

# Experimental Realisation of Elusive Multiple-bonded Aluminium Compounds: A New Horizon in the Aluminium Chemistry

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Dedication ((optional))



**Abstract:** Synthesis and isolation of stable main group compounds featuring multiple bonds has been of keen interest for the last several decades. Plethora of such multiply bonded complexes were obtained using sterically demanding substituents that provide both kinetic and thermodynamic stability. Most of these compounds have unusual structural and electronic properties that challenges the classical concept of covalent multiple bonding. In contrast, analogous aluminium compounds are scarce in spite of its high natural abundance. The parent dialumene ( $\text{Al}_2\text{H}_2$ ) has been calculated to be extremely weak, thus making Al multiple bonds a challenging synthetic target. This review provides an overview of the recent advances in the cutting edge synthetic approaches and the careful ligand design used to obtain aluminium homo- and heterodiatomic multiply bonded complexes. Additionally, the reactivity of these novel compounds towards various small molecules and reagents will be discussed herein.

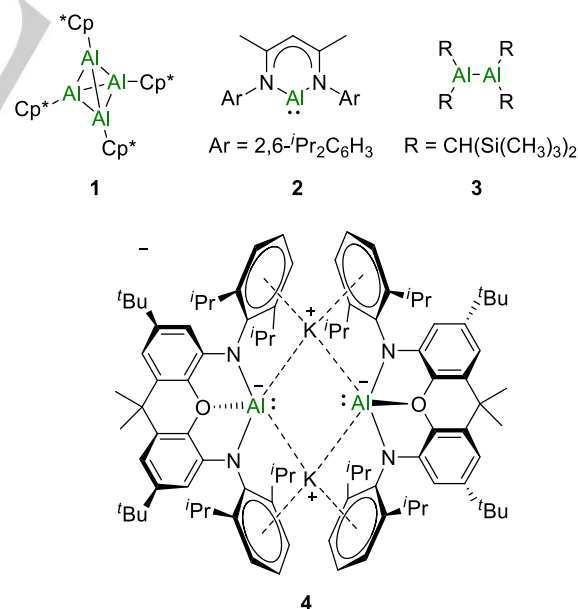
## 1. Introduction

### 1.1. Background

Aluminium is the most abundant metal found within the earth's crust. This is most commonly found as Al ore in Bauxite rock which then extracted *via* the Bayer process to yield alumina,  $\text{Al}_2\text{O}_3$ , with Al in the +3 oxidation state. Due to the large differences in electronegativity between Al and O, alumina is highly ionic in character and forms aggregates of high lattice energy in the solid state. For these reasons, alumina is inert with high temperature and electrical resistance which lends its use to a variety of applications (materials, cosmetics, catalysis etc).<sup>[1]</sup> Over 90% of the mined alumina is converted into Al metal through the smelting process, this provides the low density and corrosive resistant metal in bulk quantities.<sup>[2]</sup> These key properties of Al and its alloys have proved vital to the aerospace and construction industry.

Organometallic Al compounds came to the forefront through the use of trialkyl Al compounds in Ziegler-Natta catalysis<sup>[3]</sup> and trihalide Al salts in Friedel-Craft reactions.<sup>[4]</sup> These feature Al in the most commonly found +3 oxidation state, due to the high stability of this oxidation state for Al. Several compounds also feature Al in the +2 oxidation state<sup>[5]</sup> but isolation of Al(I) species is challenging due to the thermal instability of these compounds.<sup>[6]</sup> Low-valent Al(I) compounds such as  $\text{AlH}$ ,  $\text{AlX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{Al}_2\text{O}$  are only stable at high temperatures and low pressures, despite this reactivity studies of these compounds were possible utilising cryochemical methods and metastable solutions of  $\text{AlX}$ .<sup>[7]</sup>

The ability to isolate a stable Al(I) is an interesting synthetic challenge, due to the high Lewis acidity of the metal centre and small cation size. The first known compound in which Al was approaching +1 oxidation state was a cluster compound of the formula  $\text{K}_2[\text{Al}_2\text{Bu}_2]$ .<sup>[8]</sup> This reaction was first reported in 1976 however, it was not until 1991 that the structure was realized<sup>[8c]</sup>. Introduction of steric bulk into the ligand sphere allowed for the isolation of the widely studied Al(I) tetramer  $[(\text{Cp}^*\text{Al})_4]$  (**1**) ( $\text{Cp}^* =$  pentamethylcyclopentadienyl) (Figure 1).<sup>[9]</sup> This complex contains a tetrahedral arrangement of Al(I) centres, which dissociates at elevated temperatures in solution to yield the monomeric  $\text{Cp}^*\text{Al}$  species. The metal-metal bonding in **1** involves four highly delocalised molecular orbitals, formed from the lone-pair  $\sigma$ -orbitals of the monomers where  $\text{Cp}^*$  moiety forms  $\pi$ -bonds with Al; all others constitute of only  $\sigma$ -bonds.<sup>[10]</sup> Alternatively, Roesky and co-workers devised a rather straight forward synthetic route to the same tetrameric compound **1** (yield: 20%). Starting from easily available  $\text{AlCl}_3$ , this was reacted with  $\text{Cp}^*\text{SiMe}_3$  to form  $\text{Cp}^*\text{AlCl}_2$  and its subsequent reduction in the presence of potassium metal under refluxing conditions in toluene furnished **1**.<sup>[11]</sup> Afterwards, this prototypical Al(I) compound **1** was subjected to diverse range of reactivity which included: i) oxidation with chalcogens,<sup>[11, 12]</sup> ii) coordination behaviour towards transition metals,<sup>[13]</sup> and iii) insertion of unsaturated organic substrates into the Al-Al bonds.<sup>[14]</sup> Following this report, in 2000, Roesky and co-workers published the use of a bidentate  $\beta$ -diketiminate ligand for the successful isolation of a monomeric Al(I) compound (**2**), an aluminium analogue of N-heterocyclic carbene (Figure 1);<sup>[15]</sup> reactivity studies of both compounds **1** and **2** towards small molecules have been extensively studied.<sup>[10b, 16]</sup>



**Figure 1.** Representative examples of low oxidation state Al complexes.

This reliance on kinetic stabilisation is also necessary for Al metal-metal bonding. Since the first reported Al-Al single bond

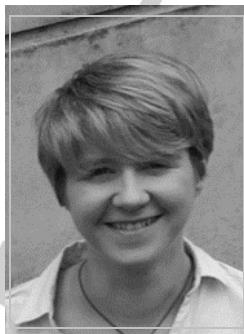
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(3) by Uhl (Figure 1)<sup>[5c]</sup> there have been many examples of singly bonded homo- and heterodiatomic Al complexes, however examples containing multiple bonds are scarce and will be discussed in this review. Very recent developments in Aluminium chemistry by Aldridge and Goicoechea have shown unprecedented reactivity in the formation of aluminium-element covalent bonds and C-H oxidative addition of benzene, through the successful isolation of the first nucleophilic, anionic Al(I) landmark compound **4** (Figure 1).<sup>[17]</sup> This dimeric compound is supported by a dimethylxanthene-derived secondary aniline which provides sufficient steric bulk and additional electronic stability from the oxygen in the ligand scaffold. This remarkable compound is likely to pave the way for new avenues of Al chemistry in the future.

Prasenjit Bag was born in 1984 and received his Ph.D in 2014 from Indian Institute of Technology Kanpur, India, under the supervision of Prof. V. Chandrasekhar. Afterwards, he spent a short time as a postdoctoral fellow at the Saarland University under Prof. David Scheschkewitz, where he worked on the multiple-bonded silicon compounds. Since March, 2016, Prasenjit is a postdoctoral fellow in the group of Prof. Shigeyoshi Inoue at the Technische Universität München (TUM). His current area of research includes the synthesis of multiple-bonded aluminium compounds and their applications in small molecule activation reactions.



Catherine Weetman was born in 1989 and obtained her MChem and PhD at the University of Bath under the supervision of Prof. Michael Hill on the development of magnesium hydroboration catalytic systems. Her first postdoctoral position was spent at the University of Edinburgh under Professors Polly Arnold and Jason Love on f-block metal NHC complexes for small molecule activation; development of air- and moisture-stable d-block NHCs for chemical warfare decontamination and perhenate catalysis. Since December 2017, Cath is a TUFF postdoctoral fellow in the group of Prof. Inoue at TUM researching aluminium multiple bond chemistry and Al dehydrocoupling catalysis.



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



## 1.2. Main group multiple bonds

The ability to stabilise metal-metal bonds is of keen interest, not only in Al chemistry but also across the periodic table. Historically, advances in metal-metal bonding (e.g. Re-Re<sup>[18]</sup>, Zn-Zn<sup>[19]</sup>, Cr-Cr<sup>[20]</sup> and Mg-Mg<sup>[21]</sup>) have led to greater understanding of the nature of chemical bonds and therefore a greater ability to exploit the chemistry available to that metal centre. Until the early 1980s it was thought that elements with a principal quantum number greater than 2 (i.e. Period 3 and below) should not form multiple bonds with themselves or other elements. Three landmark compounds discovered in 1981 proved this double bond rule wrong. First the isolation of Si=Si double bond by West and co-workers,<sup>[22]</sup> then the successful isolation of P=P containing double bond by Yoshifuji<sup>[23]</sup> and finally Brook's silene containing a Si=C double bond.<sup>[24]</sup> These remarkable discoveries have since led to a plethora of main group multiply bonded compounds which have been the subject of numerous reviews.<sup>[25]</sup>

The key to the isolation of these compounds was the use of steric bulk in the supporting ligands. This kinetic stabilisation allows for the isolation of low coordination and low oxidation state systems, preventing them from undergoing disproportionation reactions and oligomerisation or polymerisation. The use of bulky ligand substituents was pioneered by Lappert, whose seminal work in the use of bis(trimethylsilyl)methyl ligands (CH(SiMe<sub>3</sub>)<sub>2</sub>) provided access to a stannylene compound,<sup>[26a]</sup> which is a stable two coordinate tin compound, which in the solid state dimerises to form a Sn=Sn double bond.<sup>[26b]</sup> Further development in the use of bulky substituents has led to the isolation of other group 14 two coordinate species. Of these, the chemistry of silylenes is now widely established. In a similar manner to that reported by West, for the synthesis of Si=Si double bond, starting from a Si(IV) precursor and its subsequent reduction provided both cyclic and acyclic stable two coordinate silylene species, the difference here is that silylene compound generated was sufficiently bulky to prevent dimerisation to the corresponding Si=Si double bond.<sup>[27]</sup> The ability to isolate these stable two coordinate group 14 compounds has provided access to viable precursors for

group 14 multiple bond chemistry, and has indeed led to numerous examples of group 14 homo- and heterodiatomic multiple bonds.<sup>[28]</sup>

The development analogous group 13 compounds was initially hindered by the thought that the electron deficient nature of the group 13 elements precluded multiple bond formation, but again chemistry rules are made to be broken and group 13 multiple bond chemistry has now been established for the last decade.<sup>[29, 30]</sup> In general, group 13 multiple bonds are extremely reactive as they possess significant singlet diradical character which further increases their potential reactivity and reduces stability.<sup>[30]</sup> Use of Lewis basic N-heterocyclic carbenes (NHCs) has proven pivotal in the case of boron multiple bond chemistry. The landmark discovery by Robinson and co-workers utilised NHCs to stabilise the neutral parent diborene complex, this was obtained through the reductive dehalogenation of NHC-BBr<sub>3</sub> in the presence of excess potassium graphite (KC<sub>8</sub>) at room temperature.<sup>[31]</sup> Utilising a similar reductive dehalogenation methodology, but with a pre-formed B-B single bond, allowed for the isolation of the B≡B triple bond.<sup>[32]</sup>

Examples of heavier group 13 multiple bonds also exist, these have typically utilised the terphenyl ligand which exerts considerable steric bulk to kinetically stabilise dimetallenes and dimetallynes.<sup>[25e]</sup> These terphenyl ligands have a proven track record in main group and transition metal multiple bonds and have allowed for many traditional rules to be broken such as isolation of the quintuple Cr-Cr bond<sup>[20]</sup> and the controversial 'digallyne'.<sup>[33]</sup> This latter discovery caused considerable debate over the description of multiple bonds, (see section 1.3 for more detail) due to the *trans*-bent geometry observed within the crystal structure and the role in which the sodium cation played in stabilising the molecule. It is now widely accepted that descriptions used to explain lighter congeners do not apply to the heavier main group elements and in fact there are many other factors contributing to the stability of these species, such as London dispersion forces.<sup>[34]</sup> Whilst they can be considered stable, in most cases these dissociate into their corresponding monomers in hydrocarbon solvents. This has allowed these multiply-bonded compounds to exhibit a diverse range of reactivity that has traditionally been dominated by transition metal compounds.<sup>[35]</sup>

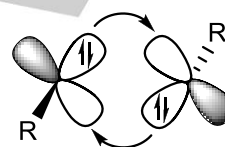
In comparison to the rest of group 13 elements, much less is known about the nature of Al multiple bonding chemistry despite its relative abundance. In fact, it was only recently that the missing member of the main group neutral double bond family was successfully isolated by our group and will be discussed herein.<sup>[36]</sup>

### 1.3 Bonding and Bond Order in Multiple Bonds

One common debate in main group multiple bonding, particularly for heavier group 13 and 14 elements, centres around the description of bond multiplicity and the ability to denote a formal double or triple bond. For carbon double and triple bonds valence bond (VB) and molecular orbital (MO) theory adequately describe the nature of bonding and the observed planar geometry, however heavier analogues exhibit

deviation from this planar geometry with considerable *trans*-bent geometries observed upon increasing atomic number.

The CGMT model provides one method for examining heavier main group analogues.<sup>[37]</sup> If you are to consider a molecule of the type REER or R<sub>2</sub>EER<sub>2</sub>, homolytic cleavage of this molecule will provide two triplet fragments. Upon descending the group (a) the singlet ground state becomes more stable and (b) the strength of the E-E bond decreases. The combination of these factors for the heavier analogues, results in insufficient energy to offset the energy required for triplet state formation prior to E=E double bond formation. Thus, heavier main group double bonds consist of increasingly singlet character and it is in fact bringing together of the two monomers in a dative bond that produces a multiple bond, as depicted below in Figure 2, resulting the observed *trans*-bent geometry, which is also thought to be due to the avoidance of steric clash. This type of polarised dative bonding was originally proposed by Lappert in the formation of the stannylene complex.<sup>[26]</sup>

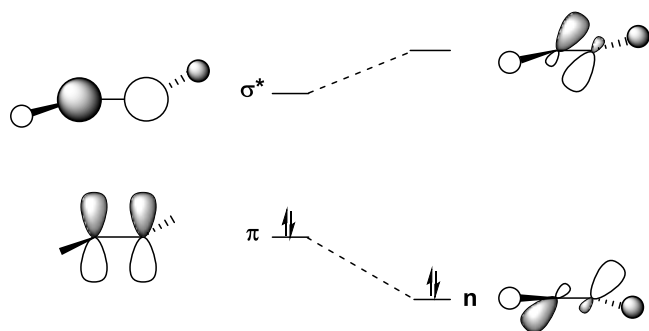


**Figure 2.** Association of two singlet fragments in multiple bond formation for the group 13 elements.

It is also possible to use MO theory to describe the observed geometries in heavier multiple bonds. Upon descending the groups there is an increase in the mixing of  $\pi$  and  $\sigma^*$  orbitals due to the lowering of  $\pi$ - $\sigma^*$  gap, resembling Jahn-Teller distortions used to describe pyridimisation. This increased mixing of the  $\sigma^*$  orbital weakens the  $\pi$  bond by increasing the lone pair character and the electron density becomes more localised on the individual atoms (Figure 3). This MO model can also be used to understand the effects of ligand substituents on the outcome multiple bond formation or the propensity to form monomers. To increase the likelihood of double bond formation, use of electropositive substituents (e.g. silyl groups) will lead to a greater stabilisation of the  $\pi$  bond through destabilisation of the lone pair bonding MO, whereas the use of electronegative substituents (e.g. amides) will strengthen the  $\sigma$  bond of R<sub>2</sub>E and provide more  $\sigma^*$  character to E providing a greater interaction between  $\pi$ - $\sigma^*$  and therefore increased lone pair character on E.<sup>[25a, 38]</sup>

Due to the nature of the bonding in heavier main group multiple bonds, the bonds themselves are weaker than compared to the carbon analogues which results in lengthening of the multiple bond. For this reason, it is difficult to quantify the exact bond order through simple analysis of the bond length observed in the X-ray structure. Several different computational methods can be used to verify the bonding in these systems. Amongst these Natural Bond Order (NBO) analysis and Wiberg Bond Index (WBI) are the most commonly used descriptions for determining values for multiple bonds and are therefore discussed throughout this review. As well as theoretical studies,

reactivity studies through on-wards reaction with small unsaturated molecules and reagents (eg. CO<sub>2</sub>, ethylene and phenylacetylene) provide an experimental insight into the nature of the multiple bond.



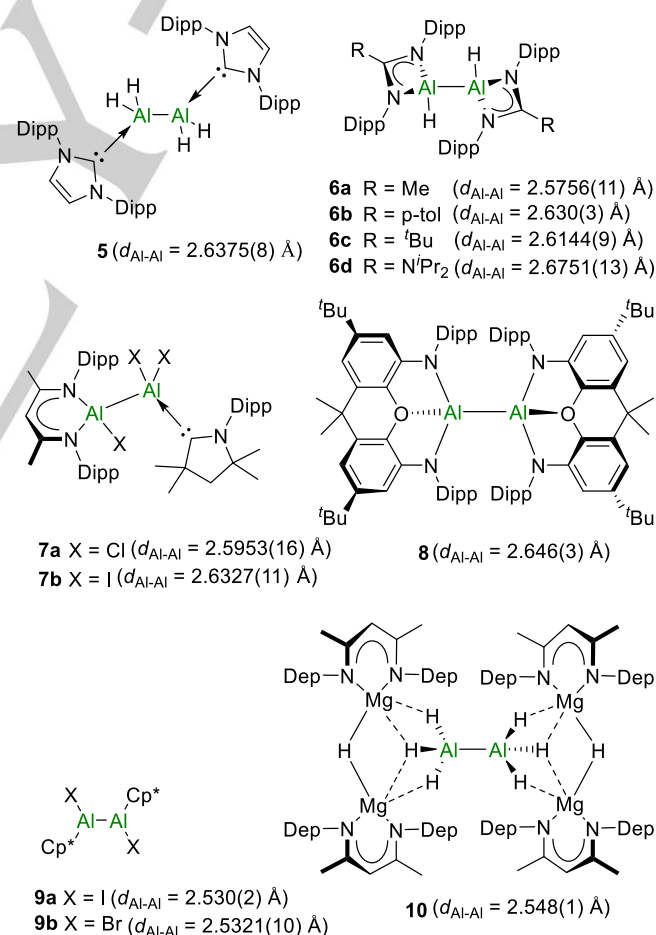
**Figure 3.** MO diagram showing the mixing of the  $\pi$  and  $\sigma^*$  orbitals and the formation of the *non-bonding* lone pair orbital in group 13 compounds.

In this review the synthesis and reactivity of numerous landmark compounds containing both hetero- and homodiatom Al multiple bonds that contributed to the recent renaissance in multiple-bonded Al chemistry will be discussed herein. We believe that in order to have better insight into the electronic structure of multiple bonded compounds our discussion should begin with single-bonded saturated Al compounds due to their intimate relationship.

## 2. Compounds with an Al–Al Single bond

Main group compounds possessing homonuclear E–E single bonds are quite common throughout group 14–16. Isolation of such compounds comprising of group 13 elements, however, remained extremely challenging until the quarter of the twentieth century. There are various reasons for such belated developments in this chemistry. One such reason is the undoubtedly weak nature of this E–E bond. This was further corroborated by combination of spectroscopic and computational data which showed E–E bond energies involving group 13 elements are considerably smaller than the corresponding E–E bonds of groups 14–16 elements. With particular reference to Al, its increased atomic radii and electropositive nature means the valence electrons lie relatively high in energy. This eventually perpetuated in its homodinuclear bonding. Calculations further highlighted Al is rather reluctant to form electron precise single bond due to its low bond dissociation energy ( $D_{0(\text{Al-Al})} = 188 \text{ kJ mol}^{-1}$ ) compared to diboranes ( $D_{0(\text{B-B})} = 293 \text{ kJ mol}^{-1}$ ) and disilanes ( $D_{0(\text{Si-Si})} = 222 \text{ kJ mol}^{-1}$ ).<sup>[39]</sup> Currently, the amount of stable disilane or diborane compounds reported to date easily outnumber the corresponding dialumane compounds. Additionally, akin to other group 13 elements, Al also possesses limited valence electrons which only form three electron pair bonds, leaving a vacant orbital on each metal centre which is responsible for their enhanced Lewis acidity. Consequently, shielding by sterically bulky substituents or stabilisation by

electronically  $\pi$ -basic ligands is crucial in order to isolate Al(II) compounds. Accordingly, in early 1960s such compounds were targeted with the aid of amide ligands, however, no compelling spectroscopic or structural characterisation were provided in support of their formation.<sup>[40]</sup> Therefore, the first structurally authenticated dialuminium compound possessing an Al–Al single bond was unambiguously reported in 1988 by Uhl [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Al–Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**3**) ( $d_{\text{Al-Al}} = 2.660(1) \text{ \AA}$ ).<sup>[5c]</sup> Since then this field has experienced considerable development and a large number of compounds have been isolated either in the tetrameric form, R<sub>4</sub>Al<sub>4</sub> (R = alkyl, aryl, silyl or amide);<sup>[9, 11, 41]</sup> dimeric form R<sub>2</sub>Al–AlR<sub>2</sub> (R = alkyl, aryl, silyl and halide); as the Lewis base adducts R<sub>2</sub>(L)Al–Al(L)R<sub>2</sub> (L = Lewis base)<sup>[42]</sup> or through use of a donor acceptor type interaction R'–Al–AlR<sub>3</sub> (R' = C<sub>6</sub>F<sub>5</sub>, R = alkyl).<sup>[43]</sup> Single-bonded aluminium compounds exhibit rich chemical reactivity, with Al–Al distances ranging from 2.5 to 2.95 Å.<sup>[10]</sup> The bonding and reactivity patterns of some of these compounds have already been subject of reviews reported in early 2000s.<sup>[6a, 44]</sup> Therefore, our discussion will mainly focus on some of the notable single bonded aluminium compounds isolated in the last decade with their potential reactivity.



**Figure 4.** Notable examples of neutral and anionic single-bonded aluminium compounds (**5–10**) isolated in the last decade.

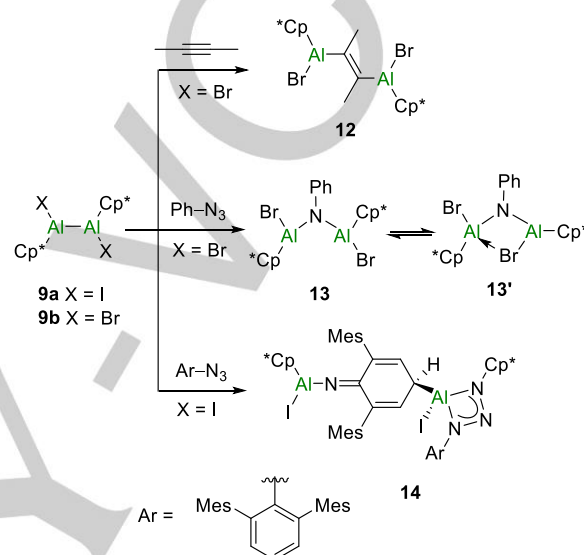
In this category, Jones and co-workers have accomplished the isolation of parent dialumane ( $\text{Al}_2\text{H}_4$ ) in the form of (bis)carbene adduct  $\text{IDipp}\cdot\text{H}_2\text{Al}-\text{AlH}_2\cdot\text{IDipp}$  (**5**) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) (Figure 4).<sup>[45]</sup> This was synthesised *via* direct hydrogen atom transfer from  $\text{IDipp}\cdot\text{AlH}_3$  adduct to Mg(I) dimer  $[\text{HC}(\text{MeCNAr})_2\text{Mg}]_2$  (Ar = Mes, Dipp).<sup>[21, 46]</sup> Compound **5** showed exceptional thermal stability (decomp. 190–192 °C), which can be undoubtedly attributed to the high nucleophilic character of the bulky NHC ligands. Moreover, utilisation of a similar synthetic method allowed them to isolate a series of 1,2-dihydrodialumane compounds  $[\text{L}(\text{H})\text{Al}-\text{Al}(\text{H})\text{L}]$  [ $\text{L} = [(\text{DippN})_2\text{CR}]^-$ , R = Me (**6a**), *p*-tolyl (**6b**), <sup>t</sup>Bu (**6c**) or  $\text{N}^i\text{Pr}_2$  (**6d**)] in moderate yields exploiting chelating bulky amidinate or guanidinate ligands (Figure 4).<sup>[45]</sup> The Al–Al bond lengths lie in the range 2.576–2.675 Å for all the dimeric compounds. The infrared spectrum analysis displayed two Al–H stretching bands at 1719  $\text{cm}^{-1}$ , 1682  $\text{cm}^{-1}$  for compound **5**, whereas the spectra of **6a–d** each exhibits one band in the region of 1748–1770  $\text{cm}^{-1}$  and these values are ~60–90  $\text{cm}^{-1}$  lower in wavenumbers compared to the starting Al(III) precursors. Moreover, the presence of Al–Al single bond was further evidenced from the strong absorption band at ~130–140  $\text{cm}^{-1}$  in Raman spectrum.

Last year, first asymmetric-substituted dialumanes  $[\text{Me}_2\text{CAAC}\cdot\text{Al}(\text{X})-\text{Al}(\text{X})\text{L}]$  (X = Cl (**7a**), I (**7b**)) were isolated by Roesky and co-workers from the facile disproportionation reaction between  $\beta$ -diketiminate ligand stabilised monomeric Al(I) compound **2** (Figure 1) and CAAC-stabilised Al(III) trihalide complexes  $\text{Me}_2\text{CAAC}\cdot\text{AlX}_3$  (CAAC = cyclic alkyl amino carbene) (Figure 4).<sup>[47]</sup> The <sup>13</sup>C NMR resonances of the carbene carbon bound to the Al centre were found at 238.6 (**7a**) and 230.8 (**7b**) ppm and as expected were downfield shifted compared to the Al(III) precursors  $\text{Me}_2\text{CAAC}\cdot\text{AlCl}_3$  (231.1 ppm) and  $\text{Me}_2\text{CAAC}\cdot\text{AlI}_3$  (223.4 ppm) respectively. Single crystal X-ray diffraction (SC-XRD) analysis showed each Al centre adopts a distorted tetrahedral geometry with the Al–Al bond lengths of 2.6327(11) Å (**7b**) and 2.5953(16) Å (**7a**) which lie well within the range of Al–Al single bonded compounds. NBO analysis suggested the CAAC bound Al centre bears less positive charge (+0.91 e (**7a**), +0.57 e (**7b**)) compared to the  $\beta$ -diketiminate bound Al centre (+1.23 e (**7a**), +1.10 e (**7b**)).

Very recently, Aldridge and coworkers synthesised dialumane compound **8**  $[\text{Al}(\text{NON})]_2$  ( $d_{\text{Al-Al}} = 2.646(3)$  Å) employing a chelating ligand (NON).<sup>[17]</sup> This was obtained in excellent yield (86 %) as off-white coloured solid from the  $\text{KC}_8$  reduction of corresponding iodo compound (NON)AlI in either toluene or benzene.

Arnold and Braunschweig groups both independently synthesised bis( $\text{Cp}^*$ ) dialane complexes  $\text{Cp}^*(\text{X})\text{Al}-\text{Al}(\text{X})\text{Cp}^*$  [X = I (**9a**,  $d_{\text{Al-Al}} = 2.5321(10)$  Å), Br (**9b**,  $d_{\text{Al-Al}} = 2.530(2)$  Å)] from the reductive dehalogenation of corresponding dihaloalane complexes  $\text{Cp}^*\text{AlX}_2$  (Figure 4).<sup>[48]</sup> The <sup>27</sup>Al NMR resonances of both compounds were identified at  $\delta = -41.7$  (**9a**) and  $-46$  (**9b**) ppm, and for the later this was shifted considerably upfield in comparison to the starting dihaloalane Al(III) precursor  $\text{Cp}^*\text{AlBr}_2$  (–11 ppm). Both the 1,2-dihydrodialumanes **9a,b** show some interesting reactivity towards electron rich alkynes or

azides which led to the formation of a diverse range of products (**12–14**) featuring varied coordination numbers on each aluminium centre (Scheme 1).<sup>[48a, 48b]</sup> In particular, the reaction with aromatic azide is highly sensitive to the halogen substitution on aluminum, as compound **8b** with bromide substitution led to simple insertion of PhN unit into the Al–Al bond to furnish compound **13**,<sup>[48b]</sup> while **8a** produces rearranged product **14**<sup>[48a]</sup> (Scheme 1). Although, the formation of **14** believed to proceed *via* intermediacy of similar type of insertion product to that of **13**.



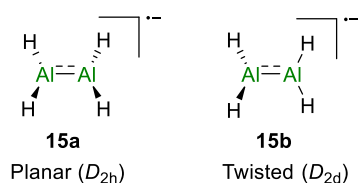
**Scheme 1.** Reaction of unsaturated organic substrates with bis(pentamethylcyclopentadienyl)dialane complexes (**9a**, **9b**).

Recent work from the Jones group reported the isolation of a low oxidation state binary, dianionic aluminium hydride (**10**)  $\{[(\text{DepNacnac})\text{Mg}]_2(\mu\text{-H})\}_2[\text{H}_3\text{Al}-\text{AlH}_3]$  (DepNacnac =  $[(\text{DepNcMe})_2\text{CH}]^-$ , Dep = 2,6-diethylphenyl), which represents the first Al-based compound which is a valence isoelectronic analogue of ethane (Figure 4).<sup>[49]</sup> Compound **10** was obtained in low yields (24 %) as a colourless compound *via* the reduction of the alane complex  $\{[(\text{DepNacnac})\text{Mg}(\mu\text{-H})_3\text{AlH}(\text{NMe}_3)]_2\}$  **11**, with a slight excess of Jones' trademark Mg(I) reagent  $\{[(\text{DepNacnac})\text{Mg}]_2\}$ .<sup>[50]</sup> The Al–Al bond length in **10** is 2.548(1) Å, which lies at the lower end of the Al–Al single bond lengths known so far and is considerably shorter than the Dipp-NHC stabilised parent dialane complex **5** (2.635(8) Å). Moreover, this bond length is also shorter than the theoretically predicted contact ion pair complex,  $\text{Li}_2[\text{H}_3\text{Al}-\text{AlH}_3]$  (2.69 Å).<sup>[51]</sup> The solid state structure of compound **10** revealed a staggered geometry as its lowest energy conformation in contrast to the theoretically predicted eclipsed structure of  $\text{Li}_2[\text{H}_3\text{Al}-\text{AlH}_3]$ .<sup>[51]</sup> It is thought that this discrepancy arises from the steric interactions between the two  $\{[(\text{DepNacnac})\text{Mg}]_2(\mu\text{-H})\}^+$  cations which contributed significantly to such structural distortion in **10**. Furthermore, NBO charge calculations suggested  $\text{Al}_2\text{H}_6$  fragment carries a negative charge of  $-1.24$  e which is mainly localised on the aluminium bound hydrogen atoms, while the Al atoms are positively charged.

### 3. Multiple-bonded ionic dialuminium compounds

#### 3.1. Mono- and dianionic compounds

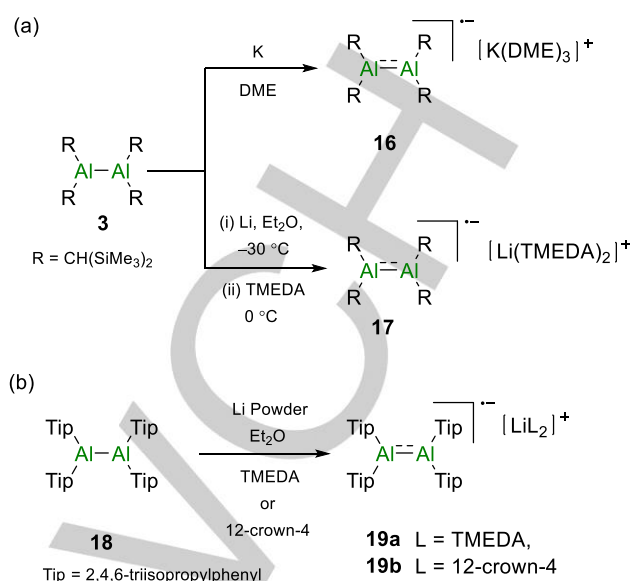
Three coordinated single bonded dialuminium compounds, namely 'dialumanes' of general formula  $R_2Al-AlR_2$ , possess an empty  $p$ -orbital at each Al centre perpendicular to the coordination plane of the metal. In principle, compounds of this type could undergo successive one or two electron reduction to provide mono- or dianionic Al compounds having formal bond orders of 1.5 or 2. In this regard, theoretical calculations by Bridgeman *et al.* showed that one electron reduction of parent dialane  $Al_2H_4$  to form radical monoanionic compound  $[Al_2H_4]^{•-}$  **15** is highly favourable from a thermodynamic point of view due to the large exothermic nature of the reduction reaction (Figure 5).<sup>[52]</sup> Thus, the generated monoanionic complex, upon one electron reduction of neutral parent dialane, prefers a planar conformation (**15a**,  $D_{2h}$ ) due to the extra electron occupying the  $\pi$ -like bonding orbital. This  $\pi$ -stabilisation is sufficient ( $\sim -60$  kJ mol<sup>-1</sup>) to favour the planar structure over the twisted geometry (**15b**,  $D_{2d}$ ), where the same electron essentially fills the non-bonding orbitals (Figure 5).<sup>[52]</sup>



**Figure 5.** Planar and twisted conformation of parent radical monoanionic dialuminium compound  $[Al_2H_4]^{•-}$

As a measure of the theoretical prediction, Uhl *et al.* first attempted the potassium metal mediated reduction of the dialane compound **3**, in dimethoxyethane (DME) (Scheme 2a). This furnished a dark blue solution which contained a radical monoanionic species, **16**  $[(Me_3Si)_2CH]_2Al-Al[CH(SiMe_3)_2]^{•-}$  which was not structurally characterised.<sup>[53]</sup> Similarly, their effort to isolate the same compound with a lithium counter cation instead of potassium, by treatment of compound **3** with neopentyl lithium or (trimethylsilyl)methyl lithium in the presence of TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) also remained unsuccessful.<sup>[53]</sup>

Shortly afterwards, Pörschke group pioneered the isolation of a black-violet coloured radical monoanionic compound  $[(Me_3Si)_2CH]_2Al-Al[CH(SiMe_3)_2][Li(TMEDA)]$  (**17**) as a solvent separated ion pair by direct Li metal reduction of the neutral dialane compound **3** in the presence of alkali metal complexing agent TMEDA (Scheme 2a).<sup>[54]</sup> Concurrently, Power and co-workers also reported the synthesis of a bulky aryl-substituted radical monoanionic species  $[(Tip)_2Al-Al(Tip)_2]^{•-}$  **19a,b**. These were isolated as dark green coloured compounds following an analogous synthetic method to that of Pörschke and co-workers (Scheme 2b) *via* the reduction of a neutral dialane compound  $[Tip_2Al-Al(Tip)_2]$  **18** (Tip = 2,4,6-triisopropylphenyl).<sup>[55]</sup>



**Scheme 2.** Synthesis of one electron  $\pi$ -bonded radical monoanionic dialuminium compounds (**16**, **17** and **19a,b**) *via* alkali metal reduction of the neutral dialane precursors.

The aforementioned results clearly signify the decisive role of counter-cation in isolating these partially double-bonded radical anionic species. SC-XRD structure of compounds **17** ( $d_{Al-Al} = 2.53(1)$  Å) and **19a,b** ( $d_{Al-Al} = 2.470(2)$  Å) showed considerable shortening of the Al–Al bond lengths ( $\sim 6\%$ ) compared to their neutral precursors **3** ( $d_{Al-Al} = 2.660(1)$  Å) and **18** ( $d_{Al-Al} = 2.647(3)$  Å). This substantial decrease of Al–Al bond length is presumably due to accumulation of negative charge density between the Al atoms which partially mitigate the ionic intermetallic  $\delta^+ - \delta^+$  repulsion, thereby drawing the Al centres much closer than anticipated. The EPR spectra measurements of all four compounds (**16**, **17** and **19a,b**) produced a strong 11 line pattern due to the coupling of the unpaired electron with the two equivalent  $^{27}Al$  nuclei ( $I = 5/2$ , 100%). In fact, in compound **16** no hyperfine splitting pattern was observed due to the coupling of the unpaired electron with four  $\beta$ -AICH protons, as the latter attains a dihedral angle of  $90^\circ$  with the SOMO (predominantly constituted of  $\pi$ -orbital), which confirms the unpaired electron mainly resides between the two Al centres. The relatively low value of hyperfine coupling constant values  $a(^{27}Al) = 1.11$ , 1.19 and 1.04 mT of the all four compounds are in line with the location of the unpaired electron in a  $\pi$ -type bonding orbital. Thus, both structural and spectroscopic data unambiguously assigned the one-electron  $\pi$ -bonded nature of the aforementioned radical monoanionic compounds (**16**, **17** and **19a,b**).

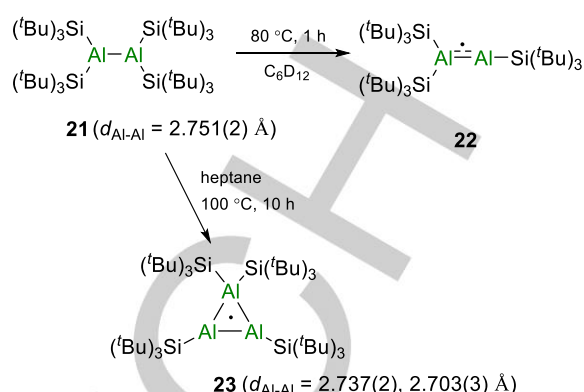
In contrast to the thermodynamically feasible one electron reduction of parent dialane, calculations by Bridgeman and co-workers further highlighted that the addition of a second electron to the monoanionic species  $[Al_2H_4]^{•-}$  to form  $[Al_2H_4]^{2-}$  dianion, isoelectronic to the neutral parent group 14 dimetallenes  $H_2E=EH_2$  (E = group 14 elements), is highly endothermic and therefore energetically unfavourable.<sup>[52]</sup> The instability of the

dianionic species arises presumably from the considerable coulombic repulsion exerted by the two anionic charges occupying the  $\pi$ -symmetry orbital. However, calculations also predicted the cation complexation, which acts to withdraw some electron density from the  $\pi$ -orbitals, could enable the isolation of such dianionic species through stabilisation of the highest occupied molecular orbital (HOMO) by suppressing the coulombic repulsion to a considerable extent.<sup>[52]</sup> It is noteworthy that by transferring two electrons to diborane species, dianionic B=B double bonded compounds owing formal bond order of 2 have been achieved.<sup>[56]</sup> In contrast, dianionic dialuminium compounds of general formula  $[R-Al=Al-R]^{2-}$  are yet to be reported. One notable attempt to achieve such species, was made by Uhl and co-workers in mid 90's through one electron reduction of radical monoanionic species **16** (Scheme 2a) in the presence of excess potassium. However, this attempted reduction only furnished three colorless anionic alkoxy/alkyl-alanate derivatives through the cleavage of dimethoxyethane (DME).<sup>[57]</sup>

Recently, Boldyrev and Bowen groups succeeded in generating a dianion in the form of a  $LiAl_2H_4^-$  cluster **20**, which confirms the formation of a conventional Al=Al double bond through electronic transmutation methodology.<sup>[58]</sup> Through a combination of theoretical calculations and photoelectron spectroscopy, the study confirmed the  $LiAl_2H_4^-$  cluster has a global minimum structure similar to that of  $Si_2H_4$ , which therefore comprises of an Al=Al double bond.

### 3.2. One electron $\pi$ -bonded neutral compounds

The lone example of a one electron  $\pi$ -bonded neutral alanyl radical, was reported by Wiberg in 1998. This was isolated as a black-green coloured compound in the form of a trisupersilyldialanyl  $[(tBu_3Si)_2Al-AlSi(tBu_3)]^\cdot$  radical **22**. This compound was synthesised *via* thermolysis of the neutral dialane  $(tBu_3Si)_2Al-Al(Si(tBu_3)_2)$  precursor **21** in a deuterated cyclohexane solution which was in a sealed NMR tube (Scheme 3).<sup>[42b, 59]</sup> The stability of the dialanyl radical arises presumably due the large steric encumbrance and electronic influence of the  $-Si(tBu)_3$  substituents. However, compound **22** could not be characterised by SC-XRD techniques. Nonetheless, the solution stability of **22** was sufficient to measure an EPR spectrum, this displayed a group of peaks due to the coupling of unpaired electron with the two non-equivalent Al nuclei possessing two- and three coordinate numbers. The observed hyperfine coupling constant values of  $a(Al)$  of 2.18 and 1.89 mT are again consistent with the  $\pi$  character of the unpaired electron at the centre of the two Al atoms. The relatively large values of coupling constants illustrated stronger s-orbital contribution than the radical monoanionic compounds **17** and **19a,b** (Scheme 2). From the above discussion compound **22** can be best described as containing  $sp^2$ - and  $sp$ -hybridised Al atoms, which are connected *via* two-electron  $\sigma$ - and one-electron  $\pi$ -bonds. Further *ab initio* calculations at the RI-DFT level of theory highlighted the dialanyl radical **22** possesses almost a planar  $Si_2AlAlSi_2$  skeleton (sum of angles at Al = 359.7 and 359.3°) with an Al-Al bond length 2.537 Å, which is comparable to that of radical monoanionic compound **17** (2.53(1) Å).



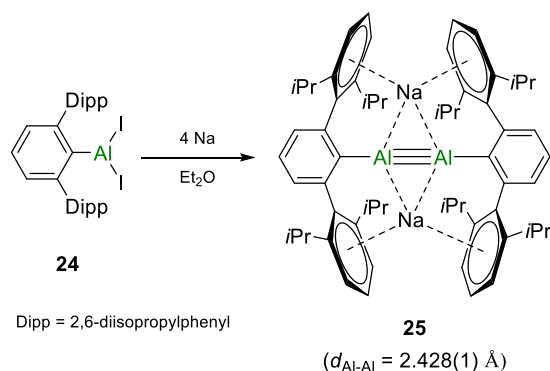
**Scheme 3.** Synthesis of one electron  $\pi$ -bonded neutral aluminium compounds.

Furthermore, heating a solution of **21** at 100 °C in heptane produced a cyclic three-membered radical compound  $[(Si(tBu_3)_4Al_3)]^\cdot$  **23** (Scheme 3).<sup>[59]</sup> As shown by the X-ray crystal structure determination three aluminium atoms occupy the corners of a triangle; one Al atom is connected with two supersilyl ( $-Si(tBu)_3$ ) groups, and the remaining two Al atoms are each bound with one  $-Si(tBu)_3$  substituent. The Al-Al distances are 2.737(2) and 2.703(3) Å. Measurement of the EPR spectrum of compound **23** at room temperature produced group of peaks due to the delocalisation of the unpaired electron across all three Al nuclei, which could not be analysed completely. However, two coupling constants were determined, one at 0.3 mT for the doubly  $-Si(tBu)_3$  substituted Al, whilst the other two Al centres were found at 1.3 mT. The hyperfine structure with such low coupling constant values confirmed predominant  $\pi$ -radical character of **23**.

### 3.3. Dianionic dialumyne and cyclotrialumene

Similar to one electron  $\pi$ -bonded monoanionic compounds, synthesis of Al-Al triple bonded compounds *via* two electron reduction of the donor free dialumene species is an appealing synthetic route. This would open the opportunity to understand the indigenous bonding nature along with their potential usefulness as synthons to acquire various Al based compounds. In 2006, Power and co-workers paved the way for the isolation of the first dianionic compound  $Na_2[ArAlAlAr]$  (**25**) as dark red almost black colour crystals in low yield (20 %). This was achieved through use of the sterically demanding *m*-terphenyl ligand, upon reduction of  $ArAlI_2$  ( $Ar = C_6H_3-2,6-(C_6H_2-2,4,6-Pr_3)_2$ ) (**24**) in the presence of four equivalents of sodium in diethylether (Scheme 4).<sup>[60]</sup> This compound was particularly significant as they claimed the molecule possesses triple bond character and therefore can be regarded as 'dialumyne' which contains a similar structural motif akin to Robinson's "digallyne"  $[Na_2Ga_2(C_6H_3-2,6-Tip_2)_2]$  ( $Tip = 2,4,6$ -triisopropylphenyl).<sup>[33a]</sup> Although, there is considerable debate over the years regarding the triply bonded nature of these compounds.



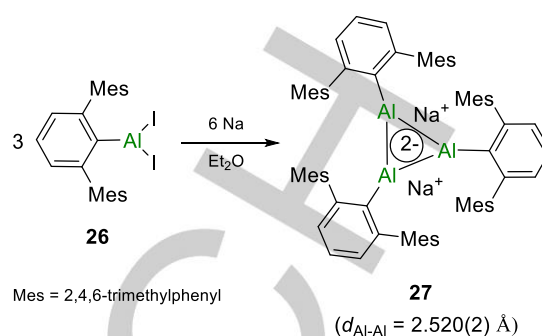


**Scheme 4.** Synthesis of dianionic dialumyne  $\text{Na}_2[\text{ArAlAlAr}]$ , **25**.

X-ray crystallographic analysis revealed compound **25** possesses a *trans*-bent structure [ $\text{C}(\text{Ar})-\text{Al}-\text{Al}-\text{C}(\text{Ar})$  dihedral:  $131.71(7)^\circ$ ] with a local  $\text{C}_{2h}$  symmetry. In the centrosymmetric  $\text{Al}_2\text{Na}_2$  core, two sodium atoms reside on either side of the Al–Al bond and are complexed in an  $\eta^6$  fashion to the flanking aryl groups of *m*-terphenyl ring. The Al–Al bond length is  $2.428(1) \text{ \AA}$  and is considerably longer ( $0.20 \text{ \AA}$ ) compared to the theoretically predicted sum of the triple-bond radii of Al ( $2.22 \text{ \AA}$ )<sup>[61]</sup> and also longer than the Ga–Ga distance ( $2.319(3) \text{ \AA}$ ) in Robinson's "digallyne". DFT calculations revealed that the HOMO-2 is clearly a  $\sigma$ -bond between the Al atoms, whereas the HOMO represents the out of plane  $\pi$  bond. The HOMO-1 designated as nonbonding pair on the Al centre and can be alternatively described as a slipped  $\pi$  bond. This was further evident from the calculated bond order of 1.13 for **25**, which is notably smaller value than the formal bond order of three for a typical triple bonded compound such as alkynes.

Recent theoretical calculations by Meng *et al.* provided some useful information regarding the vital role of the bulky terphenyl substituents and  $\text{Na}^+$  ions.<sup>[62]</sup> The natural bond orbital (NBO) analysis of compound **25** revealed the electron occupancy of these three orbitals (one  $\sigma$  and two  $\pi$ ) are 1.7150, 1.8178 and 1.6619, respectively. The  $\sigma$  bond orbital constitute of 25.92% *s*- and 73.98% *p*-character while the normal  $\pi$  bond is purely composed of the *p*-orbital of Al atoms. The slipped  $\pi$  bond mostly represents the lone pair orbital on each Al atom. The NBO analysis further highlighted the charge distribution on sodium atom is  $+0.6187$ , this indicates that electron density does shifted towards the two sodium atoms, which effectively act as electron donor in **25**, thereby increasing the bond order of the dialuminum fragment.

Use of a relatively less sterically demanding aryl group ( $\text{Ar} = \text{C}_6\text{H}_3-2,6-(2,4,6-\text{Me}_3)$ ) in comparison to the ligand used for the synthesis of the dianionic dialumyne (**25**), allowed for the isolation of a dianionic cyclotrialumene  $\text{Na}_2[(\text{AlAr})_3]$  (**27**). Compound **27** was obtained as red orange crystals under similar reaction conditions to compound **25** (Scheme 5).<sup>[60]</sup> This compound resembles the isoelectronic gallium compounds  $\text{M}_2[(\text{GaAr})_3]$  ( $\text{M} = \text{Na}$  (**28a**),  $\text{K}$  (**28b**)) isolated by Robinson and co-workers,<sup>[63]</sup> the cyclotrisilylenylium ion  $[\text{Si}_3\text{R}_2\text{R}']^+$  ( $\text{R} = \text{Si}^t\text{Bu}_3$ ,  $\text{R}' = \text{SiMe}^t\text{Bu}_2$ ) (**29a**) and the cyclotrigermanium ion  $[\text{Ge}_3\text{R}_3]^+$  ( $\text{R} = \text{Si}^t\text{Bu}_3$ ) (**29b**) published by the Sekiguchi group.<sup>[64]</sup>



**Scheme 5.** Synthesis of metalloaromatic cyclotrialumene dianion  $\text{Na}_2[(\text{ArAl})_3]$ , **27**.

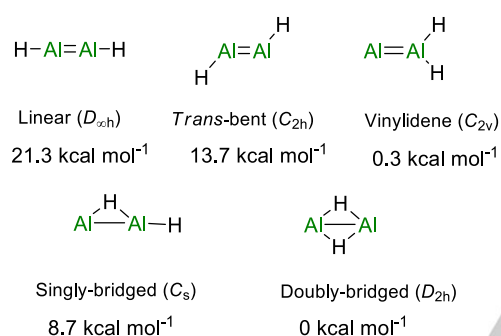
The SC-XRD structure revealed compound **27** comprised of a cyclic triangular  $\text{Al}_3$  core completed by two sodium cations perfectly placed above and below the central  $\text{Al}_3$  ring. Additional stabilisation of the  $\text{Na}^+$  cations arises from the coordination to the flanking mesityl rings. Each Al centre adopts a distorted trigonal planar geometry with Al–Al and Al–Na bond lengths of  $2.520(2)$  and  $3.285(2) \text{ \AA}$ , respectively. This Al–Al bond length is clearly shorter than the corresponding single bond lengths and is comparable to the one electron  $\pi$ -bonded radical compound **17** ( $2.53(1) \text{ \AA}$ ). Moreover, atoms-in-molecules (AIM) analysis revealed a considerable closed-shell  $\text{Na} \cdots \pi$  interaction between the Na atoms and the  $\text{Al}_3$  ring and further stability is provided from the terminal mesityl group on each aryl moiety.<sup>[65]</sup> Furthermore, DFT calculations focused on the model compound,  $\text{Na}_2[(\text{AlAr})_3]$  ( $\text{Ar} = \text{C}_6\text{H}_3-2,6-\text{Ph}_2$ ), which revealed the HOMO-2 is essentially  $\pi$ -orbital delocalised across all three Al centres whilst the HOMO and HOMO-1 represents the Al–Al  $\sigma$ -bonding orbitals. Based upon the number of electrons in the bonding orbital calculations, the formal bond order of the Al–Al bond in compound **27** could be considered as 1.33. However, the calculated WBI value in a geometry-optimised model was found to be 0.88. This low bond order is likely due to the distorted localised geometry caused by the lone pair nature at each of the Al centres coupled with polar-covalent Al–Na interactions. Compound **27** possesses two  $\pi$  electrons delocalised across all three Al atoms, which in principle obeys Hückel's rule of aromaticity in a cyclic molecule. Furthermore, in an effort to provide theoretical perspective on the metalloaromatic character within compound **27**, Li *et al.* calculated Nucleus-independent chemical shifts (NICS) values using the compound  $[(\text{AlH}_3)]^2-$  as a model complex. The observed NICS(1) value of  $-13.7$  clearly indicates the metalloaromatic character (metallic ring exhibiting aromatic character) of the cyclic trinuclear  $\text{Al}_3$  ring compound.<sup>[65]</sup>

## 4. Masked dialumenes: Barrelene type dialumanes

### 4.1. Synthesis and structure

Neutral double-bonded Al compounds defined by the general formula  $\text{R}-\text{Al}=\text{Al}-\text{R}$  remained elusive until very recently.

Synthesis of stable multiply-bonded Al compounds by means of a single substitution on each Al centre poses a formidable challenge due to the highly reactive and unstable nature of such compounds. This can be attributed to a couple of reasons: (i) very weak nature of the double bond stems from the manifestation of lone pair electron density on the orbitals comprising of Al–Al bond and (ii) presence of a vacant orbital on each Al rendered them highly reactive. Nonetheless, employing sterically demanding substituents such dimeric derivatives R–M=M–R (M = Ga,<sup>[66]</sup> In,<sup>[67]</sup> Tl<sup>[68]</sup>) of the other heavier group 13 complexes have been successfully isolated. Although, these results are in complete contrast to the computed bond dissociation energy of the dimers relative to the two monomeric :MH units which showed 10.3 kcal mol<sup>-1</sup> for Al compared to the 3 kcal mol<sup>-1</sup> for Ga–Tl.<sup>[69]</sup> This family of dimeric compounds possess *trans*-bent structures with long M–M bonds, which dissociate to the corresponding monomer in hydrocarbon solvents, emphasising the extremely weak nature of these double bonds.

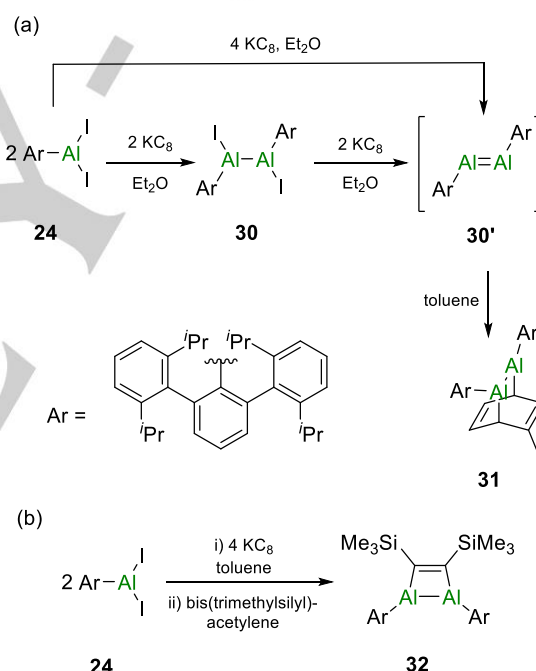


**Figure 6.** Schematic presentation of configurational isomers of Al<sub>2</sub>H<sub>2</sub> (relative energies are provided at the SCF level of theory).

To uncover the bonding features, computational studies on idealised model compounds of Al bearing hydrogen substituents were performed. The bonding in Al<sub>2</sub>H<sub>2</sub> can be best described as depicted in Figure 6. Considerably high singlet-triplet energy gap ( $\Delta E_{ST} = 28$  kcal mol<sup>-1</sup>)<sup>[69]</sup> forces parent alumylene :AlH fragment to prefer a singlet ground state over the triplet state. Therefore, in order to form a double bond two alumylene fragments interact in such a way that lone pair orbital of one fragment donates its electron density into the vacant *p*-orbital of other fragment, resulting in the formation of non-classical *trans*-bent geometry (C<sub>2h</sub>) at each Al centre (Figure 2). Calculations further revealed that *trans*-bent structure is 16 kcal mol<sup>-1</sup> more stable than the linear form (Figure 6).<sup>[69]</sup> In fact, none of the configurations represent local minima in the potential energy surface (PES) diagram (Figure 6). Doubly hydrogen bridged (D<sub>2h</sub>) isomer (Figure 6) is the global minimum on the PES. The calculated Al–Al bond distance in the *trans*-bent structure of parent dialumene is predicted to be 2.613 Å which typically lies in the range of single-bonded dialuminium compounds and 0.3 Å longer than the linear form (2.322 Å).

The first attempt to isolate double-bonded Al compound *namely* 'dialumene', was reported by Power and co-workers.

The reaction was performed in a similar manner to other heavier group 13 elements (Ga, In & Tl)<sup>[66, 67b, 68b]</sup> employing the highly sterically demanding *m*-terphenyl ligand system *via* reductive dehalogenation of aryl diiodoalane Ar–AlI<sub>2</sub> (**24**).<sup>[70]</sup> However, unlike the other cases (Ga–Tl), this reaction only led to the unprecedented formation of the bicyclo adduct (**31**) rather than much coveted dialumene (Scheme 6a). They suggested that reductive dehalogenation led to transient formation of intermediate dialumene Ar–Al=Al–Ar (**30**), which subsequently reacts in a formal [4+2] cycloaddition manner with solvent toluene to furnish the bicyclo adduct **31** (Scheme 6a). SC-XRD structure of compound **31** showed a Al–Al bond length 2.5828(7) Å, which is well within the range of normal Al–Al single bond lengths. Each Al atom adopts almost trigonal planar coordination environment with sum of bond angles being 359.25(6)° and 358.55(6)°. The low torsion angle of 24.5° pertaining to the C(Ar)–Al–Al–C(Ar) fragment clearly indicates two bulky *m*-terphenyl group (Ar) adopts a *cis*-orientation with respect to the Al–Al bond axis.

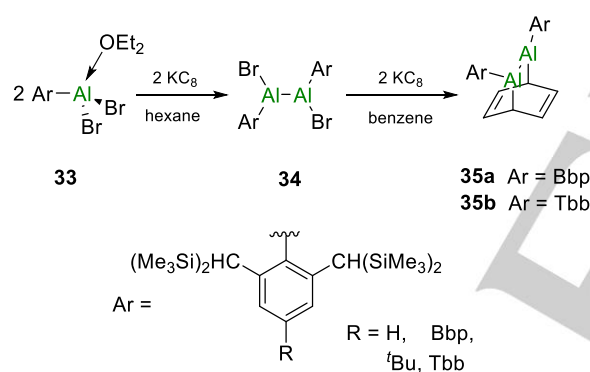


**Scheme 6.** Synthesis of formal [4+2] cycloaddition products from the incipient dialumene **30'** with toluene and (bis)trimethylsilylacetylene.

3 years later Cui *et al.* also trapped the intermediate dialumene in the form of a four-membered ring, 1,2-dialuminacyclobutene (**32**). This four-membered ring compound was isolated as orange-red crystals upon facile reductive dehalogenation of the diiodoalane (**24**) in the presence of (bis)trimethylsilylacetylene (Scheme 6b).<sup>[71]</sup> The <sup>29</sup>Si and <sup>13</sup>C NMR spectrum of the Me<sub>3</sub>SiCCMe<sub>3</sub>Si fragment in the four-membered ring appears at  $\delta = -13.2$  and 235 ppm, for Me<sub>3</sub>Si- and olefinic carbon respectively. X-ray structure showed the folded ring structure of compound **32**. The three-coordinate Al centres acquire slightly pyramidal geometry (sum of bond angles

around Al: 351.75 and 353.22°) with a considerably short Al–Al bond length (2.4946(9) Å), which is comparable to that found in the anionic radical compound [(Tip)<sub>2</sub>Al–Al(Tip)<sub>2</sub>]<sup>−</sup> **19** (2.470(2) Å). To explain the folded ring structure in **32**, theoretical calculations on the parent compound (HAl)<sub>2</sub>(CH)<sub>2</sub> were performed, this predicted a nearly planar geometry of the latter. Such puckering of the four-membered ring in **32** can be attributed to the presence of sterically demanding SiMe<sub>3</sub> and bulky aryl-groups which force the four-membered ring to deviate from planarity. The calculated HOMO is mainly located at the olefinic fragment of the ring, whereas the LUMO mainly constitutes of the empty Al 3p-orbitals with a significantly small HOMO-LUMO energy gap (13.4 kJ mol<sup>−1</sup>).

In 2013, following an analogous synthetic method to that of Power, Tokitoh and co-workers isolated the dialumene-benzene adduct, **35**. Compound **35** was isolated as air- and moisture-sensitive red crystal (100 % yield) via K<sub>2</sub>C<sub>8</sub> mediated reductive dehalogenation of 1,2-dibromodialumane **34** in benzene (Scheme 7).<sup>[42e, 72]</sup> The <sup>1</sup>H NMR spectra of both compounds (**35a**, **35b**) revealed the existence of an intermolecular exchange equilibrium between the adduct C<sub>6</sub>H<sub>6</sub> and solvent C<sub>6</sub>D<sub>6</sub>. Compound **35** features a similar structure to that of **31** (Scheme 6a) with a slightly shorter Al–Al bond length (2.5552(19) Å).

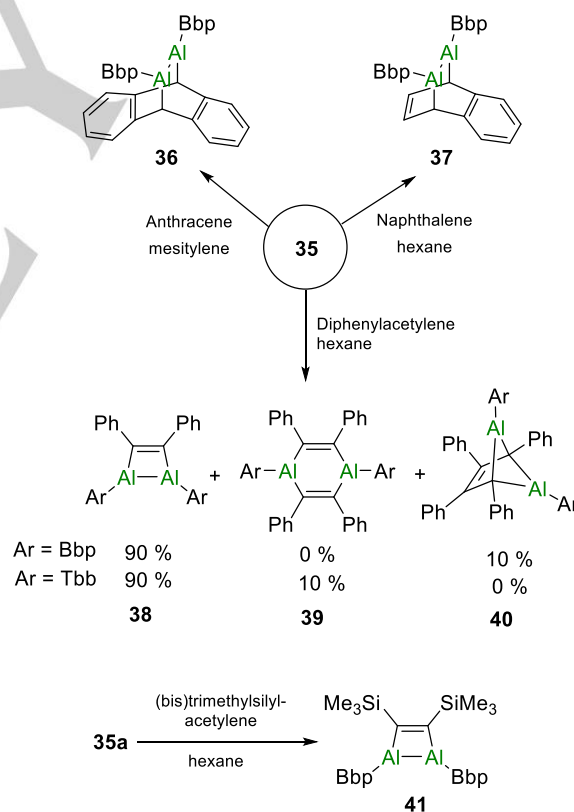


Scheme 7. Synthesis of barrelene type dialumanes **35a,b**.

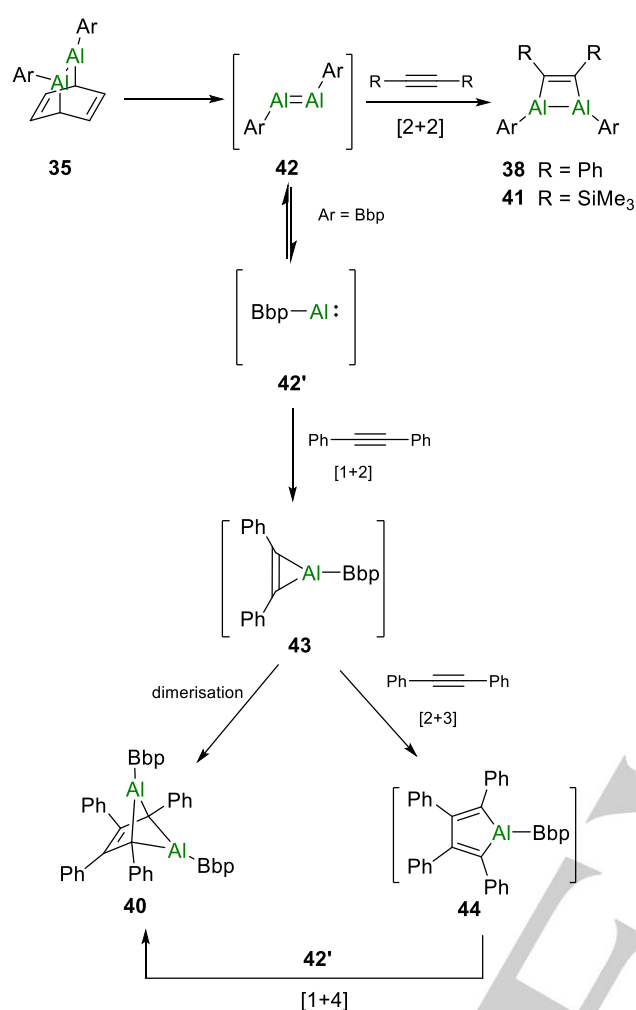
#### 4.2. Reactivity of barrelene type dialumanes as a synthetic equivalent of dialumene

Arguably, the utmost potential of bicyclo adducts **35a,b** are to serve as masked dialumenes, thereby providing potential access to various novel organoaluminium compounds. Existence of an intermolecular exchange equilibrium between the adduct C<sub>6</sub>H<sub>6</sub> and solvent C<sub>6</sub>D<sub>6</sub> in **35** allowed for exploration of its reactivity towards various unsaturated organic substrates such as internal alkynes,<sup>[72, 73]</sup> isonitriles<sup>[74]</sup> and aromatic compounds.<sup>[72]</sup> Reaction with aromatic compounds, particularly, with anthracene and naphthalene afforded arene exchange products **36** and **37**, respectively and both compounds were isolated as orange coloured compounds in excellent yields (Scheme 8).<sup>[72]</sup> On the other hand, reaction of **35** towards internal alkynes produced a variety of products depending upon the substitution pattern on both the Al centre and the alkyne

fragments. In the case of bis(trimethylsilyl)acetylene, the C<sub>6</sub>H<sub>6</sub> moiety of **35a** was smoothly exchanged to furnish the 1,2-dialuminacyclobutene (**41**) as the sole product (Scheme 8).<sup>[72]</sup> The reaction of Bbp-substituted dialumane with diphenyl acetylene produces the novel 5,6-dialuminabicyclo[2.1.1]hex-2-ene (**40**) as the minor product, in addition to the formal [2+2] cycloaddition product 1,2-dialuminacyclobutene (**38**) was isolated as the major component (Scheme 8).<sup>[73a]</sup> Additionally, the stoichiometry of the reagents and reaction conditions has a profound influence on the final product distributions. Use of 2:1 ratio of diphenylacetylene to **35** produces the 1,2-dialuminacyclobutene (**38**) as a sole component at room temperature, whilst increasing the reaction temperature to 50 °C favours the formation of **40** as the major product which possesses a tetracarba-nido-hexaalumane skeleton. In contrast, treatment of Tbb-substituted dialumane with diphenylacetylene produces a mixture of 1,2-dialuminacyclobutene **38** (90 %) and 3,6-dialuminacyclohexadiene **39** (10 %) (Scheme 8).<sup>[73b]</sup> The reaction mechanism for the formation of **40** remains unclear. Nonetheless, a reaction mechanism was proposed (Scheme 9) although no theoretical or experimental proof has been provided in support the reaction mechanism.



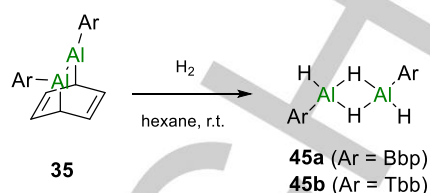
Scheme 8. Reactions of barrelene type dialumanes **35** with internal alkynes and aromatic compounds.



**Scheme 9.** Proposed reaction mechanism between internal alkynes and barrelene type dialumenes **35**.

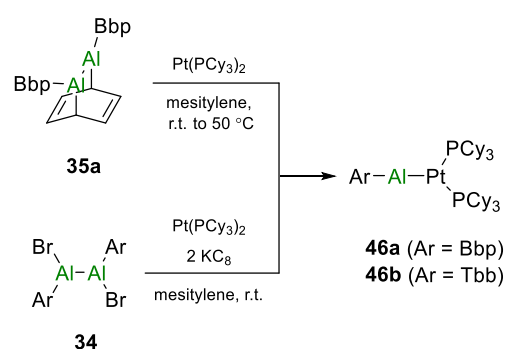
Apart from the reactivity of masked dialumenes (**35a,b**) with unsaturated organic compounds, they have also been shown to undergo metal catalyst free facile cleavage of dihydrogen at room temperature to furnish dihydrodialumane dimers as colourless compounds **45a,b** in quantitative yields (Scheme 10).<sup>[75]</sup> The <sup>1</sup>H NMR spectra for both compounds appear as broad signals which correspond to the Al bound hydrogen atoms (**45a**:  $\delta_{\text{H}} = 4.49, 4.88$  ppm and **45b**:  $\delta_{\text{H}} = 4.49, 4.89$  ppm). SC-XRD structure revealed a centrosymmetric dimeric core of **45** with two Al atoms bridged by two H atoms. The Al–Al distance is 2.632(1) Å comparable to the reported dihydroalumane dimer [Mes\*HAl( $\mu$ -H)]<sub>2</sub> (2.652(2) Å) (Mes\* = 2,4,6-(<sup>t</sup>Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).<sup>[76]</sup> The bridging and terminal Al–H distances are (1.72(2), 1.68(2) Å and 1.60(2) Å respectively. The solid-state ATR-IR spectra showed strong Al–H<sub>terminal</sub> vibrational absorption bands at 1870 cm<sup>-1</sup> (**45a**), 1872 cm<sup>-1</sup> (**45b**) and the corresponding bridging hydride appears at 1356 cm<sup>-1</sup> (**45a**), 1358 cm<sup>-1</sup> (**45b**). These values are in accordance with the calculated values corresponding to the geometry optimised

structure of both compounds ( $\nu_{\text{Al-Hterminal}} = 1922$  cm<sup>-1</sup>,  $\nu_{\text{Al-H-Al}} = 1420$  cm<sup>-1</sup>).



**Scheme 10.** Room temperature dihydrogen activation by masked dialumenes **35**.

Reaction of diaryldialumene-benzene adduct **35a** with the 14 electron transition metal complex Pt(PCy<sub>3</sub>)<sub>2</sub> furnished terminal arylaluminum complex of platinum [Bbp-Al-Pt(PCy<sub>3</sub>)<sub>2</sub>] **46a** as dark red compounds (Scheme 11).<sup>[77]</sup> Alternatively, the alumylene **46a,b** complexes could be achieved through the reduction of 1,2-dibromodialumanes (**34**) Ar(Br)Al–Al(Br)Ar (Ar = Bbp, Tbb) in the presence of [Pt(PCy<sub>3</sub>)<sub>2</sub>] (Scheme 11).<sup>[77]</sup> Both complexes show moderate thermal stability in the solid state, however, they decompose in solution even at –35 °C to produce complicated reaction mixtures containing [Pt(PCy<sub>3</sub>)<sub>2</sub>] and PCy<sub>3</sub>. The <sup>31</sup>P NMR spectra of compounds **46a** and **46b** appear at  $\delta = 69.9$  ppm (<sup>1</sup>J<sub>Pt</sub> = 4015 Hz) and  $\delta = 69.8$  ppm (<sup>1</sup>J<sub>Pt</sub> = 4033 Hz) respectively, which are downfield shifted compared to Pt(PCy<sub>3</sub>)<sub>2</sub> ( $\delta = 62.3$  ppm, <sup>1</sup>J<sub>Pt</sub> = 4160 Hz). SC-XRD structure confirmed the two coordinate environment around the Al centre with an almost linear C<sub>Ar</sub>–Al–Pt fragment for **46a** (179.2(2)°) whilst a slightly bent fragment was observed for **46b** (173.96(14)°). The Al–Pt bond distances are 2.2857(18) (**46a**) and 2.2829(13) Å (**46b**) and represents the shortest Pt–Al bond distances reported so far. DFT calculations showed a small WBI (0.59), thus indicating the highly ionic nature of Al–Pt bond, which predominantly constituted from the overlap of the 3s(Al) and 6s(Pt) orbitals. Additionally, energy decomposition analysis confirmed mainly electrostatic nature of the Al–Pt bond, which contributes 74.0% of the total attractive interaction between Ar–Al and Pt(PCy<sub>3</sub>)<sub>2</sub> moieties.

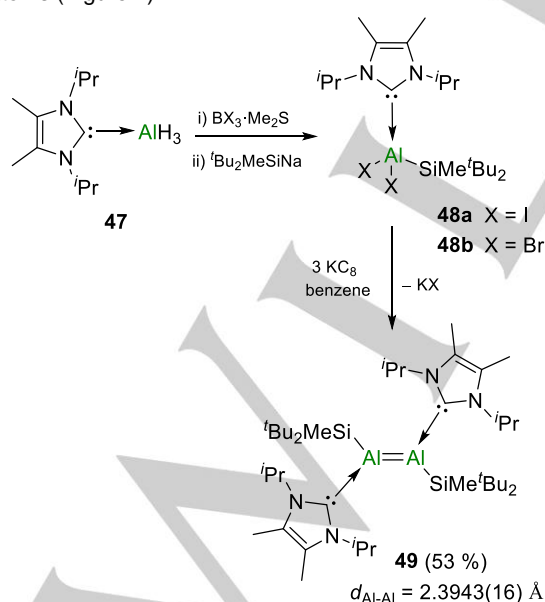


**Scheme 11.** Synthesis of Pt(PCy<sub>3</sub>)<sub>2</sub> stabilised two coordinate arylaluminum complexes **46**.

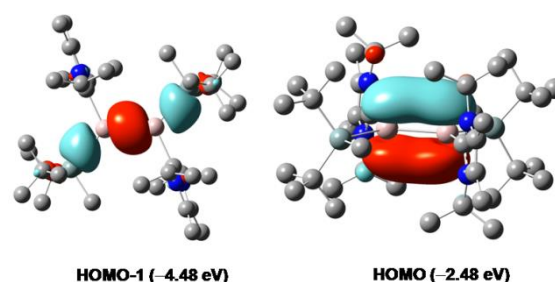
## 5. NHC-stabilised neutral dialumene

In the previous section we discussed the highly reactive nature of substituted neutral dialumene featuring an Al=Al double bond rendered them a notorious synthetic target. Theoretical calculations by Frenking *et al.* predicted that invoking the coordination of an external base such as NHCs, dialumenes of general formula  $\text{Al}_2\text{H}_2$  and  $\text{Al}_2\text{Cl}_2$  could be realised through fulfillment of the octet on each Al centre.<sup>[78]</sup> These calculations also highlighted that chloro-substituted derivatives feature longer Al–Al bonds (2.494 Å) compared to the hydrogen-substituted one (2.444 Å).

In fact very recently, our group has maneuvered the landmark synthesis of the first neutral dialumene through a two-step synthetic protocol. Sterically demanding di-*tert*-butyl(methyl)silyl groups were employed for kinetic stabilisation and  $\text{IPr}_2\text{Me}_2$  acts as external electron donor with the aim that the combination of both of these will “force” the *s*- and *p*- valence electrons of Al to hybridise and form homodinuclear double bond in order to fulfill the octet rule. The first step of the synthetic methodology involves the synthesis of the di-*tert*-butyl(methyl)silyl-substituted Al(III) dihalide precursors with coordinated NHC **48a,b** which can be obtained in good yields. Subsequently, the  $\text{KC}_8$  reduction of these Al(III) dihalide precursors led to the isolation of the dark purple coloured, crystalline, neutral dialumene **49** in moderate yields (53%) (Scheme 12).<sup>[36]</sup> SC-XRD structure analysis revealed that the dialuminium entity possesses *trans*-planar geometry and an Al–Al bond length of 2.3943(16) Å, which is the shortest distance reported for a molecular dialuminium species thus far. Each Al atom adopts an almost trigonal planar coordination environment (sum of the angles at Al: 359.99°). The DFT calculations showed that the HOMO-1 is essentially an Al–Al  $\sigma$ -bond, whereas the HOMO clearly demonstrates the Al–Al  $\pi$ -bond between the two Al atoms (Figure 7).

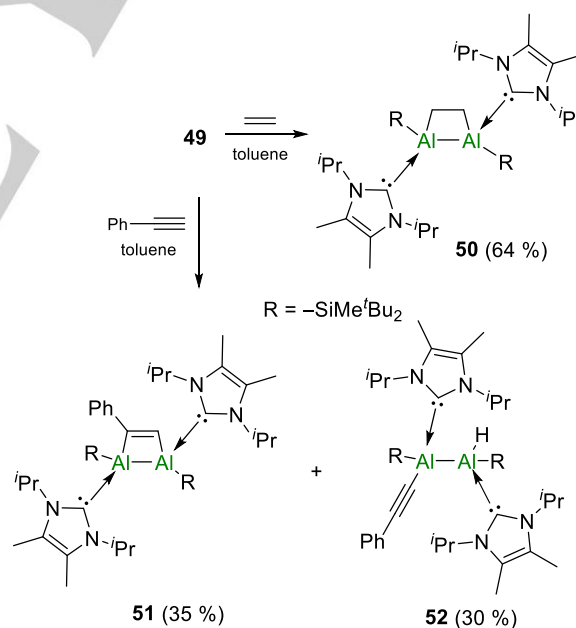


**Scheme 12.** Synthetic method for NHC-stabilised neutral dialumene, **49**.



**Figure 7.** Representation of the HOMO-1 and HOMO of neutral dialumene **49**.

The dialumene (**49**) was found to react with unsaturated organic substrates, such as ethylene and phenylacetylene to produce the four-membered rings **50** and **51** upon [2+2] cycloaddition, as well as a CH-activation product **52** (Scheme 13).<sup>[36]</sup> Solid state structure analyses of **50-52** revealed considerable elongation of the Al–Al bond lengths (2.6503(10) Å, 2.6363(11) Å and 2.6411(9) Å) compared to the dialumene **49** (2.3943(16) Å). All these bond lengths lie in the typical range of Al–Al single bonds (2.50–2.95 Å). Further, calculated WBI of compounds **50-52** were found to be 0.8274, 0.8521 and 0.8938, respectively, which are almost half of that obtained for compound **49** (WBI = 1.703). This further demonstrated the double bonding nature of compound **49**.



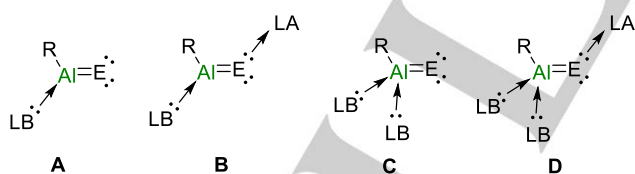
**Scheme 13.** Reactivity of neutral dialumene **49** towards ethylene and phenylacetylene.

## 6. Aluminium heterodiatomic multiple bonds

In terms of Al-E bonding (where E = s,<sup>[79]</sup> p,<sup>[44b]</sup> d<sup>[80]</sup> or f<sup>[81]</sup> block metal) there are many examples featuring heterodiatomic single bonds. Several of these compounds have relied upon the use of compounds **1** and **2** for the formation of Al-E bond formation due to the highly Lewis acidic nature of these compounds. In the case of **1** the monomeric Cp\*Al is considered to be isolobal to CO or PR<sub>3</sub>,<sup>[44b]</sup> therefore its strongly donating ability has led to many complexes with transition metals and the first examples of Al-f-block metal bonds. Despite this large number of structurally characterised examples (CCDC > 700), only a handful of compounds contain multiple bonds between Al and another metal are reported so far, these will be discussed in the following section.

### 6.1. Aluminium chalcogen multiple bonds

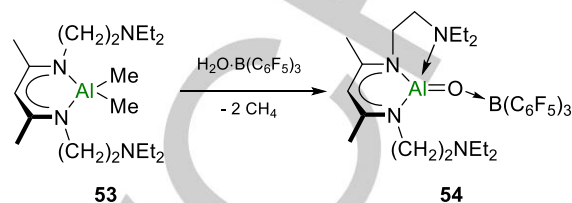
Heterodinuclear multiple bonds of the general formula L-Al=E (L = monoanionic ligand, E = chalcogen) are of great synthetic interest, currently these are limited to a few examples within the literature.<sup>[29]</sup> This is due to the large differences in electronegativities between the group 13 and 16 elements which results in highly polarised bonds and therefore increases propensity of self-oligomerisation to yield compounds of the type (RAIE)<sub>n</sub>.<sup>[11, 82]</sup> It is, however, this desire to form aggregates that makes aluminium-chalcogenides widely used in the materials industry and the ability to synthesis molecular analogues is widely sort after in order to probe the aggregation process which may lead to the development of new materials. There are a variety of different approaches to prevent this self-quenching which will be discussed within this section, an overview of the possible methods is depicted in Figure 8. The parent entity, LAIE, may be obtained through the use of very sterically demanding ligands to prevent dimerisation or oligomerisation, an alternate approach would be through the use of a combination of Lewis acids and bases to provide additional stability to the desired complexes.



**Figure 8.** Different proposed structures for the Lewis acid/base stabilised aluminium chalcogen multiple bonds.

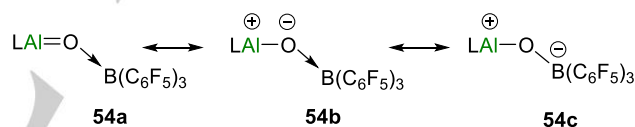
In 2002 the first isolable compound with formal Al=E bond was reported by Roesky and co-workers, this utilised a simple protonolysis route to yield a complex of the form LAI=E(LA) (Figure 8, type B).<sup>[83]</sup> As it had been previously shown that aluminium oxygen bonds could be formed through controlled addition of water to organoaluminium complexes, use of the Lewis base water adduct (H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) with compound **53** resulted in the formation of the desired compound **54** with loss of methane (Scheme 14). Additional stability of this compound

arises from the use of pendant amine arm within the β-diketiminato ligand scaffold. The amine tether is also able to coordinate to the Al centre providing a tetracoordinate Al centre, rather than a coordinatively unsaturated 3-coordinate Al complex. The Al–O bond length of 1.659(3) Å in **54** is the shortest known Al–O bond for a 4-coordinate Al centre.



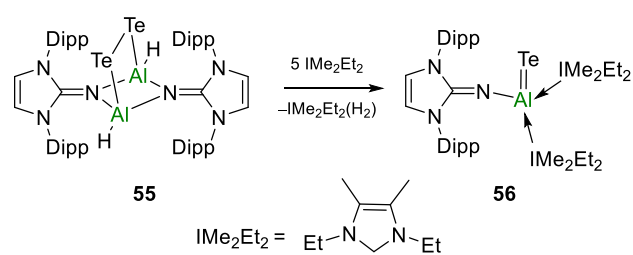
**Scheme 14.** Synthesis of the first Monoalumoxane, LAIO·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, **54**.

The isolation of this compound was considered to be the first example of a monomeric member of the (RAIO)<sub>n</sub> series. Due to the presence of the Lewis acid in the stabilisation of the Al=O bond, some debate has centred around the true bond order of this complex. Resonance forms of compound **54** can be drawn (Scheme 15) this shows considerable double bond character in **54a** however; **54b** and **54c** show the removal of electron density from the oxygen atom through dispersion of the negative charge across the boron atom thus implying more single bond character between Al and O. Therefore, isolation of a acceptor free terminal Al=O double bond is yet to be reported.



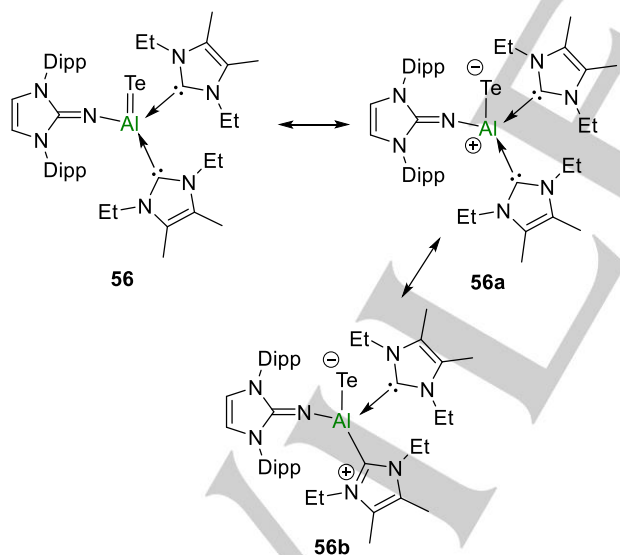
**Scheme 15.** Resonance forms of monoalumoxane, LAIO·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, **54**.

The first reported complex containing a terminal aluminium chalcogenide bond, was reported by our group.<sup>[84]</sup> This featured a N-heterocyclic imine (NHI) supported Al–Te complex with further stabilisation from NHC ligands. The parent ditopic aluminium ditelluride (**55**) was found to react with 5 eq. of NHC (NHC = 1,3-diethyl-4,5-dimethyl-imidazolin-2-ylidene) resulting in a dehydrogenative redox process to yield the monotopic aluminium telluride multiply bonded complex (compound **56**, Scheme 16). This is stabilised by the presence of two Lewis basic NHC donor ligands and therefore fits with compounds of type C in Figure 8. Structural analysis through X-ray crystallography revealed a short Al–Te bond distance of 2.5130(14) Å, in comparison to other known Al–Te containing complexes.



**Scheme 16.** Synthesis of aluminium telluride multiple bond, compound **56**.

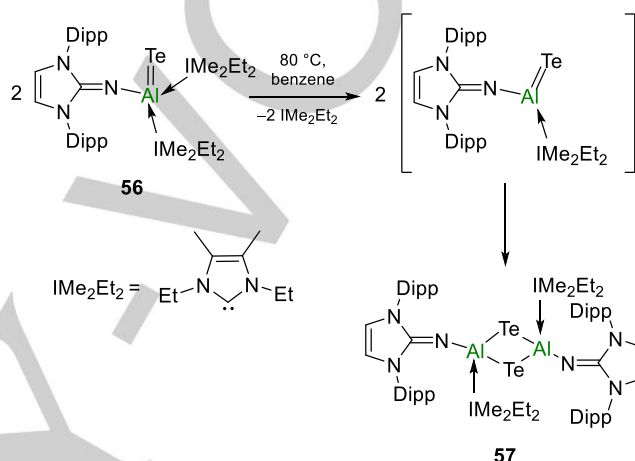
Computational analysis provided a WBI of 1.20 for Al–Te bond in compound **56**, which indicates significant multiple-bond character if the strong polarisation along the AlTe bond vector is taken into consideration. Molecular orbital analysis further indicated a higher order of bonding as the HOMO comprised of a lone pair with  $\pi$ -symmetry at the Te atom and the HOMO-1 showed a  $\pi$ -symmetric orbital lobe that expands between the Al and Te centres. It is the latter that points towards the likely double-bond character of Al–Te bond. Use of Natural Resonance Theory (NRT) provided three main resonance forms as depicted in Scheme 17. The major contribution resided in compound **56** (77%) with the remaining minor share (23%) residing in the zwitterionic species **56a** and **56b** which contain a Al–Te single bond, further supporting the identification of a terminal Al–Te multiple bond.



**Scheme 17.** Selected resonance structures of aluminium telluride **56**.

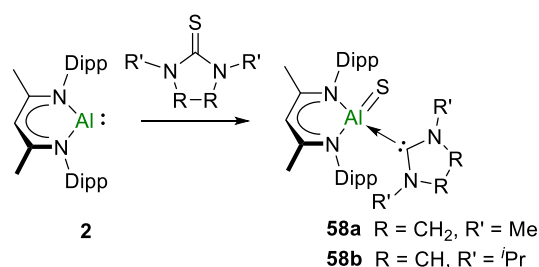
Further experimental evidence for the nature of the bonding in compound **56** was initially based on group 16 metals propensity to form aggregates, therefore a benzene solution of **56** was heated to 80 °C (Scheme 18). This resulted in the loss of NHC upon forming the dimeric Te bridged complex **57**. SC-XRD showed elongation of the Al–Te bonds to 2.6143(14) Å and

2.6211(15) Å further supporting the multiple bond character of Al–Te in compound **56**. WBI analysis of **57** calculated the AlTe interaction to be 0.75, which is considerably different for the calculated value of 1.20 for **56**. Thus, confirming the differences in single and double bonding in the two compounds. Whilst not experimentally proven, the theoretically proposed intermediate in this dimerisation mechanism provides a 3-coordinate terminal Al=Te bond. This remains a challenging synthetic target as to the best of our knowledge, no examples of 3-coordinate Al=Te multiple bonding exist.



**Scheme 18.** Dimerisation of compound **56** towards the Al–Te bridged complex **57**.

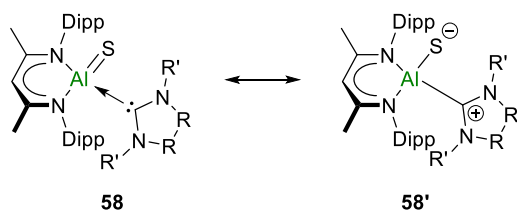
The only other report of a terminal aluminium-chalcogen double bond was reported recently by Nikonov and co-workers.<sup>[85]</sup> Utilising Roesky's Al(I) complex (**2**) reaction with a cyclic thiourea (Scheme 19), resulted in the oxidative addition to the Al centre with subsequent C=S bond cleavage to yield a terminal Al=S bond (**58**). Compound **58** comprises of a 4-coordinate Al centre, from use of the bidentate  $\beta$ -diketiminato (nacnac) ligand, terminal sulphide and the fourth coordination site occupied by the resulting carbene, with Al in the most stable +3 oxidation state.



**Scheme 19.** Synthesis of a terminal aluminium sulphide multiple bond, compound **58**.

Structural analysis revealed the short Al=S bond length of 2.104(1) Å, which is considerably shorter than the average Al–S single bond length of 2.289 Å further supporting the multiple

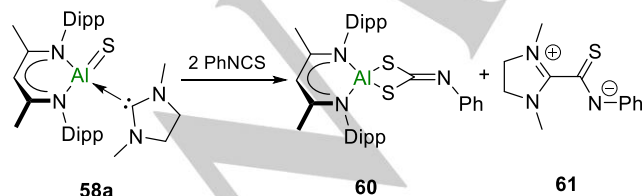
bond character of these compounds. The double bond character was further supported by examination of Mayer bond orders (Al–S 1.49) and WBI (Al–S 1.20). Consideration of the Al–NHC bonding was also examined through use of Mayer bond orders (Al–C = 0.48) this small value supports the case of the dative bonding depicted in Scheme 19, and that the Al–C interaction is mainly electrostatic in nature. Examination of the HOMO further supports the double bonding nature of the Al–S bond, as this corresponds largely to the sulphur lone pairs whilst also containing a significant contribution from Al  $p$ - $\pi$  orbital.



**Scheme 20.** Two resonance structures of compound **58**.

Using the method outlined by Bridgeman *et al.*<sup>[86]</sup> the calculated  $s$ - and  $p$ - components of the Mayer bond order were comparable ( $L_2Al=S$ : 0.89 and 0.86 respectively). Coordination of the NHC marginally decreases the  $s$ -bond order (0.81) and a noticeable reduction in the  $p$ -bond character is also observed (0.68). Combination of SC-XRD data and DFT calculations allowed for the determination of two resonance forms (Scheme 20), again the major conformer **58** is believed to be the best representation of the observed bonding in comparison to the zwitterionic form **58'**.

Extension of this chemistry to  $Ph_3P=S$  (triphenylphosphine sulphide) reagents also provided oxidative-cleavage reactivity. This required the use of 2 eq. of  $Ph_3P=S$  and resulted in the unexpected formation of  $LAl=S(SPh)_3$  **59** ( $L = \beta$ -diketiminato) however this compound was found to be thermally unstable above  $-30^\circ C$  as formation of the previously known sulphide bridged dimer occurs. Further reactivity carried out in this paper focussed on underpinning the multiple bond character of **58** through reactivity with phenyl isothiocyanate ( $PhNCS$ ). Reaction of **58a** with 2 equivalents of  $PhNCS$  resulted in the formation of the cycloaddition product (**60**) and concomitant production of a zwitterion (**61**), due to the reaction of the free NHC with  $PhNCS$  (Scheme 21).



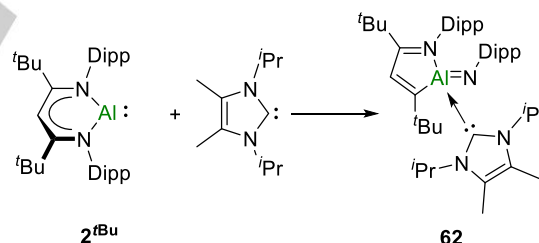
**Scheme 21.** Cycloaddition of  $PhNCS$  with the terminal aluminium sulphide complex **58a**.

To the best of our knowledge, no further examples of  $Al=Ch$  ( $Ch =$  chalcogen) multiple bonds are reported. Still of keen synthetic interest is the isolation of a donor/acceptor free terminal  $Al=O$  bond and other heavier chalcogen containing complex.

## 6.2. Aluminium pnictogen multiple bonds

Extension of this chemistry to the analogous group 15 (pnictogen) series has also proved synthetically challenging. Compounds containing group 13–15 bonds, particularly group 13–nitrogen bonds, have attracted considerable interest over recent years due to their material properties and potential application. Boron–nitride ceramics have a considerably high thermal stability and have many potential applications in nanotechnology industry due to it forming a similar structure to that of graphene but with very different properties.

Monomeric heavier group 13 iminometallanes ( $M = Ga, In$ ) have been reported by Power and co-workers, and were possible through the use of the bulky terphenyl and  $\beta$ -diketiminato ligands.<sup>[25e, 41a, 87]</sup> In terms of iminoalane complexes, a few initial attempts reported by Roesky and co-workers implied the existence of aminoalane, however these could not be structurally verified.<sup>[88]</sup> Cui and co-workers reported the first, and only, monomeric iminoalane complex **62** (Scheme 22).<sup>[89]</sup> This was prepared through the reaction of a larger version of Roesky's  $Al(I)$  complex (**2<sup>tBu</sup>**), this compound contains *tert*-butyl groups in the  $\beta$ -position. Upon reaction with a Lewis basic NHC, the supporting  $\beta$ -diketiminato ligand undergoes a ring contraction to provide a 4-coordinate Al centre.

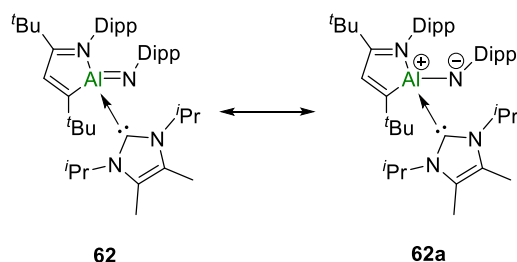


**Scheme 22.** Synthesis of a monomeric iminoalane compound, **62**.

The X-ray structure revealed a short Al–N bond length of  $1.705(2) \text{ \AA}$ , which is considerably shorter than the average reported Al–N bond lengths which are  $>1.85 \text{ \AA}$  for 4-coordinate aluminium amides. In comparison to the calculated value for the parent quasilinear iminoalane (average  $1.65 \text{ \AA}$ ) the Al–N bond is longer in compound **62**, thus leading to suggestions of multiple bond character within **62**. Natural Bond order (NBO) analysis of **62** indicated a low lying Al–N imide bond which was strongly polarised towards the nitrogen atom (94.4%). This is formed by the  $sp^3$  hybrid orbital of the Al atom with one of the two lone pairs of the  $sp$ -hybridised N atom. A large positive NBO charge of Al (1.76135) and negative charge on the imide N atom ( $-1.20923$ ) indicate a significant ionic component to the Al–N bond. Overall this indicates that the Al–N imide bond consists of a highly polarised  $\sigma$ -bond and additional ionic component.



Consideration of the resonance forms depicted in Scheme 23, the bonding in **62** may best be described as the zwitterionic form **62a**.



**Scheme 23.** Resonance forms of compound **62**.

Preliminary reactivity studies towards CO, PhCCH and PhNH<sub>2</sub> found **62** to be extremely reactive. In the case of CO a cyclic structure was obtained through the resulting Al=N cleavage and C–C and C–N coupling reactions, whilst simple addition reactions were identified in the reactions with PhCCH and PhNH<sub>2</sub>. These reactions confirmed the presence of a Al=N multiple bond, and showed that it was highly reactive. Despite this initial progress in this field of Al–pnictogen bonding this compound **62** remains the only structurally characterised example.

## 7. Conclusion and outlook

This review presents the comprehensive treatment of multiple-bonded aluminium compounds. Some of these compounds show exotic reactivity towards small molecule activations as well as exchange reactions. From the above discussion, it is clear that the isolation of multiple-bonded compounds containing aluminium is experimentally challenging and intellectually intriguing. Consequently, this particular field of chemistry still remains at the early stages of development compared to plethora of analogous boron compounds reported along with their versatile reactivity.<sup>[32b]</sup> With the advent of the seminal dianionic dialumyne Na<sub>2</sub>[ArAlAlAr] complex, which is believed to possess a formal bond order of 3, aluminium multiple bond chemistry is undergoing a renaissance. Particularly, the recent isolation of dialumene **49** and Al(I) anion **4** will likely fuel the growth of low oxidation state Al chemistry. Nonetheless, a lot of long-standing exciting multiple-bonded aluminium compounds such as Al<sub>2</sub>, Al=E (E = group 14, 15 and 16) and three coordinate aluminium chalcogenides bearing aluminium–chalcogen double bonds are yet to be discovered. Isolation of these compounds will provide the following: i) gain deeper insight into aluminium bonding nature, ii) plethora of reactivity towards transition metal free catalysis and stoichiometric activation of small molecules, iii) various potential application aspects in material chemistry, particularly, to understand the aggregation process of bulk aluminium chalcogenides from the corresponding molecular species. Evidently, the high abundance of aluminium in the earth's crust along with their great future

promise, remarkable discoveries are highly anticipated in the coming years.

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**Keywords:** Main group • aluminium • single bond • multiple bond • reactivity

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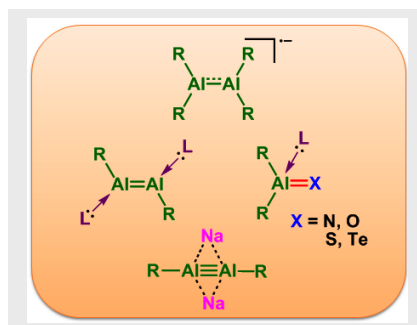
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## REVIEW

This review summarises the challenges in isolating elusive aluminium multiple bonds for both homo and heterodiatomics. Examining the development of the chemistry right from the start at single-bonds through to the missing piece of the neutral main group homonuclear double bond puzzle.



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Multiple-bonded Aluminium  
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