

LOW VALENT MAIN GROUP COMPOUNDS IN SMALL MOLECULE ACTIVATION

Catherine Weetman

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

CONTENTS

1. INTRODUCTION	1
2. S-BLOCK COMPLEXES.....	2
3. P-BLOCK MULTIPLE BONDS	4
4. NEUTRAL P-BLOCK COMPLEXES	7
5. P-BLOCK ANIONS	10
6. P-BLOCK CATIONS	12
7. SUMMARY AND OUTLOOK.....	16
8. REFERENCES	16

1. INTRODUCTION

Carbon, nitrogen, oxygen, and phosphorus are essential elements to human life and the eco-systems in which we live. They combine in a variety of different ways to provide fuel sources, both edible and non-edible, to enable us to go about our everyday life. For example, if we consider carbon, this can be combined with itself to make petrochemicals which are then used in the manufacturing of everyday items such as electronics, plastics, medicines, and cosmetics. However, these have contributed to climate change as by-products in the manufacturing processes release greenhouse gases. Sustainable methodologies to combat rising emissions and energy demands are, therefore, paramount.



Figure 1. Small molecule activation and conversion into value added products.

One method to achieve this is to find renewable sources of the basic building blocks (i.e. C, N or P) to produce value-added products (Figure 1). C₁ sources such as carbon dioxide (CO₂), carbon monoxide (CO) and methane (CH₄) can be found in waste emissions, along with nitrous oxide (N₂O), thus making them ideal candidates for further functionalisation.^[1-3] These also have the advantage of being cheap, abundant materials due to their current prevalence within the atmosphere. As the most abundant gas found within the Earth's atmosphere, dinitrogen (N₂) is also a viable building block. Historically this has been utilised in the Haber-Bosch process, wherein N₂ is converted into ammonia (NH₃) for fertiliser production.^[4-5] This process, however, is extremely energy intensive and therefore more efficient processes are required. The same is also true for the

commonly used P building block, white phosphorus (P₄). P₄ is considered a strategic and critical building block for the chemical industry,^[6] yet its production and utilisation are both energy intensive and hazardous.^[7] Thus, to truly provide sustainable methods of small molecule functionalisation the processes should involve low activation barriers and ideally be atom-efficient to minimise waste.

Use of small molecules in the production of value-added products represents a significant challenge due to the thermodynamic stability of small molecules (Figure 2). The activation of these inert bonds typically requires a catalyst, as such transition metals (TM) play a prominent role in the field of small molecule activation.^[8] This is because of the relative ease in which they coordinate substrates, their variable oxidation states and their ability to act as an electron source and/or sink within key transition states. However, due to their high cost and limited long-term supply, efforts are now focussing on the use of Earth abundant metal centres, such as those found within the *s*- and *p*-blocks of the periodic table.

$\text{N}\equiv\text{N}-\text{O}^{\ominus}$	H-H	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$
167.4	435.8	439.3
O=C=O	N≡N	C≡O
532.0	944.8	1076.4

Figure 2. Bond Dissociation Energies (BDE) for small molecules, values given in kJ mol⁻¹.^[9]

Historically speaking, main group elements have often been overlooked due to the achievements of their neighbours in the *d*-block or that of its lightest group 14 congener, carbon. The chemistry of the *s*-block is dominated by the +1 oxidation state for alkali metals (group 1) and +2 for alkaline earth (group 2) metals. It was only in 2007 that the first group 2 complex in the +1 oxidation state was isolated.^[10] Moving across to the *p*-block, more oxidation states are available, and due to the inert pair effect, these tend to be found as the Eⁿ and Eⁿ⁺² oxidation states [e.g., Si(II) and Si(IV)]. Furthermore, on descending the group the preferred electronic ground state changes from triplet to singlet state and as such for the heavier elements the lower oxidation state becomes more stable (Figure 3). The singlet state, as shown in Figure 3, highlights the reactive ambiphilic character of low valent[†] main group centres with the nucleophilic/Lewis basic (lone pair) and electrophilic/Lewis acidic (vacant *p*-orbital) active sites.

[†] In this chapter low valent is defined as low oxidation state and/or low coordinate main group centre.

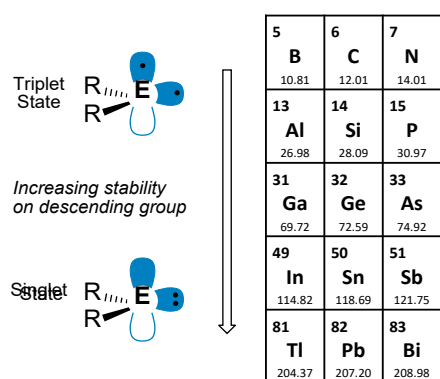


Figure 3. Singlet and triplet electronic ground states in low valent main group centres.

Increased understanding in how to isolate low valent main group centres has led to the rapid development of this field. This has largely been achieved through a combination of kinetic and thermodynamic stabilisation methods, which can be tuned through ligand design. Kinetic stabilisation is provided through use of sterically demanding ligands, whilst thermodynamic stabilisation is obtained through choice of heteroatom within the ligand scaffold. For example, use of electronegative substituents (e.g., N, S, P) allows for stabilisation of the vacant p -orbital through their π -donor properties. This partially occupies the vacant p -orbital to provide stability to the low valent main group centre (Figure 4A). In contrast, use of electropositive substituents (e.g., Si, B, C) tend to result in more reactive main group centres due to their lack of π -donor properties. They can, however, provide some stability through β -effects (Figure 4B). Additional stabilisation can be also be provided externally through coordination of Lewis acids and bases (Figure 4C and D).

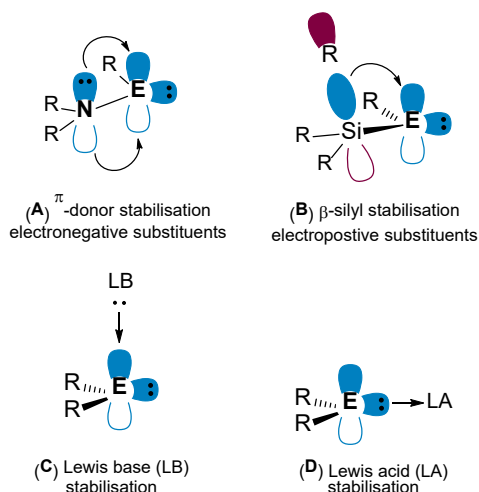


Figure 4. Different stabilisation methods for low valent main group centres (E = main group centre).

The variety of stabilisation methods has allowed for the isolation of a several new classes of low valent main group species, such as main group multiple bonds and main group compounds with either open or quasi-open coordination sites. The latter has largely been exploited in the form of frustrated Lewis pairs, providing several landmark examples of main group elements in small molecule activation^[11-13] and thus beyond the scope of this book

chapter. Comparison of main group multiple bonds and tetrylenes to transition metals have been drawn due to their similar energetically accessible frontier orbitals (Figure 5). This has enabled the activation of small molecules under ambient conditions at the low valent main group centres and is, therefore, the focus of this book chapter.

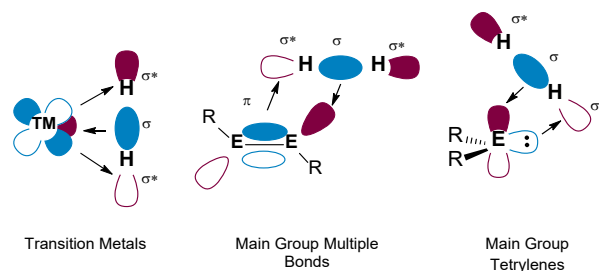
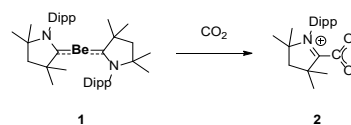


Figure 5. Frontier orbitals of transition metals, main group multiple bonds and tetrylenes and their interaction with dihydrogen.

2. S-BLOCK COMPLEXES

Despite the typical redox inactive nature of the s -block elements, they have been utilised in a variety of challenging bond activations and catalytic transformations with cycles built on a series of σ -bond metathesis and insertion reactions.^[14-15] Furthermore, the synergistic effects of alkali metals in bimetallic complexes have been widely studied and reveal enhanced reactivity over their monometallic counterparts.^[16] Due to the stability of the alkali and alkaline metals in their +1 and +2 oxidation states, respectively, these compounds are not considered low-valent. However, examples of alkaline earth compounds in their sub-oxidation state exist, with Be(0),^[17] Be(I),^[18] Mg(I)^[10] and Ca(I)^[19] now reported.

The first reported zero-valent beryllium compound (**1**, Scheme 1) was isolated using the π -acidic cyclic(alkyl)(amino)carbene (cAAC) ligand.^[17] This remarkable compound is stabilised through donor-acceptor interactions between the cAAC ligands and Be(0) which is in a $1s^2 2s^0 2p^2$ electronic configuration. The central C-Be-C core is a three-centre two-electron π -bond. This Be(0) complex has found use as a mild reducing agent capable of reducing Bi(III) to Bi(I).^[20] Currently, the only example of **1** in small molecule activation is towards CO_2 , in which a zwitterionic complex (**2**, Scheme 1) is formed along with the concomitant formation of a black precipitate which is thought to be elemental beryllium.^[17]



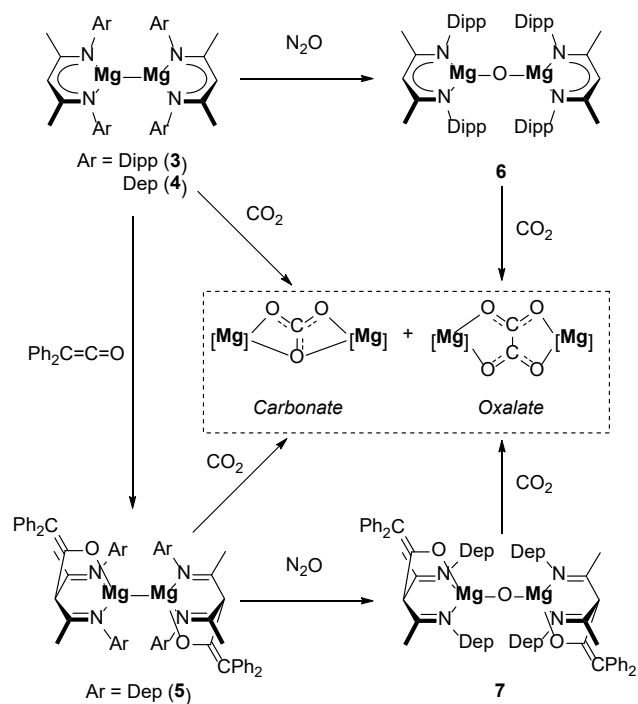
Scheme 1. CO_2 activation by a zero-valent beryllium centre (Dipp = 2,6-diisopropylphenyl).^[17]

Low valent group 2 chemistry is in its infancy and as such its use in small molecule activation is yet to be fully realised. The landmark Mg(I) dimer, however, has been established since 2007^[10] and has found use as a versatile reagent in both organic and inorganic synthesis.^[21-22] Regarding its reactivity towards small molecules, CO_2 disproportionation reactions have been investigated both experimentally and theoretically.^[23-26] Reaction of the Mg(I) dimer (**3**) with two

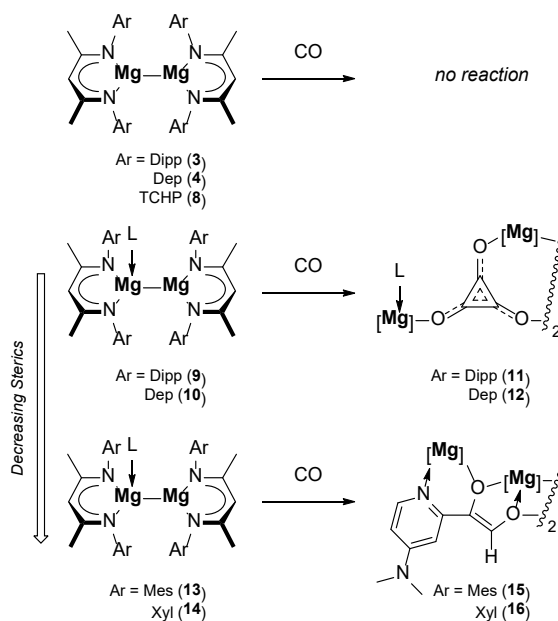
equivalents of CO₂ at ambient temperature resulted in the rapid formation of a carbonate species along with a minor amount of the reductively coupled oxalate species (Scheme 2).^[23] The reductive disproportionation to the carbonate species occurs with loss of CO, which was confirmed via *in situ* reaction monitoring with ¹³C NMR spectroscopy. Use of excess CO₂ in the reaction mixture did not increase the yield of the oxalate species but resulted in a mixture of products.

Due to the susceptible γ -position on the backbone of the β -diketiminato ligand it was thought that CO₂ may be adding across the backbone, as observed with a related Mg(II) system.^[27] Therefore, to prevent reactivity at this site the Mg(I) dimer (4) was first reacted with diphenylketene to yield the tripodal diamine-enolato Mg(I) complex (5, Scheme 2).^[25] Now, 5 reacts with an excess of CO₂ at ambient temperature to form the carbonate and oxalate products in a 60:40 ratio. Furthermore, the product formation can be controlled by temperature. At low temperature (-60 °C) oxalate formation is solely observed whereas at elevated temperatures (60 °C) near quantitative conversion to the carbonate species occurs.^[25] Mechanistic investigations into the formation of the carbonate species suggested that this reaction occurs via a magnesium-oxo species. Reaction of both Mg(I) dimers (3 and 5) with N₂O result in the formation of oxo-bridged dimagnesium complexes (6 and 7) with a central Mg-O-Mg core (Scheme 2). This can subsequently be reacted with one equivalent of CO₂ to yield the corresponding carbonate species.^[23, 25]

Further examination of Mg(I) dimers in small molecule activation has centred on the reactivity towards CO. It was found that 3 and 4 were unreactive towards CO;^[28] however, this reactivity can be turned on by simple coordination of a Lewis base [e.g., DMAP or *N*-heterocyclic carbene (NHC)] (Scheme 3).^[29] This results in the formation of 9 and 10, which have elongated Mg-Mg distances [e.g., 3 2.8457(8)^[10] Å vs. 9 3.0886(6)^[29] Å]. It was first postulated that the reason for CO activation was due to the increased bond length, therefore a highly sterically crowded Mg(I) dimer was synthesised, which contained a long Mg-Mg distance of 3.021(1) Å (compound 8, Scheme 3).^[30] This, however, resulted in no reactivity towards CO even after heating for several hours at 60 °C. It was therefore thought that CO activation is the result of an unsymmetrical, and thus, polar Mg-Mg bond. Furthermore, it was shown that sterics play a role in the resulting product formation with larger aryl groups in the β -diketiminato ligand framework (9 and 10) affording the trimeric deltate complex (11 and 12, respectively). Whilst smaller groups (13 and 14) result in ethenediolate complexes (15 and 16) (Scheme 3).^[30] The mechanism of the latter was found to proceed via reductive dimerisation of CO followed by intramolecular C-H activation of the coordinated DMAP ligand.



Scheme 2. CO₂ activation by a Mg(I) dimers (Dipp = 2,6-diisopropylphenyl, Dep = 2,6-diethylphenyl).^[23, 25]



Scheme 3. CO activation by Mg(I) dimers (L = DMAP 4-dimethylaminopyridine, Dipp = 2,6-diisopropylphenyl, TCHP = 2,4,6-tricyclohexylphenyl, Dep = 2,6-diethylphenyl, Mes = 2,4,6-trimethylphenyl, Xyl = 2,6-dimethylphenyl).^[28-30]

The exploration of new low-valent *s*-block complexes, particularly of the heavier elements, is an exciting field with huge potential in the field of small molecule activation. Despite the high stability of the *s*-block, these elements have still been used in some unique and challenging transformations, such as the nucleophilic alkylation of benzene with an organocalcium reagent.^[31] This highlights the potential of this class of compounds, both high and low-valent, as viable candidates for future sustainable processes.

3. P-BLOCK MULTIPLE BONDS

The first comparisons between transition metals and low-valent main group compounds came from the ability of a digermene (a germanium-germanium triple bond) to activate dihydrogen under mild conditions.^[32] This was possible due to the synergistic interaction of main group multiple bonds frontier orbitals with those of dihydrogen, as shown in Figure 5. Whilst this discovery happened in the early years of the 21st century, main group multiple bonds have been in existence since the early 1980s. Seminal examples reported by West (Si=Si),^[33] Yoshifuji (P=P),^[34] Brook (Si=C),^[35] and Becker (P≡C)^[36] proving that the so-called ‘double bond rule’[‡] could indeed be broken. Nowadays, homodiatomic double bonds have been isolated for all *p*-block elements (groups 13-15, rows 2-6), with selected examples highlighted in Figure 6 including **17**, **19-23**.^[37-39] Homodiatomic triple bonds for all group 14 elements have also been isolated (Figure 6, **24-27**)^[37-38] whilst only one neutral group 13 triple bond has been reported (**18**, Figure 6).^[40] Several examples of mixed *p*-block heterodiatomic multiple bonds also have been reported, in general these are rarer due to the challenges associated with stabilising an unsupported polar bond.^[37-38]

Figure 6 displays some of the seminal compounds in main group multiple bonds, along with E-E bond lengths and E-E-L bond angles (E = main group element, L = ligand). Notable trends in the geometries show elongation of E-E bond lengths on descending the group, as to be expected based on increasing atom size, which also leads to a decrease in E-E bond strengths. Of more importance, is the increase in the *trans*-bent character (E-E-L angle) on descending the group. The Carter-Goddard-Malrieu-Trinquier (CGMT) model is often used to provide an explanation for observed geometries between lighter and heavier main group element multiple bonds (Figure 7).^[41-44] If we compare to carbon based multiple bonds, alkenes and alkynes, these exhibit planar geometries due to the unhybridised carbon *p*-orbitals overlapping to form π -bonds (Figure 7A). However, on descending the group the singlet state becomes more stable and double bonds of heavier elements can be described as two monomeric units with a double dative bond (Figure 7B). This influences the observed geometries, as highlighted by the nearly 90° *trans*-bent angle for diplumblyne, which are better described as diplumblyenes with a formal single bond (**27**, Figure 6). Furthermore, the heavier elements with their weaker E-E bonds and higher stability of the singlet state, often dissociate into their monomeric counterparts in hydrocarbon solutions.^[45-48] Along with the CGMT model, Molecular Orbital (MO) theory also provides an explanation for the observed geometries of main group multiple bonds. If we compare carbon and lead (the two extremes of group 14, linear and bent geometries, respectively) the σ^* and π -orbitals differ in their energy separation. There is a large separation in the case of carbon, however on descending the group the gap becomes smaller and there is increased mixing of the π and σ^* orbitals.

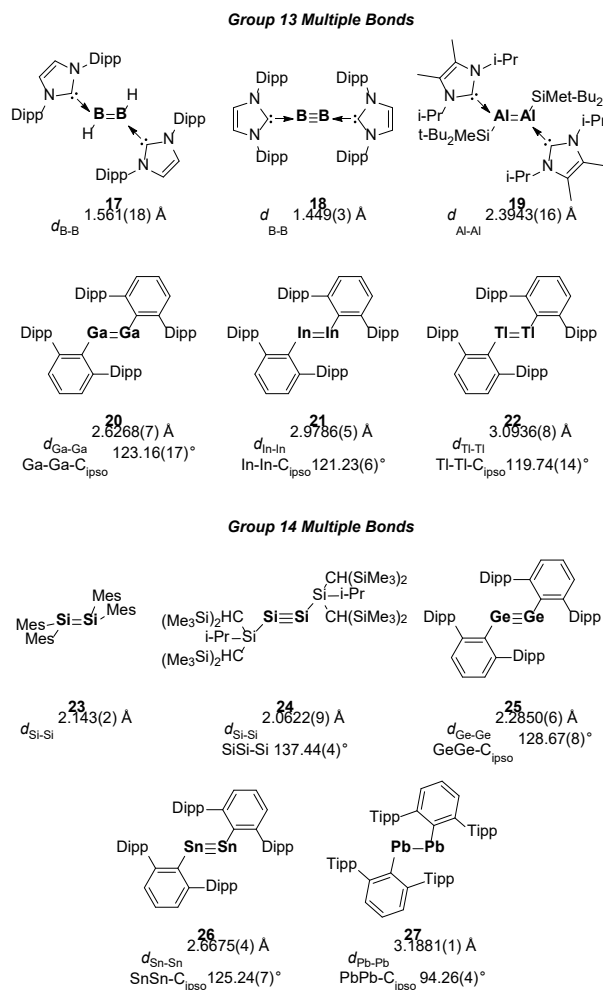


Figure 6. Selected examples of Group 13 and 14 main group multiple bonds. (Dipp = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl).^[37-40]

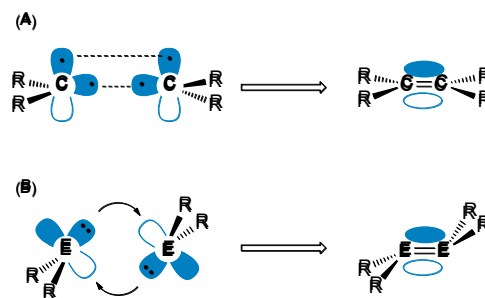


Figure 7. CGMT models for differences in observed geometries for triplet (A) and singlet multiple bonds (B).^[41-44]

This results in increased non-bonding electron density on the heavier element centre, with the observed *trans*-bent geometries a result of interelectronic repulsion between the two non-bonding lone pairs.^[37-38, 49]

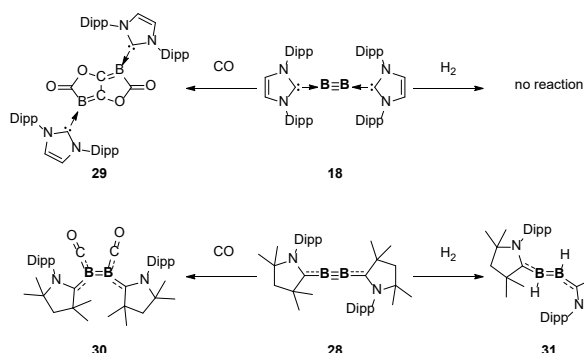
Since Power’s seminal discovery of the transition metal-like behaviour of main group multiple bonds, the field has flourished in recent years. Whilst the topic of this book chapter focusses on their ability to be used in small molecule activation, main group multiple bonds have been shown to

[‡] Double bond rule: *p*-block elements of periods > 2 (i.e. from aluminium onwards) will not form multiple bonds

be a versatile tool in a variety of synthetic transformations which have recently been reviewed.^[50-54]

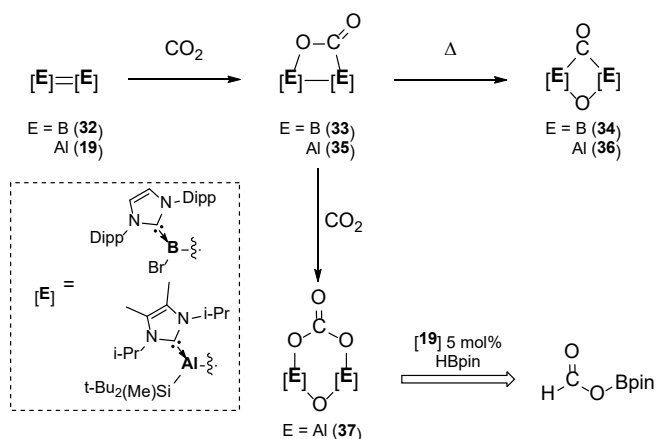
3.1 GROUP 13 MULTIPLE BONDS

Group 13 elements contain 3 valence electrons which, therefore, renders multiple bond formation more challenging than their group 14 counterparts. This is particularly true in terms of triple bond formation as all valence electrons are required, leaving only a vacant orbital for stabilisation. As shown in Figure 6, neutral double bonds for all of group 13 diatomic species have been isolated and remarkably a boron-boron triple bond, which is possible due to external stabilisation from a Lewis base (akin to Figure 4C). To date there are two main classes of diborynes, that is compounds with a boron-boron triple bond. One is stabilised by a NHC ligand (compound **18**) whilst the other is stabilised by a cAAC ligand (compound **28**), which have increased π -acceptor abilities relative to NHCs and as such shows some delocalisation across the C-B-B-C moiety. The choice of ligand influences the observed small molecule reactivity (Scheme 4), with NHC diborynes able to couple CO molecules (**29**)^[55] but are not able to activate H₂.^[56] In contrast, cAAC diborynes coordinate CO (**30**)^[57] and can activate H₂ (**31**) at room temperature.^[56]



Scheme 4. Ligand controlled reactivity of diborynes with small molecules.^[55-57]

NHC-stabilised diborenes and dialumenes, compounds with neutral double bonds, can fixate CO₂ via [2+2]-cycloaddition (Scheme 5). In the case of diborene (**32**) the fixated species (**33**) was thermally unstable and rearranged to a bridging carbonyl (**34**) complex.^[58] In the case of the heavier analogue, dialumene (**19**) the CO₂ fixated species (**35**) is isolable and indefinitely stable in the solid state at ambient temperature. However, on heating this rearranges to the bridging carbonyl (**36**) species whilst in the presence of excess CO₂ a 6-membered carbonate containing ring is isolated (**37**).^[59] Furthermore, the dialumene (**19**) was found to selectively catalyse CO₂ to a formic acid equivalent in the presence of pinacol borane (HBpin) with **37** pivotal to the calculated mechanism.^[59]



Scheme 5. CO₂ small molecule activation by neutral group 13 double bonded complexes.^[58-59]

Similar to that of diborynes, dialumene reactivity is also influenced by the choice of stabilising ligand as highlighted in Figure 8. Switching from a silyl ligand in **19** to an aryl ligand (**38**) resulted in a change in geometry from a planar to a *trans*-bent and twisted structure.^[60] Furthermore, this has a knock-on effect in terms of the electronics in the central Al₂ core as the silyl ligand is almost neutral but the aryl dialumene is highly polarised, which can be attributed to the relative differences in electronegativities ($\Delta\chi$ Al-C 0.94; $\Delta\chi$ Al-Si 0.29). This results in a more reactive dialumene, which is able to activate H₂ as well as larger substrates such as diphenylacetylene due to the increased flexibility in the aryl stabilised complex.^[60]

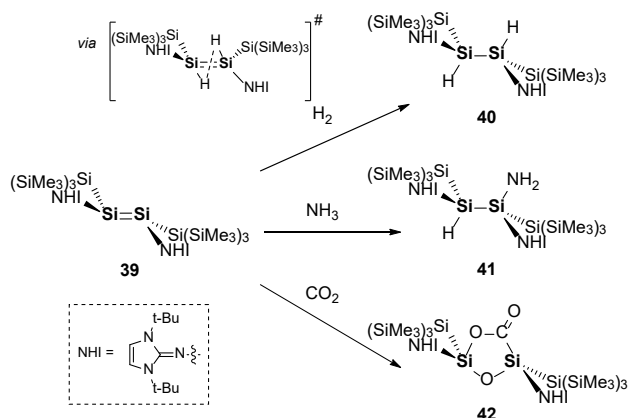
	NHC t-Bu ₂ (Me)Si	Si(Me) ₂ t-Bu ₂ NHC	Tipp NHC
Structural			
$d_{\text{Al=Al}}$	2.3943(16) Å	2.4039(8) Å	
<i>Trans</i> -bent (θ)	$\theta = 0^\circ$	$\theta = 17.25^\circ, 23.70^\circ$	
twist (τ) angles	$\tau = 0^\circ$	$\tau = 12.06^\circ$	
Electronic			
HOMO-LUMO gap	2.24 eV	1.86 eV	
NPA charge Al-Al	+0.08/+0.08	+0.48/+0.49	
Reactivity			
Large substrates (e.g. PhCCPh)	no	yes	
H ₂ activation	no	yes (50 °C)	

Figure 8. Key features of silyl and aryl stabilised dialumenes (Tipp = 2,4,6-triisopropylphenyl).^[60]

On descending further down group 13, digallene (**20**), diindene (**21**) and dithallene (**22**) have been used in small molecule activation.^[47, 61-63] Due to the higher stability of the singlet ground state compounds **20-22** readily dissociate into their monomeric forms in hydrocarbon solutions, and can form donor-acceptor complexes as the monomer can act as a Lewis base. Despite digallene's ability to dissociate, reactivity studies revealed that small molecule activation proceeds via the double bond.^[64-66]

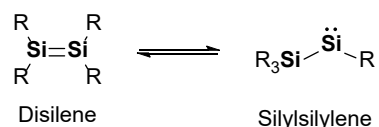
3.2 GROUP 14 MULTIPLE BONDS

Group 14 multiple bonds are arguably the most widely studied main group multiple bonds, particularly if you consider the lightest congeners: alkenes and alkynes. As shown in Figure 6 triple bonds have been isolated for all members of group 14 but owing to the inert pair effect diplumbylenes (**27**) are best considered to contain a single bond.^[37-38] It was group 14 multiple bonds that first drew comparisons to the transition metal-like ability of main group elements, as digermynes (**25**) showed ambient temperature activation of H₂.^[32] Despite disilenes being one of the earliest examples of an isolated main group multiple bond, it was only recently that H₂ activation was achieved. A highly *trans*-bent and twisted disilene (**39**), which may be better described as a weak double donor-acceptor complex due to its long Si-Si double bond [2.3134(7) Å average ~2.22 Å], undergoes facile H₂ activation to yield 1,2-disilane (**40**, Scheme 6).^[67] In contrast to alkene hydrogenation, anti-addition occurs due to the staggered ligand arrangement which pre-organises the central Si=Si bond. Furthermore, disilene **39** has been shown to react with several other small molecules (Scheme 6). N-H bond cleavage was observed with NH₃ (**41**), and decarbonylation and 5-membered ring formation with excess CO₂ (**42**).^[68]



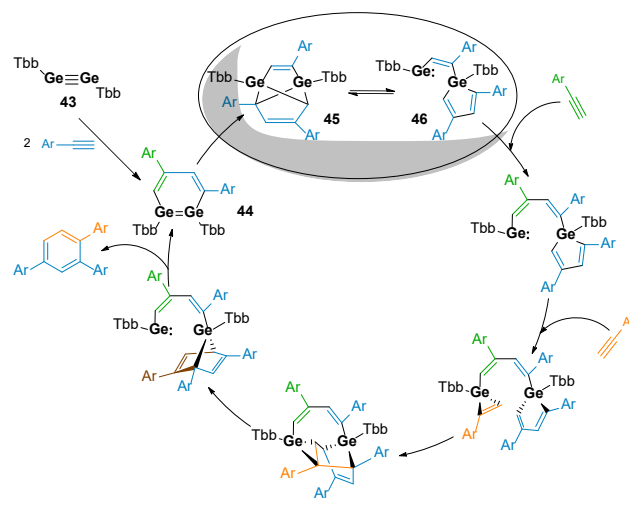
Scheme 6. Small molecule activation with a highly *trans*-bent and twisted disilene.^[67-68]

One notable aspect of disilene chemistry is the proposed disilene-silylsilene equilibria (Scheme 7). This equilibrium has been used to access transient silylsilylenes which show exceptional reactivity due to the strongly σ -donating silyl ligands, representing an alternative mechanism of small molecule activation by a main group multiple bond. This equilibria has previously been invoked to account for the observed reactivity, (e.g. [2+1]-cycloaddition with ethene rather than [2+2]-cycloaddition)^[69] direct experimental evidence for this equilibrium was achieved recently by Cowley and co-workers using a base coordination strategy.^[70] This is an important observation as the ability to control this equilibria will have a direct influence on product formation.



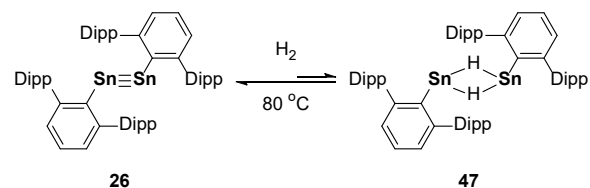
Scheme 7. Disilene-silylsilylene equilibria

Digermynes have been pivotal in highlighting the potential of main group multiply bonded species. Following the first report of H₂ activation, they were also used in the first catalytic application of main group multiple bonds. Regioselective cyclotrimerisation of phenylacetylene (PhCCH) is achieved using digermynes (**43**) as a pre-catalyst (Scheme 8).^[71] This reaction proceeds via initial [2+2+2]-cycloaddition to form **44**, addition of a third PhCCH molecule results in **45** which is in equilibrium with a germole-germylene species **46**. Mechanistic studies revealed **46** to be key in facilitating turnover, as it provides access to the low valent Ge(II) centre which has the vacant coordination site for additional substrates to bind. The stability of this system arises due to the equilibrium that exists between **45** and **46**.



Scheme 8. Digermine catalysed cyclotrimerisation of phenylacetylene. Tbb = 4-*t*-Bu-2,6-[CH-(SiMe₃)₂]-C₆H₂.^[71]

The heaviest group 14 diatomic multiple bonds (Sn, Pb) have a higher tendency to dissociate in solution owing to their weaker bonds.^[72-73] Distannylene **26** was found to be in equilibrium with the corresponding product of H₂ activation (**47**, Scheme 9). Both the equilibrium constant ($K_{eq} = 2.33 \times 10^{-4} \pm 4.9\%$ by ¹H NMR) and the Gibbs free energy ($\Delta G^\circ = 5.89 \text{ kcal mol}^{-1} \pm 0.68\%$) strongly favoured the Sn(II) hydride species (**47**).^[74] Additional studies on distannylene **26** found the Sn-Sn triple bond undergoes reversible cleavage to afford two Sn(I) radicals in toluene.^[75]

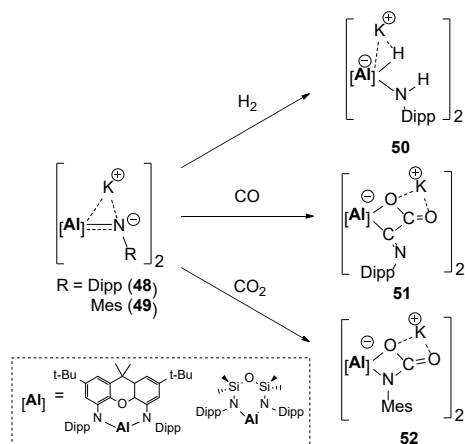


Scheme 9. Reversible H₂ activation by distannynes.^[74]

3.3 HETERODIATOMIC MULTIPLE BONDS

Heterodiatomic multiple bonds are of interest due to the novel materials properties that are associated with pnictogen (group 15) and chalcogen (group 16) bonded complexes.^[50, 76] For example boron-nitrides are used in the ceramics industry due to their high thermal and chemical stability,^[77] whilst alumina (Al₂O₃) is an electrical insulator and owing to its high strength its widely used as an abrasive material.^[78] The ability to isolate a discrete heterodiatomic units and study the aggregation process is key to fine tuning material properties, however this is challenging due to the highly polarised nature of these species. As such, sterically demanding ligands or use of external Lewis acid/base stabilisation is necessary yet this can be detrimental to the small molecule reactivity of the heterodiatomic multiply bonded complex.

Several examples of group 13 pnictogen and chalcogen multiply bonded complexes have been reported.^[52, 79] Recent achievements have centred around the use of anionic group 13 nucleophiles (*see section 5.1*) to access aluminium-nitrogen (**48**^[80], **49**^[81]) or chalcogen multiple bonds.^[82-84] As shown in Scheme 10, aluminium-imides have been reported to react with various small molecules. Aldridge and co-workers reported H₂ cleavage with **48** which occurs in a 1,2-fashion across the polar Al-N bond to yield compound **50**, whereas reaction with CO results in C-C coupling C-O cleavage to form **51**.^[80] Alternatively, Coles and co-workers showed **49** undergoes [2+2]-cycloaddition with CO₂ to yield the carbamate dianion **52**.^[81]



Scheme 10. Aluminium-imide reactivity towards small molecules.^[80-81]

Examples of intragroup multiple bonds exist but are scarce, there is one example of a mixed group 13 multiple bond (B=Al)^[85] and a handful of heavier group 14 mixed species also exist (e.g. Si=Sn,^[86] Ge=Sn^[87]). These have been shown to react with small molecules and tend to react in accordance with the polarity of the double bond. Alternate mixed intra-group 14 compounds have focussed on combinations with the lightest congener carbon, this yields metallalkenes^[88-90] and metallavinylidenes^[91] as well as group 14-carbon triple bonds.^[92-94]

4. NEUTRAL P-BLOCK COMPLEXES

The most widely studied compounds that fit the ‘low-valent’ criteria within the main group is carbenes. The ability to fine tune the steric and electronic demands of carbenes have led to them being ubiquitous in modern day transition metal and main group chemistry.^[95] Whilst carbenes can access both the singlet and triplet state, borylenes, alumylenes, silylenes, germlyenes *etc.*, have so far all been isolated in the singlet state although some reactivity is reported to occur via the triplet state (Figure 9). They are often considered to be ambiphilic due to the presence of a lone pair (Lewis base) and empty *p*-orbital (Lewis acid). As such these species are often highly reactive and capable of the most challenging bond activations.

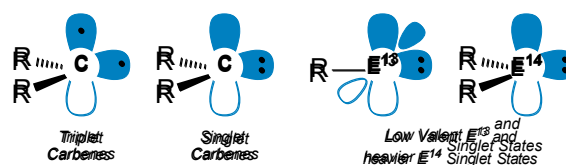
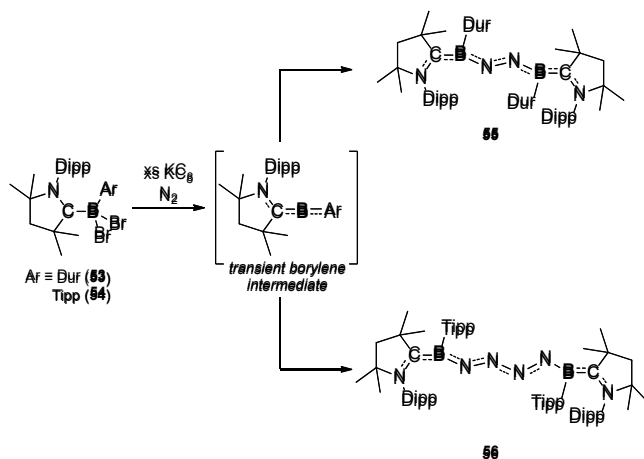


Figure 9. Ground state electronic configurations.

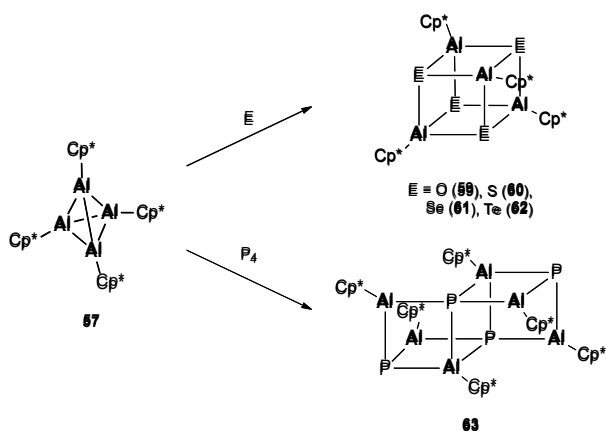
4.1 GROUP 13 COMPLEXES

E¹³ carbene analogues have two vacant *p*-orbitals and therefore require additional Lewis base stabilisation to be isolated. The first stable terminal borylene was reported by Braunschweig and co-workers in 1998 and is coordinated to a transition metal centre,^[96] further examples of isolobal borylenes have used mono- or bis-(Lewis base) stabilisation strategies.^[97] Several examples of small molecule activation have been reported with borylenes,^[98] but the standout example of a low-valent main group compound in small molecule activation was reported by Braunschweig and co-workers in 2018. Nitrogen fixation was achieved due to the *in situ* generated borylene intermediate. This was the first time such a transformation had been achieved by a low valent main group centre. In the initial report reduction of [(CAAC)DurBBr₂] (**53**) (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 N₂ under ambient conditions to yield [(CAAC)DurB]₂(μ-N₂) (**55**)(Scheme 11).^[99] Whilst in subsequent work, exchange of the aryl substituent to Tipp (**54**) (2,4,6-triisopropylphenyl) results in the reductive coupling of dinitrogen (**56**)(Scheme 11).^[100] Furthermore, the group showed it was possible to use **53** in a one pot reaction to yield ammonium chloride under ambient conditions.^[101]



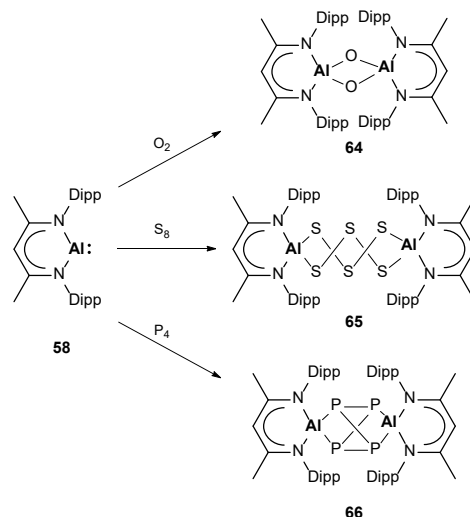
Scheme 11. Nitrogen fixation and reductive coupling at a low valent boron centre.^[99-100]

On descending the group, alumylene chemistry is dominated by the Al(I) tetramer $[\text{Cp}^*\text{Al}]_4$ (**57**) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$),^[102] which dissociates into its monomeric unit at elevated temperatures, and the monomeric β -diketiminate supported Al(I) (**58**).^[103] The Lewis basic character of Al(I) has been utilised in coordination chemistry, owing to its isolobal nature with CO several examples of Al(I)-transition metal^[104] complexes and Al-*f*-element^[105-106] complexes have been reported. In terms of their chemistry Al(I) complexes have been used in a variety of bond activations, with a particular emphasis on the oxidative addition reactions of strong σ -bonds with the driving force being the formation of the inherently more stable Al(III) compound.^[107-109] In terms of small molecule activation the Al(I) tetramer $[\text{Cp}^*\text{Al}]_4$ (**57**) has been shown to react with O_2 or N_2O to yield the heterocubane structure **59**, additionally reactions with the heavier elemental chalcogens also yielded heterocubane structures (compounds **60-62**, Scheme 12).^[110-111] These structures arise due to the highly polarised Al-E bonds and the insufficient kinetic stabilisation provided by the Cp^* unit. Reaction of **57** with P_4 results in the formation of a unusual P_4Al_6 cage through cleavage of the P-P bonds.^[112]



Scheme 12. Reactions of tetrameric Al(I) with small molecules.^[110-112]

Similar small molecule reactions performed with the monomeric alumylene (**58**) results in a series of discrete complexes due to the increased size of the supporting β -diketiminate ligand (Scheme 13). A dimeric complex (**64**) is obtained on reaction with oxygen,^[113] whilst an eight membered Al_2S_6 ring (**65**) (can alternatively be described as two $\mu\text{-S}_3$ chains between two Al centres) is isolated on reaction with elemental sulfur.^[114] Extension to P_4 reactivity results in the partial reduction of P_4 to yield a $[\text{P}_4]^{4-}$ anion bridged between two Al centres (**66**).^[115] Alumylene **58** has also been used for a wide range of E-H bond activations which have been recently reviewed.^[107, 109]

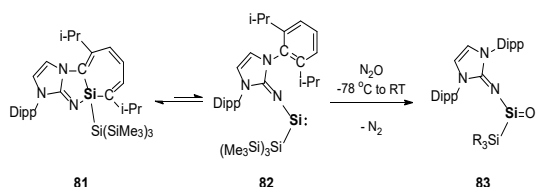


Scheme 13. Reactions of monomeric Al(I) complex **58** with small molecules.^[113-115]

Descending further down the group results in increased stability of the lone pair, and as such the reactivity of Ga(I),^[116] In(I)^[117] and Tl(I)^[118] is more driven by the basicity (or nucleophilicity) of the metal centres compared to the acidic (or electrophilic) boron and aluminium centres.^[119]

4.2 GROUP 14 COMPLEXES

E^{14} complexes of the general formula R_2E , also known as tetrylenes, have provided some of the most notable low-valent main group transformations over the last decades. Of this class of compounds, carbenes are the most widely studied and now ubiquitous in both transition metal and main group chemistry.^[95] Whilst they have largely been employed as ligands to stabilise low-valent metal centers they are reactive species in their own right. This is highlighted by both the previously mentioned cyclic(alkyl)(amino)carbenes (cAAC, **67**) and acyclic(alkyl)(amino)carbenes (aACs, **68**) ability to cleave dihydrogen at a single carbon site (Scheme 14).^[120] This was enabled by the ability to fine tune both the steric and electronic properties of the carbene carbon to enhance its nucleophilic character as di(amino)carbenes (e.g., NHCs) are incapable of dihydrogen activation. This was also attributed to the differences in the singlet-triplet energy gaps (cAAC 46 kcal mol⁻¹ vs. NHCs 68 kcal mol⁻¹). In contrast to transition metals, where coordination is often observed, reaction of **67** and **68** with NH_3 results in N-H cleavage to yield compounds **71** and **72** (Scheme 14).^[120]



Scheme 14. Reactivity of CAACs and aAACs towards H₂ and NH₃.^[120]

The singlet or triplet ground states of carbenes can be manipulated depending on the nature of the substituents, however on descending further down the group the heavier tetrylenes exhibit a singlet ground state. In general, silylenes are highly reactive with short lifetimes, they often undergo dimerisation to form multiple bonds and therefore requires sterically demanding groups to prevent this from occurring. The first stable Si(II) compound was isolated in 1986 by Jutzi (**73**, Figure 10),^[121] whilst a landmark achievement it is not strictly low-valent due to the 10-fold coordination of the Cp* rings. Two-coordinate silylenes were first isolated by Denk and co-workers as the silicon analogue of NHCs (**74**)^[122] namely N-heterocyclic silylenes (NHSi). This was extended to a 6 membered ring system (**75**)^[123] by Driess and co-workers in 2006. Also in 2006, Roesky reported a three-coordinate silylene chloride (**76**)^[124] this has paved the way for many additional transformations due to its labile Si-Cl bond.^[125]

These cyclic species are reactive towards a range of small molecules and substrates,^[126-127] however their acyclic counterparts are much more reactive. This is due to the change in R-Si-R angle, which in turn influences the singlet-triplet energy gap and HOMO-LUMO gap. This influence of geometry is highlighted by the ability to cleave dihydrogen or not,^[128] compounds **77**^[129] and **78**^[130] with obtuse angles readily form the corresponding silanes whilst compounds **79**^[131] and **80**^[132] with narrow bite angles are unreactive towards H₂ (Figure 11).

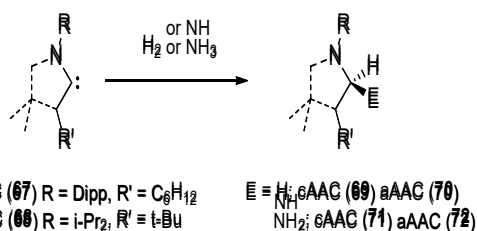


Figure 10. Selected examples of ground-breaking Si(II) compounds.^[121-124]

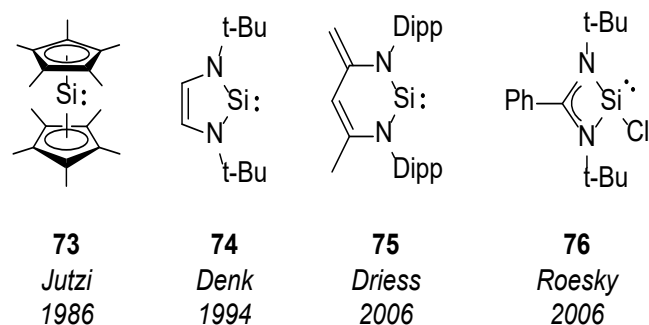
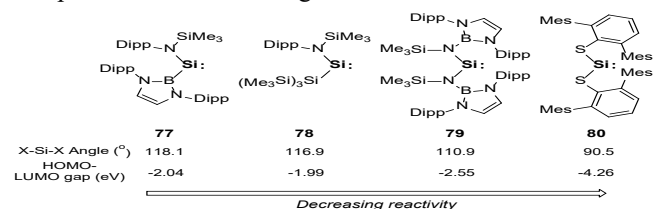


Figure 11. Selected examples of acyclic silylenes with key parameters.^[129-132]

One strategy for accessing reactive silylenes is the use of masked species. Inoue and co-workers reported the use of a silepin Si(IV) compound (**81**) which has a thermally accessible Si(II) silylene (**82**), due to the reversible insertion into the C=C bond of the supporting Dipp group of the N-heterocyclic imino (NHI) ligand (Scheme 15).^[133] Reactivity towards small molecules revealed the desired Si(II) reactivity, which is exemplified by the isolation of ‘Kipping’s dream’ a long sought after silanone (**83**) complex and heavier analogue of ketones.^[134]



Scheme 15. Reversible intramolecular C-C bond activation for masked silylenes and synthesis of a three coordinate silanones.^[133-134]

One of the most recent break throughs in silylene chemistry (and main group chemistry in general) is the isolation of silacarbonyl species. Previously on reaction of CO with group 14 tetrylenes reductive homologation reactions were observed.^[135] In contrast to the heavier elements, reaction of CO with carbenes result in the formation oxidation of the central C atom to yield ketenes (R₂C=C=O).^[136] This contrasts with transition metals, where TM complexes often form coordination compounds with the carbonyl in various bonding motifs (e.g., terminal, bridging and isocarbonyl). Commonly TM-CO complexes contain terminal CO bonds with σ-donation from CO lone pair to the empty orbital on the TM centre with concurrent π-backdonation from the filled d-orbital of the TM centre to the empty π*-orbital of CO (Figure 12a). In 2020, two different examples of a room temperature stable silicon carbonyl complex were reported (Figure 12b). These both utilised strong σ-donating and electropositive stabilising ligands [gallyl (**84**)^[137] and silyl (**85**)^[138]], which increases the electron density at the Si centre and induces π-backdonation from Si to CO. In a similar manner as witnessed in TM-CO complexes, σ-donation from the CO lone pair to the Si centre is also observed (Figure 12a).

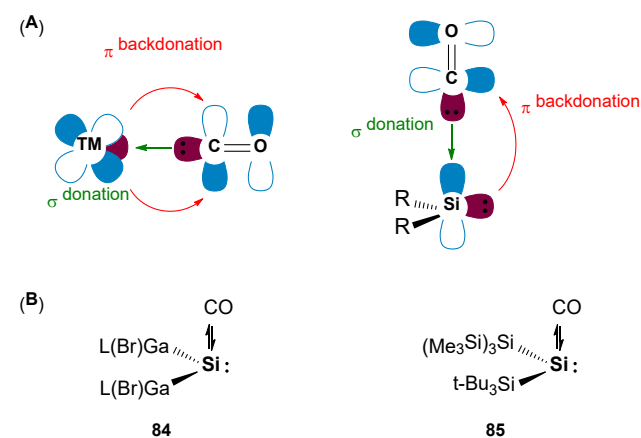
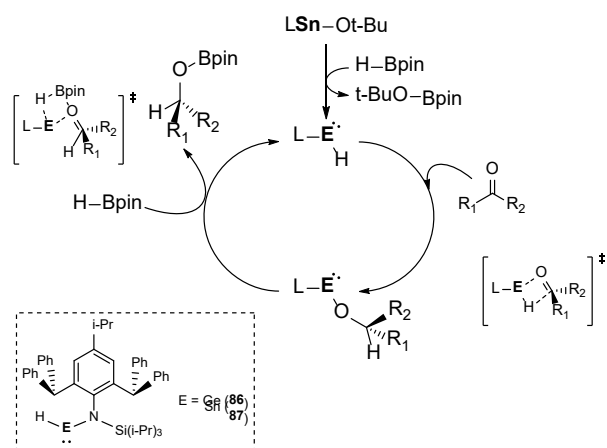


Figure 12. a) TM-CO and Si-CO frontier molecular orbital interactions; b) room temperature stable silicon carbonyl compounds (L = β-diketiminate).^[137-138]

Small molecule activation with tetrylenes is relatively well understood; however, the challenge of reductive elimination from the resulting stable E(IV) compound still presents a barrier towards achieving turnover and catalytic application.^[139-140] Jones and co-workers achieved catalytic turnover through a non-redox cycle, based on a series of insertion and σ -bond metathesis steps (Scheme 16).^[141] The active hydrido-germylene (**86**) and stannylene (**87**) (with the latter generated *in situ* from the corresponding alkoxy complex) enabled hydroboration of aldehydes and ketones with high turnovers and very low catalyst loadings.



Scheme 16. Proposed catalytic cycle for the hydroboration of carbonyl compounds by *in situ* generated E(II)-hydrides.^[142]

Whilst it is possible to circumvent traditional redox catalytic cycles, reversible bond activations highlight the feasibility of E(IV) to E(II) transformations without the need for reducing agents or forcing conditions. This has been achieved for tetrylenes with several different substrates including C=C,^[143-145] P-P,^[146] Si-H^[147] and P-H^[147] bonds. These transformations show the potential for non-transition metal redox catalysis.

5. P-BLOCK ANIONS

With most low valent species containing a lone pair and empty *p*-orbital they can be described as ambiphilic. To enhance the nucleophilic character this can be achieved by increasing the negative charge on the central element. In a similar manner to that employed in organic chemistry, where conjugate bases are stronger nucleophiles (e.g., HO⁻ vs. H₂O).

5.1 GROUP 13 COMPLEXES

Owing to their electron deficient nature, the chemistry of group 13 elements has largely been dictated by their Lewis acidic character. This is particularly the case for the lightest elements. Transition metal catalysed borylation of organic substrates has been widely studied,^[148-149] but it was not until 2006 that an isolable boryl species was achieved. Yamashita, Nozaki and co-workers reported the landmark lithium boryl complex **88** (Figure 13), which is stabilised through the electronegative nitrogen substituents within the *N*-heterocyclic ring and the electrostatic interaction of the boron lone pair with the lithium cation.^[150] In this instance, the boron centre in **88** was found to be in the singlet state

rather than its triplet configuration which was found to be 20 kcal mol⁻¹ higher in energy.^[151] The reactivity of **88** has been widely studied over the last decade, with several examples of bond activations of strong σ - and π -bonds reported.^[152] Additionally, the directional lone pair on the boron centre has enabled their use as ligands in coordination chemistry.^[153]

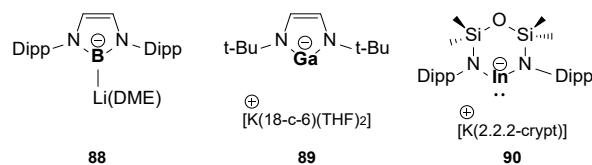
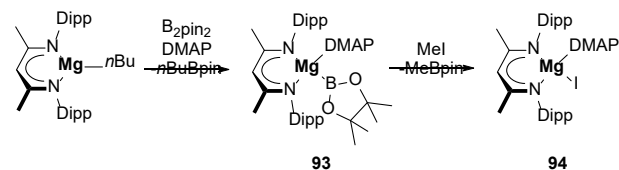


Figure 13. The first reported examples of boryl,¹⁵⁰ gallyl¹⁵⁴ and indyl¹⁵⁵ anions.

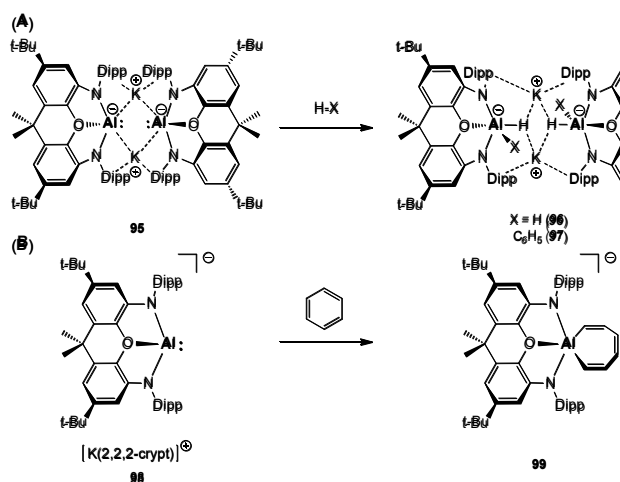
Whilst anionic boryl species have gathered notable attention in the last decades, it was the gallyl species that was first anionic group 13 complex. This was reported in 1999 and also incorporated the Ga anion into a *N*-heterocycle (**89**, Figure 13).^[154] Despite being around for longer, as well as several more examples, the small molecule reactivity is scarce.^[127, 155] Further descending down the group, the heaviest group 13 anion known is the recently reported indyl anion, this can be isolated as a separated ion pair (**90**) and as an indyllithium contact ion pair (**92**) analogous to the boryllithium species.^[156]

Compounds **88-90**, and their analogues, all require harsh reducing conditions to access the anionic species. This, therefore, impedes their use as viable synthons to the wider synthetic community. In 2017 Hill, McMullin and co-workers reported a facile route to nucleophilic boron through diboronate to magnesium boryl metathesis (**93**, Scheme 17).^[157] The nucleophilic character of boron was verified both experimentally [via reactions with methyl iodide (forming **94**), benzophenone and carbodiimides where B-C bond formations were observed] and computationally.



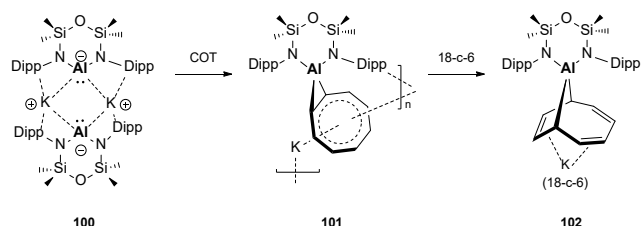
Scheme 17. Facile synthesis of a nucleophilic boron (**93**) and proof of nucleophilic character. DMAP = 4-dimethylaminopyridine.^[157]

Despite the established boryl and gallyl chemistry, aluminyls were first discovered in 2018.^[158] The anionic Al(I) species (**95**) was stabilised by a xanthene-based diamido ligand and, importantly, through potassium π -arene interactions which stabilise the dimeric structure in both the solution and solid state. Whilst the initial report proved the unprecedented nucleophilic behaviour of aluminyls, notably through the observed dihydrogen activation (**96**), C-H activation of C₆H₆ (**97**, Scheme 18a) and aluminium-element bond forming reactions.^[158] A subsequent report further enhanced the nucleophilic power through sequestration of the potassium counterion (**98**), using a crown ether, which resulted in the more challenging C-C bond cleavage of C₆H₆ (**99**, Scheme 18b).^[159]



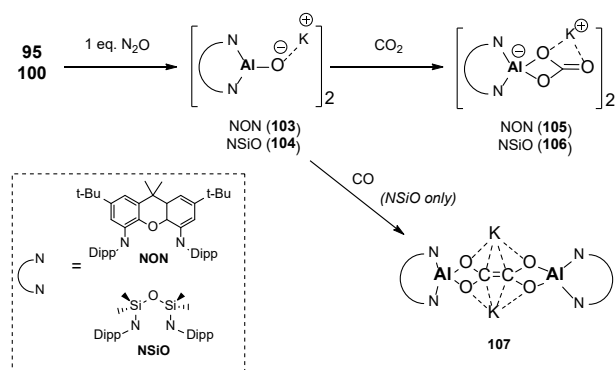
Scheme 18. a) H-X activation of hydrogen and benzene by aluminylium dimer **95**.^[158] b) C-C activation of benzene by monomeric aluminylium **98**.^[159]

The second example of an aluminylium (**100**) was reported by Coles and co-workers, again the dimeric species is held together by a potassium counterion. This showed the potential of Al(I) anions to be used as reducing agents as it was capable of a 2 electron reduction of 1,3,5,7-cyclooctatetraene (COT) (**101**, Scheme 19).^[160] Addition of 18-crown-6 to the reaction mixture breaks the polymeric structure and leads to a formal [1+4]-cycloaddition product (**102**).



Scheme 19. Aluminylium (**100**) reduction of COT.^[160]

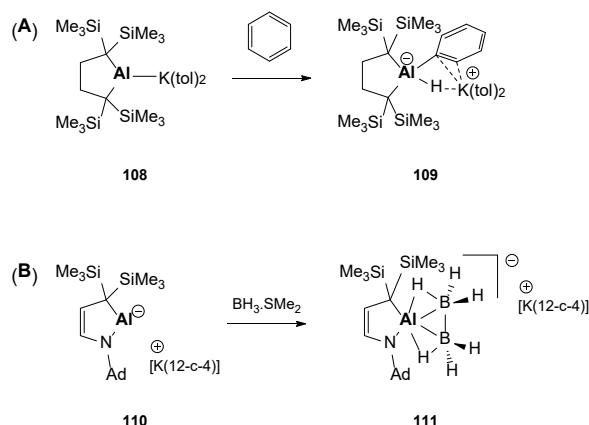
The reactivity of **95** and **100** towards small molecules is similar, both react with CO₂ to form carbonate species (**105** and **106**, respectively) with loss of CO. Both of these proceed via an aluminium-oxide ion (**103**, **104** Scheme 20), which was isolated in both cases through reaction with N₂O.^[83-84] The oxide ion (**104**) was further used to yield the unprecedented ethenetetraolate ligand (**107**), through the reductive homology of CO.^[161]



Scheme 20. Small molecule reactivity of aluminylium anions.^[83-84, 161]

Both **95** and **100** have utilised bidentate diamido ligands to enable the isolation of Al(I) anions, Yamashita and co-workers reported the first alkyl stabilised aluminylium (**108**).^[162] Rather than a dimeric unit held together by potassium- π -arene interactions, **108** is a monomeric species with a two centre-two electron Al-K bond. Compound **108** has shown to have enhanced basicity compared to **95** and **100** owing to its narrower HOMO-LUMO gap, and as such C-H activation of C₆H₆ is observed at room temperature within a few hours (Compound **109**, Scheme 21a).^[162] Both **95** and **108** have also reported *meta*-selective C-H aluminium of mono-substituted arenes owing to the high reactivity of these systems.^[163-164]

A second alkyl stabilised aluminylium (**110**) was reported by Kinjo and co-workers, which was isolated as a 'naked' aluminylium ion as the potassium counterion is sequestered.^[165] The reactivity of **110** towards BH₃·SMe₂ resulted in a unique AlB₂ ring (**111**, Scheme 21b) through B-B coupling reactions, in addition **110** showed it was capable of bond cleavage reactions to both polar and non-polar bonds through oxidative addition to the Al(I) centre.^[165]

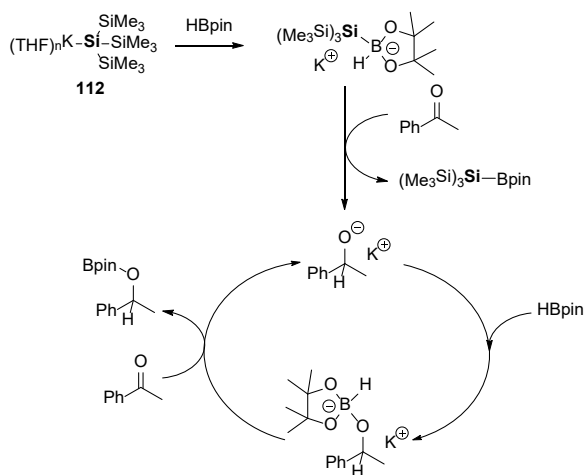


Scheme 21. Reactivity of alkyl aluminylium: a) deprotonation of benzene;^[162] b) B-B forming reaction with BH₃·SMe₂.^[165]

5.2 GROUP 14 COMPLEXES

Amongst the group 14 anions, carbanions are the most widely studied. The trivalent *sp*³ hybridised carbon centre, with its negative charge, is highly reactive towards a range of electrophiles. Electron withdrawing groups are often used to stabilise the negative charge through inductive effects but are more commonly found stabilised by electropositive atoms (*i.e.*, alkali or alkaline earth metals) either as contact ion pairs or solvent separated ion pairs. As synthetic reagents carbanions are found in the form of organolithiums or Grignard reagents in the condensed phase. Whilst not strictly pure carbanions, the highly polarised M^{δ+}-C^{δ-} bond makes them versatile reagents for nucleophilic additions and deprotonation reactions. Alternative reagents, based on mixed metal systems, have found themselves to be stronger metalation reagents with increased selectivity and higher functional group tolerance compared to organolithium reagents. These include Schlosser's base, turbo-Grignards and alkali-metal mediated metalations where the non-alkali metal can be readily exchanged to form bespoke dianionic-dicationic structures for regioselective metalations.^[16, 166-167]

Heavier analogues are also often found with an alkali metal counterpart. They are prepared by reaction of silyl chlorides and lithium metal or through cleavage of Si-Si bonds with lithium reagents.^[168] Silyl anions have largely been utilised in synthesis, providing access to cyclic oligomers or disilenes.^[169] Their use in small molecule activation is currently not developed but a recent example from Cowley and co-workers showcased the ability of a silyl anion (**112**) to mimic transition metals in catalytic transformation of carbonyls.^[170] Typically, hydroboration of carbonyls proceeds *via* metal-hydride species however in this case the silyl anion is devoid of a silyl-hydride. This reaction is therefore a base promoted mechanism, owing to the increased nucleophilic silicon centre, which coordinates to the pinacolborane to form the active borohydride species (Scheme 22).



Scheme 22. Proposed mechanism for the silyl anion initiated hydroboration of carbonyls.^[170]

Alternative methods for the stabilisation of heavier anions has involved incorporation of the heavier group 14 element into a phenyl ring, to yield heavy analogues of the phenyl anion. This has recently been achieved for both the germanium (**113**)^[171-172] and tin (**114**)^[173] analogues (Figure 14). In the germanium case, this shows considerable aromatic character (A) with a contribution from the tetrylene (B) form.^[171] When moving to tin (**114**) the contribution of the resonance forms change depending on the solvation of the potassium counterion. In the solvate free complex (**114-K**) there is a larger contribution of the stannylene form (B) whereas **114-K(THF)** has a larger contribution of the stannabenzene anion.^[173] Currently the reactivity of these species is limited but **113** has shown interesting coupling chemistry on reaction with $\text{Me}_2(\text{t-Bu})\text{SiCl}$ resulting in the trimerization of the germabenzene skeleton.^[174]

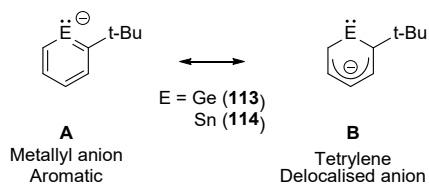
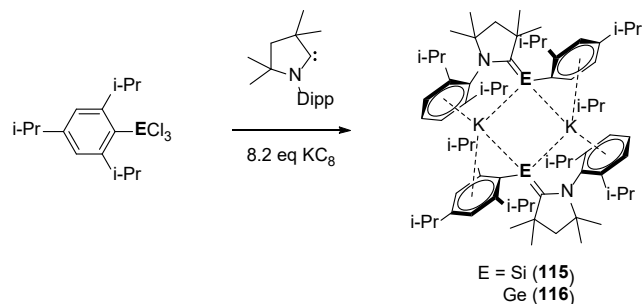


Figure 14. Resonance structures of heavier phenyl anions.^[171, 173]

Currently reports of small molecule of activation with group 14 anions are scarce, however a new class of compounds look set to provide some unique bond activations. Valence-isoelectronic to phosphinidenes (R-P species), silanylidene and germanyldiene compounds are a new class of acyclic group 14 anions ($[\text{R-E}]^-$ where $\text{E} = \text{Si}$ (**115**), Ge (**116**)).^[175] Compounds **115** and **116** are synthesised through reduction of the metal halide complex in the presence of a cAAC ligand (Scheme 23). Single crystal X-Ray diffraction studies revealed a dimeric structure which is held together by potassium π -arene interactions in a similar fashion to those seen with group 13 aluminums.



Scheme 23. Synthesis of silanylidene and germanyldiene anions.^[175]

6. P-BLOCK CATIONS

Opposite to anions with their enhanced nucleophilic character, cations are positively charged species with increased electrophilicity compared to their neutral counterparts. In 1994 Olah won the Nobel Prize for his seminal work on carbocations.^[176] The citation '*Carbocations: from hypothetical intermediate products to well defined molecules*' broadly applies to the current state of affairs in the rest of the *p*-block elements. In many cases, particularly of the heavier elements, cations are still considered hypothetical but in the case of boron or silicon the cation chemistry is relatively well defined and understood. This section will cover the advances in *p*-block cation chemistry towards small molecule activation.

6.1 GROUP 13 COMPLEXES

Group 13 elements, of the type R_3E , are stable high oxidation state compounds which are isoelectronic to carbocations (Figure 15). Removal of one substituent creates a cationic species (Type A, Figure 15) and satisfies the low valent criteria due to the sub-coordinate nature. As expected R_2E^+ species are highly reactive and often found in combination with Lewis bases to aid stability. Due to the already present vacant orbital, removal of R_2E species contain two vacant orbitals and as such can be stabilised by either one or two Lewis bases (Type B and C, respectively). In these complexes choice of Lewis base is key, as short-range coulombic interactions can lead to electron precise bonds and thus quenching the desired cationic reactivity. Weakly coordinating anions (WCAs) (*e.g.*, carboranes) provide long-range electrostatic interactions and maintenance of the vacant coordination site, and therefore have found use in stabilisation of cationic species.

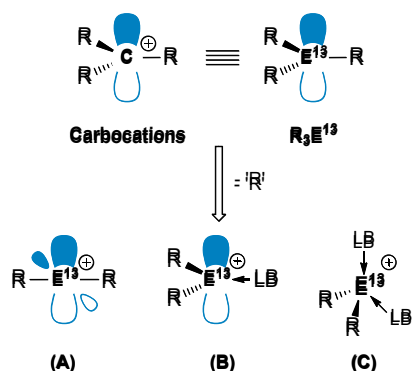
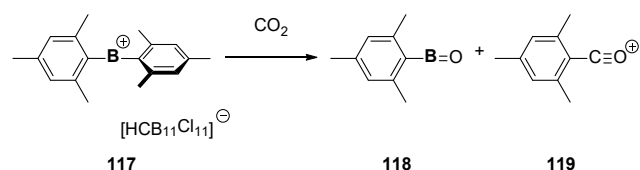


Figure 15. Isoelectronic nature of carbocations and R_3E^{13} . (A) Two-coordinate E^{13} cation; three- (B) and four- (C) coordinate Lewis base stabilised E^{13} cations.

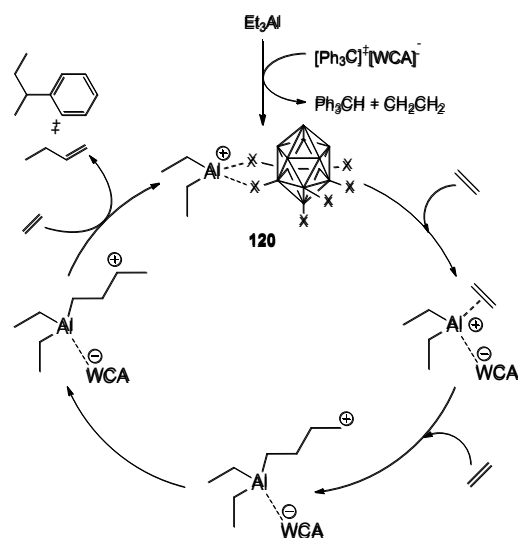
Boron is the most widely studied of the group 13 cations with borinium, borenium, and boronium the nomenclature for the two-, three- and four-coordinate boron cations as drawn in Figure 15, respectively. A seminal study by Shoji and co-workers in 2014 reported a cationic dimesityl boron complex (**117**), with a near linear C-B-C coordination.^[177] This two-coordinate borinium cation is stabilised by p_π – interactions between the mesityl group and the boron centre, with no interactions found between the boron centre and the carborane counterion. Additionally, inspection of the molecular orbitals by DFT studies further supported the borinium nature as the LUMO and LUMO+1 was found to consist of the vacant $2p$ orbitals of boron. Compound **117** was found to exhibit unprecedented Lewis acid behaviour, as on reaction with CO_2 cleavage of the C-O bond was observed to yield compounds **118** and **119** in an arylation-deoxygenation reaction (Scheme 24).^[177]

Several other examples of boron cations exist and have been used in many small molecule activation reactions as well as catalytic application, as such this is beyond the scope of this book chapter as they have also been widely reviewed.^[178-181]



Scheme 24. Arylation-deoxygenation of CO_2 with borinium cation (**117**).^[177]

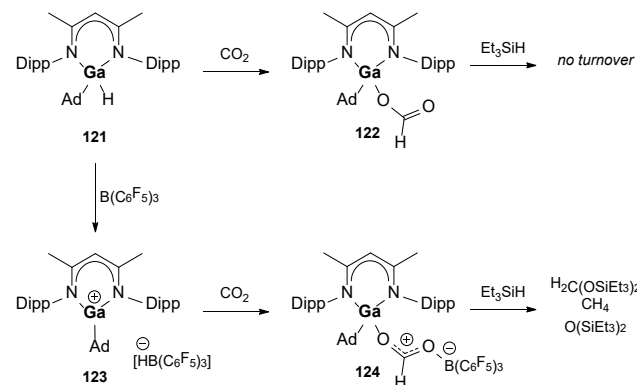
Two-coordinate aluminium ions, namely alumenium, have been used in small molecule catalysis. Reed and Sen reported the use of Et_2Al^+ (**120**), stabilised by carborane anions ($[CB_{11}H_6X_6]$ X= Cl or Br), in ethylene oligomerisation catalysis.^[182] Whilst butene was the major product, alkylated benzene derivatives were also observed due to the use of benzene as the reaction solvent (Scheme 25). Et_2Al^+ has also been used in polymerisation of cyclohexane oxide^[182] and the alkylative defluorination of fluorocarbons.^[183]



Scheme 25. Proposed catalytic cycle for ethylene oligomerisation mediated by an alumenium ion. $WCA = [CB_{11}H_6X_6]$ X= Cl or Br.^[182]

Wehmschulte and co-workers reported the use of Et_2Al^+ in the catalytic hydrosilylation of CO_2 .^[184-185] It was shown that the choice of carborane anion had a strong influence on the activity and selectivity of the catalysis. Due to the small alkyl substituents on the Al centre there is considerable anion-cation interactions with the halocarboranes. Comparison of $[CH_6B_{11}I_6]$ and the less basic $[CHB_{11}Cl_{11}]$, anions found that the chlorine containing carborane resulted in an order of magnitude higher catalytic activity in contrast to the iodo-analogue. Additionally it was shown that the gallium analogue was also much lower in activity due to the decrease in Lewis acidity on descending the group.^[185]

This decrease in Lewis acidity can also be seen in the recent report by Aldridge and co-workers.^[186] Use of a β -diketiminate stabilised gallium hydride (**121**) was found to react with CO_2 to form the formate species **122**, however regeneration of the gallium hydride species (**121**) could not be observed on addition of Et_3SiH (Scheme 26). Use of a borane co-catalyst $[B(C_6F_5)_3]$ enables efficient turnover due to the formation of a three-coordinate gallium cation (**123**). The enhanced reactivity observed with the cationic species allows for reduction of CO_2 to $H_2C(OSiEt_3)_2$, CH_4 and $O(SiEt_3)_2$ under mild conditions ($60^\circ C$) (Scheme 26).^[186]



Scheme 26. Neutral vs. cationic reactivity of gallium towards hydrosilylation of CO_2 . Ad = 1-adamantane.^[186]

Recent efforts in the main group community have focussed on mimicking transition metal chemistry. In this

regard transition metal olefin compounds are widely established and have key roles in multiple transformations due to accessible M^n and M^{n+2} oxidation states. Whilst reactions of main group metal centres and olefins have been reported, a homoleptic olefin complex was only very recently isolated. Crossing and co-workers successfully isolated $[Ga(COD)_2]^+$ complex in high yields.^[187] The cationic Ga^+ is coordinated to four double bonds of the two COD ligands in a *pseudo*-tetrahedral arrangement. Theoretical studies showed there is no back-bonding to the COD ligands, implying a dominant electrostatic interaction of Ga^+ and COD. Future reactivity is anticipated as $Ga(I)$ cations have previously shown themselves to be efficient π -acid catalysis.^[188]

6.2 GROUP 14 COMPLEXES

As the lightest group 14 element, carbon, its cations can be classified into two main groups: Carbenium ions $[R_3C^+]$ and carbonium ions $[R_5C^+]$, with the former being widely studied as reactive intermediates.^[189-190] Heavier analogues of carbenium ions are called tetrylium ions and are highly reactive species owing to the inherent differences between the heavier and lighter elements within the same group. To compare R_3C^+ vs R_3Si^+ , silicon is more electropositive with a larger covalent radius which makes it more polarisable. Whilst R_3Si^+ is thermodynamically favoured and easier to generate in the gas phase compared to R_3C^+ , its highly electrophilic nature makes it more challenging to isolate in the condensed phase as it strongly interacts with both σ - or π -donors. As such, the first 'true' silylium ion (**125**, Figure 16)^[191] was isolated over a 100 years after the first carbenium ion. Further examples of silylium ions have subsequently been reported, they can be classified into the following groups: A – free ions, B – intramolecular stabilised ions and C – intermolecular stabilised ions (Figure 16). Class A type (**125-127**)^[191-193] are often referred to as 'true' tetrylium ions and require sterically demanding ligands to prevent solvent and counterion interactions. Class B type (**128-130**)^[194-196] are also 'free' ions but are stabilised by either σ - or π -intramolecular interactions. Additionally, the unique α -ferrocenyl substituted silylium ion (**130**) is intramolecularly stabilised due to two three-centre-two-electron ($3c2e$) bonds across the C_{ipso}^{Cp} , Si and Fe centres.^[196] Finally, Class C type (**131-133**)^[197-199] are arguably the most common type of tetrylium ions and are stabilised by σ - or π -intermolecular interactions often with solvent molecules or in some cases transition metal complexes.

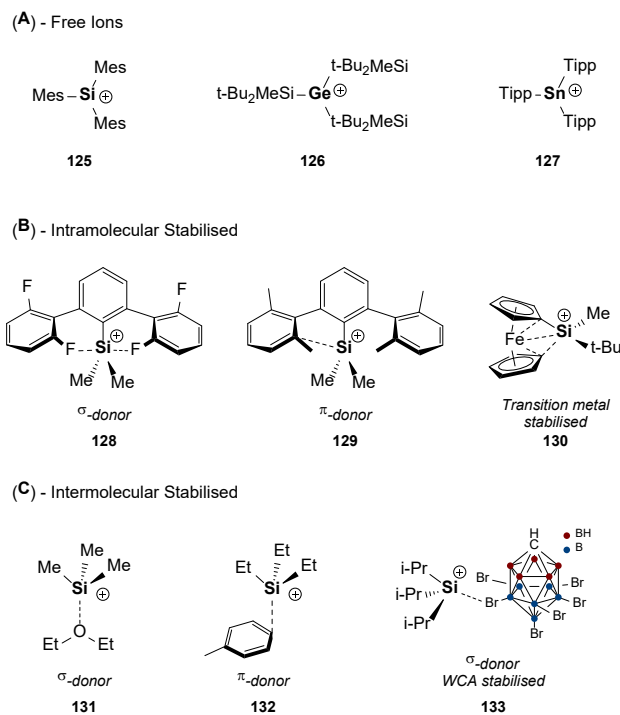
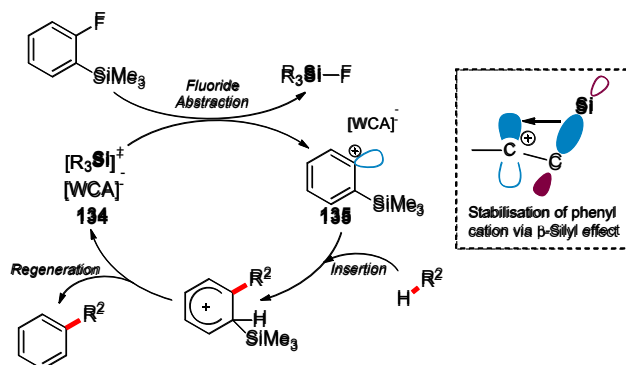


Figure 16. Examples of different stabilisation methods for tetrylium ions. Anions omitted for clarity.^[191-199]

Owing to their high Lewis acidity, silylium ions have been shown to be efficient catalysts in a range of transformations such as cycloaddition reactions, hydrosilylation of $C=X$ bonds, and hydrodefluorination of $C-F$ bonds.^[200-202] A notable example of $C-C$ bond forming reactions, contains both silylium and phenyl cations as key intermediates in the catalytic cycle. Fluoroarenes with β -silyl groups undergo fluoride abstraction reactions with silylium ions ($[Me_3Si^+]$, **134**, Scheme 27). This generates a phenyl cation (**135**) which is additionally stabilised by the β -silyl group. **135** undergoes $C-H$ insertion reactions with both sp^3 and sp^2 $C-H$ bonds to yield new $C-C$ coupled products and regeneration of the active silylium ion (Scheme 27).^[203] Heavier analogues have also been reported in catalysis, with gerylium ions been shown to be effective in dehydrofluorination of alkanes^[204] and stannylum ions showing versatile hydrogenation catalysis towards imines, aldehydes, and ketones.^[205]



Scheme 27. Arylation of hydrocarbons mediated by silylium ions. $WCA = [HCB_{11}Cl_{11}]^-$ ^[203]

Further amplification of the cationic reactivity of group 14 compounds can be achieved through use of

tetryliumylidenes. This class of compounds combines the reactive aspects of both tetrylium ions and tetrylenes (Figure 17). As such, tetryliumylidenes are highly reactive species which again require careful ligand design (kinetic and thermodynamic stabilisation), non-coordinating anions and non-coordinating solvents.

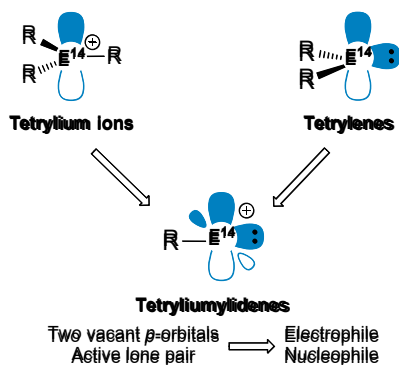


Figure 17. Key electronic features of tetryliumylidenes.

Of the tetrel elements, silyliumylidenes are the most widely studied with advances in this area only achieved in the last 15 years (Figure 18a). Jutzi reported the first Si(II) cation (**136**) in 2004,^[206] this was stabilised by a η^5 -Cp* ligand and therefore not strictly mono-coordinate. However, the hyper-coordinate complex can be regarded as the ‘resting state’ of the mono-coordinate Si(II) centre as the reactivity of **136** is in line with the silyliumylidene character. The first two-coordinate silyliumylidene (**137**)^[207] was formed by protonation of the ligand backbone of the corresponding zwitterionic silylene and remains one of the few examples of two-coordinate species to date.^[208-209]

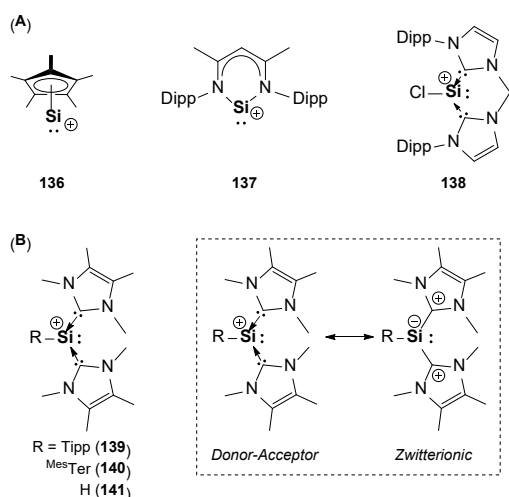
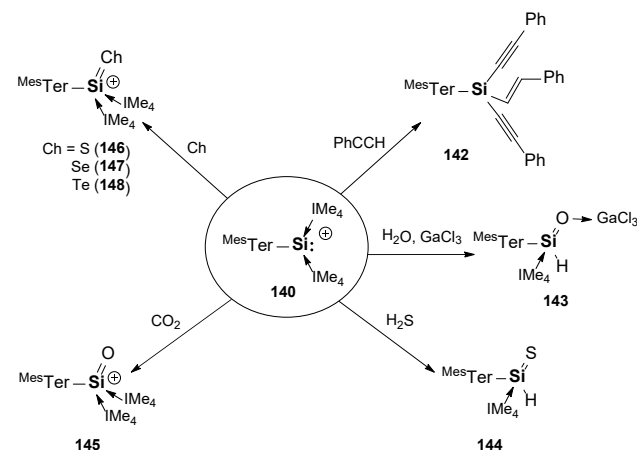


Figure 18. (A) – Notable milestones in silyliumylidene cations.^[206-207, 210] (B) – NHC stabilised silyliumylidenes and their different resonance forms.^[211-212] Anions omitted for clarity.

The vast majority of silyliumylidenes (and tetryliumylidenes) reported to date are three-coordinate complexes, which are often isolated in combination with NHC donor ligands to partially occupy the vacant *p*-orbitals and provide additional stability. The use of NHCs in combination with tetryliumylidenes influences the positive charge and thus an alternate zwitterionic resonance form can

be drawn (Figure 18b). The first use of NHC to stabilise a chloro-silyliumylidene (**138**)^[210] was reported by Driess in 2013, where a chelating bis-NHC ligand was utilised. One of the initial drawbacks in this field was the challenging synthesis required to obtain the desired complexes, however it was shown that use of a small excess of NHC ligand (3 equivalents) with substituted Si(IV)hydrochlorides results in facile synthesis of silyliumylidenes via a dehydrochlorination process. This was utilised to provide access to aryl substituted complexes **139** and **140**.^[211] Finally, a notable achievement in this field was the reported isolation of the parent silyliumylidene ($[H-Si:]^+$ **141**).^[212] This highly reactive species has subsequently been shown to be active in a range of catalytic transformations including the hydroboration of carbonyls (aldehydes, ketones, and CO₂) and pyridines.^[213]

In terms of small molecule activation, Inoue and co-workers have employed their silyliumylidenes (**139** and **140**) in a variety of transformations (Scheme 28). This includes C-H activation of terminal alkynes (**142**),^[211] and the formation of heavy analogues of aldehydes (**143**)^[214] and thioaldehydes (**144**).^[215] Owing to the high polarity of Si-O bonds, additional Lewis acid stabilisation (GaCl₃) is required to prevent oligomerisation and therefore allow for isolation of a discrete SiO unit. Reaction of **140** and CO₂ resulted in decarbonylation of CO₂ to yield a heavier sila-acylium ion (**145**).^[216] The same compound could also be obtained on reaction with N₂O with elimination of N₂.

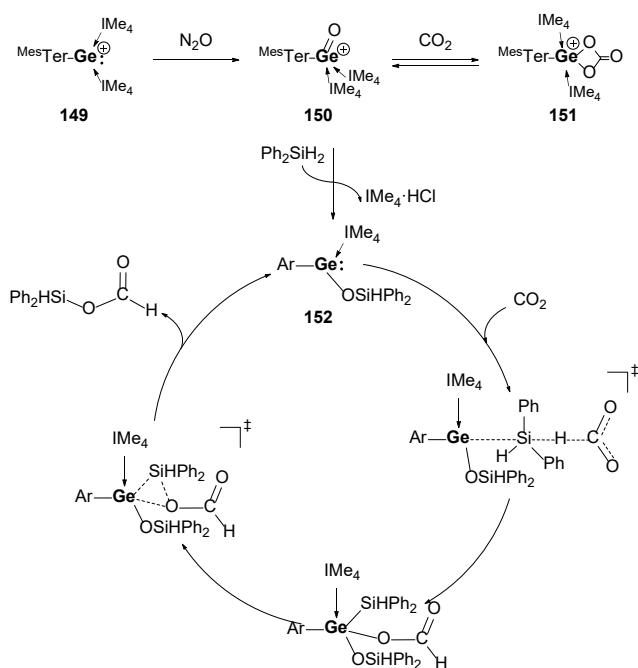


Scheme 28. Small molecule activation by NHC-stabilised silyliumylidenes.^[211, 214-217]

Heavier sila-acylium ions could also be obtained on reaction with elemental chalcogens (**146-148**, Scheme 28). Notably regeneration of **140** could be achieved on reaction of **146-148** with AuI, which is a rare example of facile reductive elimination from Si(IV) to Si(II).^[217] Germyliumylidenes, stannylumylidenes and plumblyliumylidenes have all been reported,^[218] although they are much less studied in comparison to silyliumylidenes. Limited examples of germyliumylidenes in small molecule activation have been reported,^[219-221] and recently they have been used in the catalytic hydroboration of carbonyls.^[222-223]

A notable breakthrough in this field, combines many of the areas discussed in this chapter. An NHC-stabilised

germyliumylidene (**149**) was reacted with N₂O to yield a heavier analogue of an acylium ion (**150**) (Scheme 29).^[224] The Ge-O bond in **150** was found to be in the range of other Ge-O donor-acceptor stabilised double bonds but also contained a strong influence of the zwitterionic resonance form (*i.e.* single bond). **150** was found to react reversibly with CO₂ to form carbonate species **151**, drawing comparisons to transition metal oxides. This reversibility, and thus relative ease in which the Ge(II)/Ge(IV) redox couple could be accessed, prompted an attempt at the catalytic reduction with diphenylsilane. This was found to be successful and reduction to formic acid equivalents was observed. Mechanistic investigations found that this reaction initially proceeds via the formation of a siloxygermylene species (**152**) which is the active catalyst in this system. DFT studies further supported the mechanism in which it is proposed that the germylene lone pair coordinates to the silane to create a hypervalent silane which facilitates the CO₂ reduction (Scheme 29). Additional reactivity of **150** was shown to facilitate the N-formylation of amines further drawing comparisons to transition metal oxide chemistry. Furthermore, classical acylium ion like reactivity was observed as **150** provided access to heavier novel germanium analogues of carbonyls and heavier chalcogen derivatives, such as the first example of a germanium ester. This highlights the diverse electronic features of **150** with its comparison to classical organic and transition metal chemistry.^[224]



Scheme 29. Synthesis of a germaacylium ion (**150**) and its reversible reactivity with CO₂ as well as its utility in the catalytic reduction of CO₂ via a germylene (**152**) catalyst.^[224]

7. SUMMARY AND OUTLOOK

With global efforts focussing on new methodologies and processes to enable a more sustainable future, main group elements present themselves as ideal candidates for a future green economy. In this regard, small molecule activation

has been at the forefront in the renaissance of main group chemistry. Activation of dihydrogen by a main group multiple bond led to the first comparisons to transition metals, owing to their similarly accessible frontier molecular orbitals. Since this seminal discovery, advances in main group chemistry have led to an increased understanding of chemical bonding and the different tricks required to stabilise reactive low-valent centres. These developments in ligand design have also allowed for fine tuning of the reactivity. For example, the varying steric demands of ligands in group 14 tetrelenes has been shown to influence their reactivity towards dihydrogen, with the resulting narrow R-E-R angles unreactive.

In the last 10 or so years, the diverse chemistry of the main group elements has prevailed. From multiple bonds, to anions, cations and neutral complexes several ground-breaking discovery's have been made. New complexes have been discovered (*e.g.* aluminyls) and new reactivity has also been achieved (*e.g.* nitrogen fixation). Moving forward it is anticipated that main group chemistry will continue to flourish. Many more examples of low-oxidation state *s*-block complexes are expected, particularly with the heavier group 2 elements. Main group multiple bonds have started to emerge as viable catalysts, with the additionally stability to the active catalyst provided by the combination of two metal centres. Neutral low valent species have shown themselves to be a powerful tool in the main group chemists toolkit. Many examples of strong bond activations have now been reported and their transition metal like behaviour is well established. Challenges in this field still arise with reductive elimination to revert to the low-valent metal centre once the small molecule has been activated. In order to truly surpass transition metals and their use in catalysis, facile reductive elimination will be required to enable high turnovers. Further advances in main group chemistry have centred on enhancing the nucleophilic (anionic) or electrophilic (cationic) character of the *p*-block element. This has enabled many unique transformations and will pave the way for diverse application of the main group elements.

8. REFERENCES

- [1] IPCC, *Climate Change 2007: Synthesis Report* Geneva, **2007**.
- [2] IPCC, *Special Report on Carbon Dioxide Capture and Storage*, Cambridge University Press, Cambridge, UK, **2005**.
- [3] S. D. Allen, C. M. Byrne, G. W. Coates, in *Feedstocks for the Future*, Vol. 921, American Chemical Society, **2006**, pp. 116-129.
- [4] *Catalytic Ammonia Synthesis—Fundamentals and Practice*, Springer Science + Business Media, New York, **1991**.
- [5] R. Schlög, in *Handbook of Homogeneous Catalysis*, (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley, **2008**.
- [6] W. Schipper, *The Elemental Phosphorus Market in 2014 - Applications and Technology*, CRU Group, Paris, **2014**.
- [7] H. Diskowski, T. Hofmann, *Phosphorus*, Wiley, **2000**.

- [8] *Activation of Small Molecules: Organometallic and Bioinorganic Perspectives*, Wiley, **2006**.
- [9] *CRC Handbook of Chemistry and Physics*, 87 ed., Taylor and Francis, Boca Raton, FL, **2007**.
- [10] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754-1757.
- [11] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124-1126.
- [12] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2009**, *49*, 46-76.
- [13] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441.
- [14] M. S. Hill, D. J. Liprot, C. Weetman, *Chem. Soc. Rev.* **2016**, *45*, 972-988.
- [15] M. D. Anker, M. S. Hill, *Encyclopedia of Inorganic and Bioinorganic Chemistry* **2017**, 1-23.
- [16] S. D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* **2019**.
- [17] M. Arrowsmith, H. Braunschweig, M. A. Celik, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, T. Kramer, I. Krummenacher, J. Mies, K. Radacki, J. K. Schuster, *Nat. Chem.* **2016**, *8*, 890.
- [18] G. Wang, J. E. Walley, D. A. Dickie, S. Pan, G. Frenking, R. J. Gilliard, *J. Am. Chem. Soc.* **2020**, *142*, 4560-4564.
- [19] S. Kriech, H. Görls, L. Yu, M. Reiher, M. Westerhausen, *J. Am. Chem. Soc.* **2009**, *131*, 2977-2985.
- [20] G. Wang, L. A. Freeman, D. A. Dickie, R. Mokrai, Z. Benkő, R. J. Gilliard Jr, *Chem. Eur. J.* **2019**, *25*, 4335-4339.
- [21] A. Stasch, C. Jones, *Dalton Trans.* **2011**, *40*, 5659-5672.
- [22] C. Jones, *Nat. Rev. Chem.* **2017**, *1*, 0059.
- [23] R. Lalrempuia, A. Stasch, C. Jones, *Chem. Sci.* **2013**, *4*, 4383-4388.
- [24] C. E. Kefalidis, A. Stasch, C. Jones, L. Maron, *Chem. Commun.* **2014**, *50*, 12318-12321.
- [25] A. J. Boutland, I. Pernik, A. Stasch, C. Jones, *Chem. Eur. J.* **2015**, *21*, 15749-15758.
- [26] C. E. Kefalidis, C. Jones, L. Maron, *Dalton Trans.* **2016**, *45*, 14789-14800.
- [27] M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Köhn, D. J. Liprot, M. F. Mahon, C. Weetman, *Chem. Sci.* **2014**, *5*, 2826-2830.
- [28] R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch, C. Jones, *J. Am. Chem. Soc.* **2015**, *137*, 8944-8947.
- [29] K. Yuvaraj, I. Douair, A. Paparo, L. Maron, C. Jones, *J. Am. Chem. Soc.* **2019**, *141*, 8764-8768.
- [30] K. Yuvaraj, I. Douair, D. D. L. Jones, L. Maron, C. Jones, *Chem. Sci.* **2020**, *11*, 3516-3522.
- [31] A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinioi, L. Maron, *Science* **2017**, *358*, 1168.
- [32] G. H. Spikes, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232-12233.
- [33] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.
- [34] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587-4589.
- [35] A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc., Chem. Commun.* **1981**, 191-192.
- [36] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1981**, *36*, 16-19.
- [37] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463-3504.
- [38] R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877-3923.
- [39] P. Bag, A. Porzelt, P. J. Altmann, S. Inoue, *J. Am. Chem. Soc.* **2017**, *139*, 14384-14387.
- [40] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420-1422.
- [41] E. A. Carter, W. A. Goddard, *J. Phys. Chem.* **1986**, *90*, 998-1001.
- [42] G. Trinquier, J. P. Malrieu, P. Riviere, *J. Am. Chem. Soc.* **1982**, *104*, 4529-4533.
- [43] G. Trinquier, J. P. Malrieu, *J. Am. Chem. Soc.* **1987**, *109*, 5303-5315.
- [44] J. P. Malrieu, G. Trinquier, *J. Am. Chem. Soc.* **1989**, *111*, 5916-5921.
- [45] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667-2679.
- [46] Z. Zhu, R. C. Fischer, B. D. Ellis, E. Rivard, W. A. Merrill, M. M. Olmstead, P. P. Power, J. D. Guo, S. Nagase, L. Pu, *Chem. Eur. J.* **2009**, *15*, 5263-5272.
- [47] R. J. Wright, A. D. Phillips, S. Hino, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 4794-4799.
- [48] E. Rivard, P. P. Power, *Inorg. Chem.* **2007**, *46*, 10047-10064.
- [49] P. P. Power, *Organometallics* **2007**, *26*, 4362-4372.
- [50] C. Weetman, *Chem. Eur. J.* **2020**, *n/a*.
- [51] M. Arrowsmith, H. Braunschweig, T. E. Stennett, *Angew. Chem. Int. Ed.* **2017**, *56*, 96-115.
- [52] P. Bag, C. Weetman, S. Inoue, *Angew. Chem. Int. Ed.* **2018**, *57*, 14394-14413.
- [53] C. Präsang, D. Scheschkewitz, *Chem. Soc. Rev.* **2016**, *45*, 900-921.
- [54] A. Rammo, D. Scheschkewitz, *Chem. Eur. J.* **2018**, *24*, 6866-6885.
- [55] H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan, A. Vargas, *Nat. Chem.* **2013**, *5*, 1025.
- [56] M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, T. Dellermann, K. Hammond, *Chem. Eur. J.* **2016**, *22*, 17169-17172.
- [57] J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, J. Mies, *Angew. Chem. Int. Ed.* **2015**, *54*, 13801-13805.
- [58] A. Stoy, J. Böhnke, J. O. C. Jiménez-Halla, R. D. Dewhurst, T. Thiess, H. Braunschweig, *Angew. Chem. Int. Ed.* **2018**, *57*, 5947-5951.
- [59] C. Weetman, P. Bag, T. Silvási, C. Jandl, S. Inoue, *Angew. Chem. Int. Ed.* **2019**, *58*, 10961-10968.
- [60] C. Weetman, A. Porzelt, P. Bag, F. Hanusch, S. Inoue, *Chem. Sci.* **2020**, *11*, 4817-4827.
- [61] N. J. Hardman, R. L. Wright, A. D. Phillips, P. P. Power, *Angew. Chem. Int. Ed.* **2002**, *41*, 2842-2844.
- [62] R. J. Wright, A. D. Phillips, N. J. Hardman, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 8538-8539.
- [63] Z. Zhu, X. Wang, Y. Peng, H. Lei, J. C. Fettinger, E. Rivard, P. P. Power, *Angew. Chem. Int. Ed.* **2009**, *48*, 2031-2034.
- [64] C. A. Caputo, J.-D. Guo, S. Nagase, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 7155-7164.
- [65] C. A. Caputo, P. P. Power, *Organometallics* **2013**, *32*, 2278-2286.
- [66] C. A. Caputo, J. Koivistoinen, J. Moilanen, J. N. Boynton, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2013**, *135*, 1952-1960.
- [67] D. Wendel, T. Szilvási, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 9156-9159.
- [68] D. Wendel, T. Szilvási, D. Henschel, P. J. Altmann, C. Jandl, S. Inoue, B. Rieger, *Angew. Chem. Int. Ed.* **2018**, *57*, 14575-14579.

- [69] D. Reiter, R. Holzner, A. Porzelt, P. J. Altmann, P. Frisch, S. Inoue, *J. Am. Chem. Soc.* **2019**, *141*, 13536-13546.
- [70] M. W. Stanford, J. I. Schweizer, M. Menche, G. S. Nichol, M. C. Holthausen, M. J. Cowley, *Angew. Chem. Int. Ed.* **2019**, *58*, 1329-1333.
- [71] T. Sugahara, J. D. Guo, T. Sasamori, S. Nagase, N. Tokitoh, *Angew. Chem. Int. Ed.* **2018**, *57*, 3499-3503.
- [72] P. P. Power, *J. Chem. Soc., Dalton Trans.* **1998**, 2939-2951.
- [73] P. P. Power, *Chem. Commun.* **2003**, 2091-2101.
- [74] S. Wang, T. J. Sherbow, L. A. Berben, P. P. Power, *J. Am. Chem. Soc.* **2018**, *140*, 590-593.
- [75] T. Y. Lai, L. Tao, R. D. Britt, P. P. Power, *J. Am. Chem. Soc.* **2019**, *141*, 12527-12530.
- [76] E. M. Leitao, T. Jurca, I. Manners, *Nat. Chem.* **2013**, *5*, 817.
- [77] M. A. Malik, M. Afzaal, P. O'Brien, *Chem. Rev.* **2010**, *110*, 4417-4446.
- [78] J. R. Davis, *Aluminum and Aluminum Alloys*, ASM International: Almere, Netherlands, **1993**.
- [79] D. Franz, S. Inoue, *Dalton Trans.* **2016**, *45*, 9385-9397.
- [80] A. Heilmann, J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2020**, *59*, 4897-4901.
- [81] M. D. Anker, R. J. Schwamm, M. P. Coles, *Chem. Commun.* **2020**, *56*, 2288-2291.
- [82] M. D. Anker, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 13452-13455.
- [83] M. D. Anker, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 18261-18265.
- [84] J. Hicks, A. Heilmann, P. Vasko, J. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2019**, *58*, 17265-17268.
- [85] A. Hofmann, M.-A. Légaré, L. Wüst, H. Braunschweig, *Angew. Chem. Int. Ed.* **2019**, *58*, 9776-9781.
- [86] A. Sekiguchi, R. Izumi, V. Y. Lee, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 14822-14823.
- [87] A. Schäfer, W. Saak, M. Weidenbruch, *Organometallics* **2003**, *22*, 215-217.
- [88] A. Sekiguchi, V. Y. Lee, *Chem. Rev.* **2003**, *103*, 1429-1448.
- [89] H. Ottosson, A. M. Eklöf, *Coord. Chem. Rev.* **2008**, *252*, 1287-1314.
- [90] K. K. Milnes, L. C. Pavelka, K. M. Baines, *Chem. Soc. Rev.* **2016**, *45*, 1019-1035.
- [91] W.-P. Leung, Y.-C. Chan, C.-W. So, *Organometallics* **2015**, *34*, 2067-2085.
- [92] C. Bibal, S. Mazières, H. Gornitzka, C. Couret, *Angew. Chem. Int. Ed.* **2001**, *40*, 952-954.
- [93] W. Setaka, K. Hirai, H. Tomioka, K. Sakamoto, M. Kira, *J. Am. Chem. Soc.* **2004**, *126*, 2696-2697.
- [94] D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossío, A. Bacciredo, *Angew. Chem. Int. Ed.* **2010**, *49*, 6585-6588.
- [95] V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**.
- [96] H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem. Int. Ed.* **1998**, *37*, 3179-3180.
- [97] M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10282-10292.
- [98] M.-A. Légaré, C. Prankevicus, H. Braunschweig, *Chem. Rev.* **2019**, *119*, 8231-8261.
- [99] M.-A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels, H. Braunschweig, *Science* **2018**, *359*, 896-900.
- [100] M.-A. Légaré, M. Rang, G. Bélanger-Chabot, J. I. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M. C. Holthausen, H. Braunschweig, *Science* **2019**, *363*, 1329.
- [101] M.-A. Légaré, G. Bélanger-Chabot, M. Rang, R. D. Dewhurst, I. Krummenacher, R. Bertermann, H. Braunschweig, *Nat. Chem.* **2020**.
- [102] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem. Int. Ed.* **1991**, *30*, 564-565.
- [103] C. M. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. J. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.* **2000**, *39*, 4274-4276.
- [104] H. W. Roesky, S. S. Kumar, *Chem. Commun.* **2005**, 4027-4038.
- [105] M. T. Gamer, P. W. Roesky, S. N. Konchenko, P. Nava, R. Ahlrichs, *Angew. Chem. Int. Ed.* **2006**, *45*, 4447-4451.
- [106] S. G. Minasian, J. L. Krinsky, V. A. Williams, J. Arnold, *J. Am. Chem. Soc.* **2008**, *130*, 10086-10087.
- [107] T. Chu, I. Korobkov, G. I. Nikonov, *J. Am. Chem. Soc.* **2014**, *136*, 9195-9202.
- [108] T. Chu, Y. Boyko, I. Korobkov, G. I. Nikonov, *Organometallics* **2015**, *34*, 5363-5365.
- [109] T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608-3680.
- [110] A. C. Stelzer, P. Hrobárik, T. Braun, M. Kaupp, B. Braun-Cula, *Inorg. Chem.* **2016**, *55*, 4915-4923.
- [111] S. Schulz, H. W. Roesky, H. J. Koch, G. M. Sheldrick, D. Stalke, A. Kuhn, *Angew. Chem. Int. Ed.* **1993**, *32*, 1729-1731.
- [112] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem. Int. Ed.* **1994**, *33*, 199-200.
- [113] H. Zhu, J. Chai, V. Jancik, H. W. Roesky, W. A. Merrill, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 10170-10171.
- [114] Y. Peng, H. Fan, V. Jancik, H. W. Roesky, R. Herbst-Irmer, *Angew. Chem. Int. Ed.* **2004**, *43*, 6190-6192.
- [115] Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chem. Int. Ed.* **2004**, *43*, 3443-3445.
- [116] R. J. Baker, C. Jones, *Dalton Trans.* **2005**, 1341-1348.
- [117] J. A. J. Pardoe, A. J. Downs, *Chem. Rev.* **2007**, *107*, 2-45.
- [118] C. Janiak, *Coord. Chem. Rev.* **1997**, *163*, 107-216.
- [119] S. Aldridge, A. J. Downs, *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*, John Wiley & Sons, Ltd., Chichester, United Kingdom, **2011**.
- [120] G. D. Frey, V. Lavallo, B. Donnadiu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439-441.
- [121] P. Jutzi, D. Kanne, C. Krüger, *Angew. Chem. Int. Ed.* **1986**, *25*, 164-164.
- [122] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691-2692.
- [123] M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628-9629.
- [124] C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3948-3950.
- [125] S. Khan, H. W. Roesky, *Chem. Eur. J.* **2019**, *25*, 1636-1648.
- [126] Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479-3511.
- [127] M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354-396.
- [128] N. Kuriakose, K. Vanka, *Dalton Trans.* **2014**, *43*, 2194-2201.
- [129] A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500-6503.
- [130] V. Protchenko Andrey, D. Schwarz Andrew, P. Blake Matthew, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Angew. Chem. Int. Ed.* **2012**, *52*, 568-571.

- [131] T. J. Hadlington, J. A. B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones, *Chem. Commun.* **2016**, 52, 1717-1720.
- [132] B. D. Rekken, T. M. Brown, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2012**, 134, 6504-6507.
- [133] D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, 139, 8134-8137.
- [134] D. Wendel, D. Reiter, A. Porzelt, P. J. Altmann, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, 139, 17193-17198.
- [135] R. Y. Kong, M. R. Crimmin, *Dalton Trans.* **2020**.
- [136] V. Lavallo, Y. Canac, B. Donnadiou, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2006**, 45, 3488-3491.
- [137] C. Ganesamoorthy, J. Schoening, C. Wölper, L. Song, P. R. Schreiner, S. Schulz, *Nat. Chem.* **2020**, 12, 608-614.
- [138] D. Reiter, R. Holzner, A. Porzelt, P. Frisch, S. Inoue, *Nat. Chem.* **2020**.
- [139] S. Yadav, S. Saha, S. Sen Sakya, *ChemCatChem* **2015**, 8, 486-501.
- [140] T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, 47, 4176-4197.
- [141] T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2014**, 136, 3028-3031.
- [142] T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2014**, 136, 3028-3031.
- [143] R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossío, A. Baceiredo, *Angew. Chem. Int. Ed.* **2011**, 50, 10414-10416.
- [144] F. Lips, J. C. Fettinger, A. Mansikkamäki, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2014**, 136, 634-637.
- [145] T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *Chem. Sci.* **2015**, 6, 7249-7257.
- [146] J. W. Dube, C. M. E. Graham, C. L. B. Macdonald, Z. D. Brown, P. P. Power, P. J. Ragoon, *Chem. Eur. J.* **2014**, 20, 6739-6744.
- [147] R. Rodriguez, Y. Contie, R. Nougé, A. Baceiredo, N. Saffon-Merceron, J.-M. Sotiropoulos, T. Kato, *Angew. Chem. Int. Ed.* **2016**, 55, 14355-14358.
- [148] I. A. I. Mkhaldid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, 110, 890-931.
- [149] J. F. Hartwig, *Acc. Chem. Res.* **2012**, 45, 864-873.
- [150] Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, 314, 113.
- [151] Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, 130, 16069-16079.
- [152] L. Weber, *Eur. J. Inorg. Chem.* **2017**, 2017, 3461-3488.
- [153] L. Dang, Z. Lin, T. B. Marder, *Chem. Commun.* **2009**, 3987-3995.
- [154] E. S. Schmidt, A. Jockisch, H. Schmidbaur, *J. Am. Chem. Soc.* **1999**, 121, 9758-9759.
- [155] R. J. Baker, C. Jones, *Coord. Chem. Rev.* **2005**, 249, 1857-1869.
- [156] R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, C. M. Fitchett, *Angew. Chem. Int. Ed.* **2018**, 57, 5885-5887.
- [157] A.-F. Pecharman, A. L. Colebatch, M. S. Hill, C. L. McMullin, M. F. Mahon, C. Weetman, *Nat. Commun.* **2017**, 8.
- [158] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, 557, 92-95.
- [159] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, 141, 11000-11003.
- [160] R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, 58, 1489-1493.
- [161] M. D. Anker, C. L. McMullin, N. A. Rajabi, M. P. Coles, *Angew. Chem. Int. Ed.* **2020**, 59, 12806-12810.
- [162] S. Kurumada, S. Takamori, M. Yamashita, *Nat. Chem.* **2020**, 12, 36-39.
- [163] S. Kurumada, K. Sugita, R. Nakano, M. Yamashita, *Angew. Chem. Int. Ed.* **2020**, 59, 20381-20384.
- [164] J. Hicks, P. Vasko, A. Heilmann, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2020**, 59, 20376-20380.
- [165] K. Koshino, R. Kinjo, *J. Am. Chem. Soc.* **2020**.
- [166] R. E. Mulvey, *Acc. Chem. Res.* **2009**, 42, 743-755.
- [167] R. E. Mulvey, T. X. Gentner, *Angew. Chem. Int. Ed.* **2020**, DOI:10.1002/anie.202010963.
- [168] V. Y. Lee, *Organosilicon Compounds: Theory and Experiment (Synthesis)*, Elsevier Science, **2017**.
- [169] C. Präsang, D. Scheschkewitz, in *Functional Molecular Silicon Compounds II: Low Oxidation States* (Ed.: D. Scheschkewitz), Springer International Publishing, Cham, **2014**, pp. 1-47.
- [170] M. W. Stanford, A. Bismuto, M. J. Cowley, *Chem. Eur. J.* **2020**, 26, 9855-9858.
- [171] Y. Mizuhata, S. Fujimori, T. Sasamori, N. Tokitoh, *Angew. Chem. Int. Ed.* **2017**, 56, 4588-4592.
- [172] S. Fujimori, Y. Mizuhata, N. Tokitoh, *Chem. Eur. J.* **2019**, 25, 6284-6289.
- [173] S. Fujimori, Y. Mizuhata, N. Tokitoh, *Chem. Eur. J.* **2018**, 24, 17039-17045.
- [174] Y. Mizuhata, S. Fujimori, N. Tokitoh, *Phosphorus, Sulfur, and Silicon and the Related Elements* **2020**, 195, 936-939.
- [175] M. M. Siddiqui, S. Sinhababu, S. Dutta, S. Kundu, P. N. Ruth, A. Münch, R. Herbst-Irmer, D. Stalke, D. Koley, H. W. Roesky, *Angew. Chem. Int. Ed.* **2018**, 57, 11776-11780.
- [176] G. A. Olah, (Ed.: N. Prize), NobelPrize.org, **1994**.
- [177] Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama, T. Fukushima, *Nat. Chem.* **2014**, 6, 498-503.
- [178] W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem. Int. Ed.* **2005**, 44, 5016-5036.
- [179] D. Franz, S. Inoue, *Chem. Eur. J.* **2019**, 25, 2898-2926.
- [180] M. J. Ingleson, in *Synthesis and Application of Organoboron Compounds*, Springer, **2015**.
- [181] K. Stefkova, L. Gierlichs, D. Willcox, R. L. Melen, *Encyclopedia of Inorganic and Bioinorganic Chemistry* **2020**, 1-37.
- [182] K.-C. Kim, C. A. Reed, G. S. Long, A. Sen, *J. Am. Chem. Soc.* **2002**, 124, 7662-7663.
- [183] W. Gu, M. R. Haneline, C. Douvris, O. V. Ozerov, *J. Am. Chem. Soc.* **2009**, 131, 11203-11212.
- [184] M. Khandelwal, R. J. Wehmschulte, *Angew. Chem. Int. Ed.* **2012**, 51, 7323-7326.
- [185] M. Saleh, D. R. Powell, R. J. Wehmschulte, *Organometallics* **2017**, 36, 4810-4815.
- [186] A. Caise, J. Hicks, M. Á. Fuentes, J. Goicoechea, S. Aldridge, *Chem. Eur. J.* **2020**, n/a.
- [187] K. Grootz, A. Barthélemy, I. Krossing, *Angew. Chem. Int. Ed.* **2020**, DOI:10.1002/anie.202011466.
- [188] Z. Li, G. Thiery, M. R. Lichtenthaler, R. Guillot, I. Krossing, V. Gandon, C. Bour, *Adv. Synth. Catal.* **2018**, 360, 544-549.
- [189] G. A. Olah, *J. Am. Chem. Soc.* **1972**, 94, 808-820.
- [190] G. A. Olah, *J. Org. Chem.* **2001**, 66, 5943-5957.
- [191] K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, *Science* **2002**, 297, 825.
- [192] A. Sekiguchi, T. Fukawa, V. Y. Lee, M. Nakamoto, M. Ichinohe, *Angew. Chem. Int. Ed.* **2003**, 42, 1143-1145.
- [193] J. B. Lambert, L. Lin, S. Keinan, T. Müller, *J. Am. Chem. Soc.* **2003**, 125, 6022-6023.
- [194] P. Romanato, S. Duttwyler, A. Linden, K. K. Baldrige, J. S. Siegel, *J. Am. Chem. Soc.* **2010**, 132, 7828-7829.

- [195] S. Duttwyler, Q.-Q. Do, A. Linden, K. K. Baldrige, J. S. Siegel, *Angew. Chem. Int. Ed.* **2008**, *47*, 1719-1722.
- [196] K. Mütter, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2011**, *133*, 12442-12444.
- [197] M. Kira, T. Hino, H. Sakurai, *J. Am. Chem. Soc.* **1992**, *114*, 6697-6700.
- [198] J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917.
- [199] C. A. Reed, Z. Xie, R. Bau, A. Benesi, *Science* **1993**, *262*, 402.
- [200] J. S. Siegel, *Nat. Rev. Chem.* **2020**, *4*, 4-5.
- [201] H. F. T. Klare, M. Oestreich, *Dalton Trans.* **2010**, *39*, 9176-9184.
- [202] J. C. L. Walker, H. F. T. Klare, M. Oestreich, *Nat. Rev. Chem.* **2020**, *4*, 54-62.
- [203] B. Shao, A. L. Bagdasarian, S. Popov, H. M. Nelson, *Science* **2017**, *355*, 1403.
- [204] M. Talavera, G. Meißner, S. G. Rachor, T. Braun, *Chem. Commun.* **2020**, *56*, 4452-4455.
- [205] D. J. Scott, N. A. Phillips, J. S. Sapsford, A. C. Deacy, M. J. Fuchter, A. E. Ashley, *Angew. Chem. Int. Ed.* **2016**, *55*, 14738-14742.
- [206] P. Jutzi, A. Mix, B. Rummel, W. W. Schoeller, B. Neumann, H.-G. Stammler, *Science* **2004**, *305*, 849.
- [207] M. Driess, S. Yao, M. Brym, C. van Wüllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 6730-6733.
- [208] Y. Xiong, S. Yao, S. Inoue, E. Irran, M. Driess, *Angew. Chem. Int. Ed.* **2012**, *51*, 10074-10077.
- [209] H.-X. Yeong, H.-W. Xi, Y. Li, K. H. Lim, C.-W. So, *Chem. Eur. J.* **2013**, *19*, 11786-11790.
- [210] Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147-7150.
- [211] S. U. Ahmad, T. Szilvási, S. Inoue, *Chem. Commun.* **2014**, *50*, 12619-12622.
- [212] Y. Li, Y.-C. Chan, B.-X. Leong, Y. Li, E. Richards, I. Purushothaman, S. De, P. Parameswaran, C.-W. So, *Angew. Chem. Int. Ed.* **2017**, *56*, 7573-7578.
- [213] B.-X. Leong, J. Lee, Y. Li, M.-C. Yang, C.-K. Siu, M.-D. Su, C.-W. So, *J. Am. Chem. Soc.* **2019**, *141*, 17629-17636.
- [214] D. Sarkar, V. Nesterov, T. Szilvási, P. J. Altmann, S. Inoue, *Chem. Eur. J.* **2019**, *25*, 1198-1202.
- [215] A. Porzelt, I. J. Schweizer, R. Baierl, J. P. Altmann, C. M. Holthausen, S. Inoue, *Inorganics* **2018**, *6*, 54-68.
- [216] S. U. Ahmad, T. Szilvási, E. Irran, S. Inoue, *J. Am. Chem. Soc.* **2015**, *137*, 5828-5836.
- [217] D. Sarkar, D. Wendel, S. U. Ahmad, T. Szilvási, A. Pöthig, S. Inoue, *Dalton Trans.* **2017**, *46*, 16014-16018.
- [218] V. S. V. S. N. Swamy, S. Pal, S. Khan, S. S. Sen, *Dalton Trans.* **2015**, *44*, 12903-12923.
- [219] Y. Xiong, S. Yao, S. Inoue, A. Berkefeld, M. Driess, *Chem. Commun.* **2012**, *48*, 12198-12200.
- [220] A. Rit, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2016**, *55*, 378-382.
- [221] X. Zhou, P. Vasko, J. Hicks, M. Á. Fuentes, A. Heilmann, E. L. Kolychev, S. Aldridge, *Dalton Trans.* **2020**, *49*, 9495-9504.
- [222] M. M. D. Roy, S. Fujimori, M. J. Ferguson, R. McDonald, N. Tokitoh, E. Rivard, *Chem. Eur. J.* **2018**, *24*, 14392-14399.
- [223] S. Sinhababu, D. Singh, M. K. Sharma, R. K. Siwatch, P. Mahawar, S. Nagendran, *Dalton Trans.* **2019**, *48*, 4094-4100.
- [224] D. Sarkar, C. Weetman, S. Dutta, E. Schubert, C. Jandl, D. Koley, S. Inoue, *J. Am. Chem. Soc.* **2020**, *142*, 15403-15411.

Abstract:

Since the discovery that main group elements can mimic transition metals, efforts have focussed on harnessing main group elements abilities to break strong bonds to enable new sustainable methodologies. In this regard, use of small molecules, such as those found in greenhouse gases, are a prime target for incorporation into catalytic cycles to produce value-added products. Initial challenges in main group chemistry focussed on the ability to isolate these highly reactive low-oxidation state species, whilst also maintaining the reactive sites. An array of low valent compounds have been

successfully isolated (*i.e.*, multiple bonds, tetrylenes, anions and cations), through careful ligand design, and have challenged traditional bonding models and pre-conceptions of the main group elements. Current advances have highlighted how reactive these low-valent sites are with the ability to activate strong bonds, such as those found in small molecules (*e.g.*, H₂, CO, CO₂ etc.). This represents the first step in a redox-based catalytic cycle, as the low-valent main group centre undergoes oxidative addition reactions. Current challenges remain in reductive elimination, and thus functionalisation of the small molecule, but examples of low-valent main group elements in catalysis are starting to emerge and represent a bright future for main group chemistry. This book chapter highlights the achievements of low valent main group elements, with a focus on group 2, 13, and 14 elements, in small molecule activation as well as the fundamental concepts that have aided the development of this rapidly advancing field.

Keywords: s-block, p-block, Low Valent, Anions, Cations, Multiple Bonds, Oxidative Addition, Small Molecule Activation, Homogeneous Catalysis.