 3 and 4). In order to obtain reactive species, compounds with wide bite angles, which provide small HOMO-LUMO energy gaps, should be targeted to enable efficient oxidative addition reactions.

Reductive elimination is gaining much attention, with reversible bond activations paving the way towards catalytic application. This is exemplified in the catalytic trimerisation of alkynes mediated by a digermyne complex. The reversible step allows for switching between the resting and active catalyst states, thus providing additional stability to this system whilst allowing for efficient turnover to occur. Key reversible steps have also observed within our group, albeit stoichiometrically, wherein the isolation of a 'silepin' has allowed for use of a stable Si(IV) species which formally undergoes reductive elimination to react as a Si(II) centre. Again, this work highlights the differences in ligand design

as moving from an aryl to alkyl substituent in the NHI ligand results in the formation of a disilene complex. These examples, highlight the importance of reversible bond activations towards achieving redox based catalytic cycles with main group elements.

In the last 10 years main group chemistry has surpassed imaginations and is expected to continue on this trend in the future. With a number of new complexes recently isolated (eg. aluminyl, dialumene, silepin) their reactivity has yet to be fully explored and will surely lead to a plethora of new bond breaking and forming reactions. In terms of catalysis, it is highly likely that more examples of redox based cycles will be fully achieved. Use of main group multiply bonded compounds for this has also shown to be promising (digermyne alkyne trimerisation). The combination of the two metal centres within the same complex and the ability to switch between redox states is an area that is likely to succeed in further catalytic application. This use of two metal centres has also been recently shown to be successful in the case of non-redox based catalytic cycles. The synergistic effect of two distinct metal centres allows for increased bond polarisation of key intermediates enabling increased turnover in comparison to their monometallic counterparts. Use of cations or anions in catalysis is also one that has started to be realised and therefore is also expected to provide further examples in the future.

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Catherine Weetman and obtained her MChem and PhD at the University of Bath under the supervision of Prof. Michael Hill on the development of magnesium hydroboration catalytic systems. Her first postdoctoral position was spent at the University of Edinburgh under Professors Polly Arnold and Jason Love on f-block metal NHC complexes for small molecule activation; development of air- and moisture-stable d-block NHCs for chemical warfare decontamination and perrhenate catalysis. In December 2017, Cath was joined the group of Prof. Inoue at TU München as a TUFF postdoctoral fellow and in July 2018 she was awarded a Eurotech-Marie Curie Fellowship for aluminium multiple bond chemistry which will be carried out at TUM/EPFL.

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Shigeyoshi Inoue studied at the University of Tsukuba and carried out his doctoral studies under the supervision of Prof. Akira Sekiguchi, obtaining his Ph.D. in 2008. As a Humboldt grantee as well as a JSPS grantee, he spent the academic year 2008-2010 at the Technische Universität Berlin in the group of Prof. Matthias Driess. In 2010 he established an independent research group within the framework of the Sofja Kovalevskaja program at the Technische Universität Berlin. Since 2015 he has been on the faculty at the Technische Universität München, where he holds a tenure-track professorship of silicon chemistry. His research interests focus on the investigation of the synthesis and reactivity of low-valent main group compounds with the goal of finding novel applications.

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This concept article presents the last 10 years of molecular main group chemistry since Power's seminal review and the progress made towards catalysis.
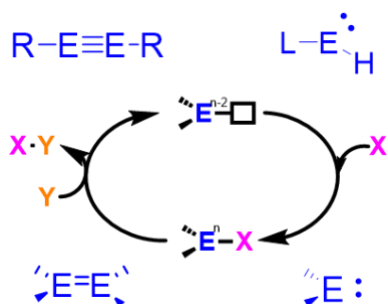
Catherine Weetman and Shigeyoshi Inoue*

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The Road Travelled: After Main-group

Elements as Transition Metals