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

Prasenjit Bag, Catherine Weetman and Shigeyoshi Inoue*

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 (Al₂H₂) 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, Al₂O₃, 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.). 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. 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[8] and trihalide Al salts in Friedel-Craft reactions.[9] 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[10] but isolation of Al(II) species is challenging due to the thermal instability of these compounds.[11] Low-valent Al(II) compounds such as AlH, AlX (X = F, Cl, Br, I) and Al₆O₆ 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 AlX.[7]

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 K₂[Al₅(μ₃-O)][12]. This reaction was first reported in 1976 however, it was not until 1991 that the structure was realized[13]. Introduction of steric bulk into the ligand sphere allowed for the isolation of the widely studied Al(I) tetramer [(Cp*Al₂)₄] (Cp* = pentamethylcyclopentadienyl) (Figure 1).[14] This complex contains a tetrahedral arrangement of Al(I) centres, which dissociates at elevated temperatures in solution to yield the monomeric Cp*Al species. The metal-metal bonding in 1 involves four highly delocalised molecular orbitals, formed from the lone-pair σ-orbitals of the monomers where Cp* moiety forms π-bonds with Al; all others constitute of only σ-bonds.[10]

Alternatively, Roesky and co-workers devised a rather straightforward synthetic route to the same tetrameric compound 1 (yield: 20%). Starting from easily available AlCl₃, this was reacted with Cp*SiMe₃ to form Cp*AlCl₂ and its subsequent reduction in the presence of potassium metal under refluxing conditions in toluene furnished 1.[15] Afterwards, this prototypical Al(I) compound 1 was subjected to diverse range of reactivity which included: i) oxidation with chalcogens,[11, 12] ii) coordination behaviour towards transition metals,[13] and iii) insertion of unsaturated organic substrates into the Al–Al bonds.[14]

Following this report, in 2000, Roesky and co-workers published the use of a bidentate β-diketiminate ligand for the successful isolation of a monomeric Al(I) compound 2, an aluminium analogue of N-heterocyclic carbene (Figure 1).[16] Reactivity studies of both compounds 1 and 2 towards small molecules have been extensively studied.[10b, 16]

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
(3) by Uhl (Figure 1)[25] 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).[17] 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
double bond rule wrong. First the isolation of Si=Si double bond by West and co-workers,[22] then the successful isolation of P=P containing double bond by Yoshifuji[23] and finally Brook’s silene containing a Si=C double bond.[24] These remarkable discoveries have since led to a plethora of main group multiply bonded compounds which have been the subject of numerous reviews.[25]

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(SiMe3)2) provided access to a stannylene compound,[26a] which is a stable two coordinate tin compound, which in the solid state dimerises to form a Sn=Sn double bond.[26b] 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.[27] The ability to isolate these two stable 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. 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, 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. 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 diborone complex, this was obtained through the reductive dehalogenation of NHC-BBr, in the presence of excess potassium graphite (KC) at room temperature. Utilising a similar reductive dehalogenation methodology, but with a pre-formed B-B single bond, allowed for the isolation of the BiB triple bond.

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 dimetallalynes. 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 and the controversial ‘digallyne’. 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. 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.

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.

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. If you are to consider a molecule of the type REER or RERE, 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 intense 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.

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 π and σ* orbitals due to the lowering of π-σ* gap, resembling Jahn-Teller distortions used to describe pyrimidisation. This increased mixing of the σ* orbital weakens the π 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 electronegative substituents (e.g. silyl groups) will lead to a greater stabilisation of the π bond through destabilisation of the lone pair bonding MO, whereas the use of electronegative substituents (e.g. amides) will strengthen the σ bond of R=E and provide more σ character to E providing a greater interaction between π-σ* and therefore increased lone pair character on E.

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 onwards reaction with small unsaturated molecules and reagents (e.g., CO₂, ethylene and phenylacetylene) provide an experimental insight into the nature of the multiple bond.

![MO diagram showing the mixing of the π and σ* orbitals and the formation of the non-bonding lone pair orbital in group 13 compounds](image)

In this review the synthesis and reactivity of numerous landmark compounds containing both hetero- and homodiatomic 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 group 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_{D(B-E)} = 188 KJ mol⁻¹) compared to diboranes (D_{D(B-B)} = 293 KJ mol⁻¹) and disilanes (D_{D(Si-Si)} = 222 KJ mol⁻¹) [39]. Currently, the amount of stable disilane or diborane compounds reported to date easily outnumber the corresponding diatomic 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 π-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 [40]. Therefore, the first structurally authenticated dialuminium compound possessing an Al–Al single bond was unambiguously reported in 1988 by Uhl [[Me₃Si]₂C]₂Al–Al[CH(SiMe₃)₂][2] (3) (d_{Al-Al} = 2.660(1) Å) [56]. Since then this field has experienced considerable development and a large number of compounds have been isolated either in the tetrameric form, R₄Al₄ (R = alkyl, aryl, silyl or amide) [57, 58], dimeric form R₂Al–AlR₂ (R = alkyl, aryl, silyl and halide), as the Lewis base adducts R₂(L)Al–Al(L)R₂ (L = Lewis base) [52] or through use of a donor acceptor type interaction R₃Al–AlR₃ (R’ = CsF, R = alkyl) [59]. Single-bonded aluminium compounds exhibit rich chemical reactivity, with Al–Al distances ranging from 2.5 to 2.95 Å [10]. The bonding and reactivity patterns of some of these compounds have already been subject of reviews reported in early 2000s [60, 61]. Therefore, our discussion will mainly focus on some of the notable single bonded aluminium compounds isolated in the last decade with their potential reactivity.

![Notable examples of neutral and anionic single-bonded aluminium compounds (5-10) isolated in the last decade](image)
In this category, Jones and co-workers have accomplished the isolation of parent dialumane (AlH₂) in the form of bis(carbene adduct IDipp₂H₂Al−AlH₂IDipp (5) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) (Figure 4). This was synthesised via direct hydrogen atom transfer from IDipp₂AlH₂ adduct to Mg(I) dimer [HC(MeCN)₂]₂Mg₂ (Ar = Mes, Dipp).[21, 46] 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-dihydridodialumane compounds [L(H)Al(III)AI(L)] (L = [(Dipp)₂C]R, R = Me (6a), p-tolyl (6b), Bu (6c) or NPr₂ (6d)) in moderate yields exploiting chelating bulky amidinate or guanidinate ligands (Figure 4).[45] 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 cm⁻¹, 1682 cm⁻¹ for compound 5, whereas the spectra of 6a–d each exhibits one band in the region of 1748-1770 cm⁻¹ and these values are ~60-90 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 cm⁻¹ in Raman spectrum.

Last year, first asymmetric-substituted dialumanes [Me₆CAAC·Al(X)−Al(X)Me₆] (X = Cl (7a), Br (7b)) were isolated by Roesky and co-workers from the facile disproportionation reaction between β-diketiminate ligand stabilised monomeric Al(II) compound 2 (Figure 1) and CAAC-stabilised Al(III) trihalide complexes [Me₆CAAC·AlX₃ (CAAC = cyclic alkyl amino carbene) (Figure 4).[47] The ¹³C 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 [Me₆CAAC·AlCl₃ (231.1 ppm)] and [Me₆CAAC·AlI₃ (223.4 ppm)] respectively. Single crystal X-ray diffraction (SCXRD) analysis showed each 1 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 β-diketiminate bound Al centre (+1.23 e (7a), +1.10 e (7b)).

Very recently, Aldridge and coworkers synthesised dialumane compound 8 [Al(NON)]₂ (dono = 2.646(3) Å) employing a chelating ligand (NON).[48] This was obtained in excellent yield (86 %) as off-white coloured solid from the KC₈ reduction of corresponding iodo compound (NON)All in either toluene or benzene.

Arnold and Braunschweig groups both independently synthesised bis(Cp*) dialane complexes Cp*Al−Al(Cp*) (X = I (9a, d(oAl−Al) = 2.532(1) Å), Br (9b, d(oAl−Al) = 2.530(2) Å)) from the reductive dehalogenation of corresponding dihaloalane complexes Cp*AlX₂ (Figure 4).[49] The ²³⁷Al NMR resonances of both compounds were identified at δ = −41.7 (9a) and −46 (9b) ppm, and for the later this was shifted considerably upfield in comparison to the starting dihaloalane (AlIII) precursor Cp*AlBr₂ (~11 ppm). Both the 1,2-dihalodialumanes 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).[48a, 48b] In particular, the reaction with aromatic azide is highly sensitive to the halogen substitution on aluminium, as compound 8b with bromide substitution led to simple insertion of PhN unit into the Al–Al bond to furnish compound 13,[48c] while 8a produces rearranged product 14[48a] (Scheme 1). Although, the formation of 14 believed to proceed via intermediary of similar type of insertion product to that of 13.

Scheme 1. Reaction of unsaturated organic substrates with bis(pentamethylcyclopentadieny)alane complexes (9a, 9b).

Recent work from the Jones group reported the isolation of a low oxidation state binary, dianionic aluminium hydride (10) [(⁵⁰Nacnac)Mg₂(μ-H)₂][H₂Al−AlH₃] (⁵⁰Nacnac = [(⁵⁰Nacnac)Me₂]CH). Dep = 2,6-diethylphenyl), which represents the first Al-based compound which is a valence isoelectronic analogue of ethane (Figure 4).[49] Compound 10 was obtained in low yields (24 %) as a colourless compound via the reduction of the alane complex [(⁵⁰Nacnac)Mg(μ-H)₂Al(NMe₃)] with a slight excess of Jones’s trademark Mg(I) reagent [(⁵⁰Nacnac)Mg]₂.[50] 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, Li₂[H₂Al−AlH₃] (2.69 Å).[51] 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 Li₂[H₂Al−AlH₃].[51] It is thought that this discrepancy arises from the steric interactions between the two [(⁵⁰Nacnac)Mg(μ-H)]⁺ cations which contributed significantly to such structural distortion in 10. Furthermore, NBO charge calculations suggested Al₃H₆ 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 bond dialuminium compounds, namely ‘dialumanes’ of general formula R₂Al – AlR₂, possess an empty π- 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 Al₂H₄ to form radical monoanionic compound [Al₂H₄]⁻ 15 is highly favourable from a thermodynamic point of view due to the large exothermic nature of the reduction reaction (Figure 5). This, therefore, generated the first ionic species, upon one electron reduction of neutral parent dialane, which prefers a planar conformation (15a, D₃h) due to the extra electron occupying the π-like bonding orbital. This π-stabilisation is sufficient (~−60 kJ mol⁻¹) to favour the planar structure over the twisted geometry (15b, D₂h), where the same electron essentially fills the non-bonding orbitals (Figure 5).

![Figure 5. Planar and twisted conformation of parent radical monoanionic dialuminium compound [Al₂H₄]⁻](image)

As a measure of the theoretical prediction, Uhl et al. first attempted the potassium metal mediated reduction of the dialane compound 3, in dimethoxethane (DME) (Scheme 2a). This furnished a dark blue solution which contained a radical monoanionic species, 16 [(Me₂Si)₂CH₂]₂Al–Al[(CH₂SiMe₃)₂][Li(TMEDA)]⁻ which was not structurally characterised. Similarly, their efforts to isolate the same compound with a lithium counter cation instead of potassium, by treatment of compound 3 with neopentyllithium (or trimethylsilylmethyl lithium in the presence of TMEDA (TMEDA = N,N,N,N’-tetramethylethylenediamine) also remained unsuccessful.

![Scheme 2. Synthesis of one electron π-bonded radical monoanionic dialuminium compounds (16, 17 and 19a, b) via alkali metal reduction of the neutral dialane precursors.](image)

Shortly afterwards, Pörschke group pioneered the isolation of a black-violet coloured radical monoanionic compound [(Me₂Si)₂CH₂]₂Al–Al[(CH₂SiMe₃)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). Concurrently, Power and co-workers also reported the synthesis of a bulky aryl-substituted radical monoanionic species [(Tp)₂Al–Al(Tp)]⁻ 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 [Tp₂Al–Al(Tp)]₂ 18 (Tp = 2,4,6-trisopropylphenyl).
dianionic species arises presumably from the considerable columbic repulsion exerted by the two anionic charges occupying the π-symmetry orbital. However, calculations also predicted the cation complexation, which acts to withdraw some electron density from the π-orbitals, could enable the isolation of such dianionic species through stabilisation of the highest occupied molecular orbital (HOMO) by suppressing the columbic repulsion to a considerable extent. 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. 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 monoaionic species 16 (Scheme 2a) in the presence of excess potassium. However, this attempt reduction only furnished three colorless anionic alkoxy/alkyl-alanate derivatives through the cleavage of dimethoxysilane (DMET).

Recently, Boldyrev and Bowen groups succeeded in generating a dianion in the form of a LiAlH4− cluster 20, which confirms the formation of a conventional Al=Al double bond through electronic transmutation methodology. Through a combination of theoretical calculations and photoelectron spectroscopy, the study confirmed the LiAlH4− cluster has a global minimum structure similar to that of Si2H4, which therefore comprises of an Al=Al double bond.

### 3.2. One electron π-bonded neutral compounds

The lone example of a one electron π-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 ([Bu3Si]3-Al-Al-[Bu3Si]) radical 22. This compound was synthesised via thermolysis of the neutral dialane ([Bu3Si]3-Al-Al-[SiBu3]2) precursor 21 in a deuterated cyclohexane solution which was in a sealed NMR tube (Scheme 3). The stability of the dialanyl radical arises presumably due the large steric encumbrance and electronic influence of the −Si(Bu3)2 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 π character of the unpaired electron at the centre of the two Al atoms. The relatively large values of coupling constants illustrated strong 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 sp2- and sp3-hybridised Al atoms, which are connected via two electron σ- and one electron π-bonds. Further ab initio calculations at the “RI-DFT” level of theory highlighted the dialanyl radical 22 possesses almost a planar Si2Al2AlSi2 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).

### 3.3. Dianionic dialumyne and cyclostilumene

A similar to one electron π-bonded monoanionic compounds, synthesis of Al−Al triple bonded compounds via two electron reduction of the donor free dialumyne 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 Na2[ArAlA] (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 ArAl2 (Ar = C6H4-2,6-((C6H4-2,4,6-Pr3)2) (24) in the presence of four equivalents of sodium in diethylether (Scheme 4). 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” [Na2Ga2(C6H4-2,6-TiP3)2] (TIP = 2,4,6-trisopropylphenyl), Although, there is considerable debate over the years regarding the truly bonded nature of these compounds.
X-ray crystallographic analysis revealed compound 25 possesses a trans-bent structure [C(Ar)−Al−Al−C(Ar) dihedral: 131.71(7)°] with a local C₃ᵥ symmetry. In the centrosymmetric Al₂Na₃ core, two sodium atoms reside on either side of the Al−Al bond and are complexed in an n²-fashion to the flanking aryl groups of m-terphenyl ring. The Al−Al bond length is 2.428(1) Å and is considerably longer (0.20 Å) compared to the theoretically predicted sum of the triple-bond radii of Al (2.22 Å) and also longer than the Ga−Ga distance (2.319(3) Å) in Robinson’s “digallyne”. DFT calculations revealed that the HOMO-2 is clearly a σ-bond between the Al atoms, whereas the HOMO represents the out of plane π bond. The HOMO-1 designated as nonbonding pair on the Al centre and can be alternatively described as a slipped π 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 Na⁺ ions. The natural bond orbital (NBO) analysis of compound 25 revealed the electron occupancy of these three orbitals (one σ and two π) are 1.7150, 1.8178 and 1.6619, respectively. The σ bond orbital constitutes of 25.92% s- and 73.98% p-character while the normal π bond is purely composed of the p-orbital of Al atoms. The slipped π 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 shift 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 (Ar = C₆H₄-2,6-(2,4,6-Me₃)) in comparison to the ligand used for the synthesis of the dianionic dialumine (25), allowed for the isolation of a dianionic cyclotrialumine Na₂[Al₂Ar₃] (27). Compound 27 was obtained as red orange crystals under similar reaction conditions to compound 25 (Scheme 5). This compound resembles the isoelectronic gallium compounds M₂[Ge₆Ar₆] (M = Na (28a), K (28b)) isolated by Robinson and co-workers, the cyclostilbilenium ion [Si₆R₆⁺] (R = SiBu₃, R' = SiMe₃Bu₂) (29a) and the cyclostilbelenium ion [Ge₆R₆⁺] (R = SiBu₃) (29b) published by the Sekiguchi group.

4. Masked dialumenes: Barrelene type dialumenes

4.1. Synthesis and structure

Neutral double-bonded Al compounds defined by the general formula R−Al=Al−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=R (M = Ga, In[36], Tl[37, 38]) 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\(^{-1}\) for Al compared to the 3 kcal mol\(^{-1}\) for Ga-Tl[39]. 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](image_url)  
**Figure 6.** Schematic presentation of configurational isomers of AlH\(_2\) (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\(_2\)H\(_2\) can be best described as depicted in Figure 6.26] Consequently high singlet-triplet energy gap (\(\Delta E_{ST} = 28\) kcal mol\(^{-1}\)[36]) 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 the other fragment, resulting in the formation of non-classical trans-bent geometry (\(C_{2n}\)) at each Al centre (Figure 2). Calculations further revealed that trans-bent structure is 16 kcal mol\(^{-1}\) more stable than the linear form (Figure 6).[39] In fact, none of the configurations represent local minima in the potential energy surface (PES) diagram (Figure 6). Doubly hydrogen bridged (\(D_{2n}\)) isomer (Figure 6) is the global minimum on the PES. The calculated Al–Al bond distance in the trans-bent structure of parent alumylene is predicted to be 2.613 Å which typically lies in the range of single-bonded dialuminyd 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)[36, 67b, 68b] employing the highly sterically demanding m-terphenyl ligand system via reductive dehalogenation of aryl diiodoalane Ar–AI\(_2\) (24). However, unlike the other cases (Ga-Tl), this reaction only led to the unprecedented formation of the bicyclic adduct (31) rather than much coveted dialumene (Scheme 6a). They suggested that reductive dehalogenation led to transient formation of intermediate dialumene Ar–AI–Al–Ar (30), which subsequently reacts in a formal \([4+2]\) cycloaddition manner with solvent toluene to furnish the bicyclic 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(aryl)–Al–Cl–C(aryl) fragment clearly indicates two bulky m-terphenyl group (Ar) adopts a cis-orientation with respect to the Al–Al bond axis.

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

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)trimethylsilacycylene (Scheme 6b).[67a] The \(^{29}\)Si and \(^{13}\)C NMR spectrum of the Me\(_3\)SiCCMe\(_3\)Si fragment in the four-membered ring appears at \(\delta = -13.2\) and 235 ppm, for Me\(_3\)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\textdegree with a considerably short Al–Al bond length (2.4946(9) Å), which is comparable to that found in the anionic radical compound [(Tip)\textsubscript{2}Al–Al(Tip)\textsubscript{2}]- 19 (2.470(2) Å). To explain the folded ring structure in 32, theoretical calculations on the parent compound (HAl\textsubscript{3}(CH)\textsubscript{2}) 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\textsubscript{3} 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\textsuperscript{-1}).

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 KC\textsubscript{2} mediated reductive dehalogenation of 1,2-dibromodialumane 34 in benzene (Scheme 7).\textsuperscript{[42a, 72]} The 1H NMR spectra of both compounds (35a, 35b) revealed the existence of an intermolecular exchange equilibrium between the adduct C\textsubscript{8}H\textsubscript{6} and solvent C\textsubscript{6}D\textsubscript{6}. Compound 35 features a similar structure to that of 31 (Scheme 6a) with a slightly shorter Al–Al bond length (2.5552(19) Å).

\textbf{Scheme 7.} Synthesis of barrelene type dialumanes 35a,b.

\textbf{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\textsubscript{8}H\textsubscript{6} and solvent C\textsubscript{6}D\textsubscript{6} in 35 allowed for exploration of its reactivity towards various unsaturated organic substrates such as internal alkynes,\textsuperscript{[72, 79]} isonitriles\textsuperscript{[84]} and aromatic compounds.\textsuperscript{[73]} 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).\textsuperscript{[73]} 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\textsubscript{6}H\textsubscript{5} moiety of 35a was smoothly exchanged to furnish the 1,2-dialuminacyclobutene 41 (as the sole product) (Scheme 8).\textsuperscript{[72]}

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] cycloadition product 1,2-dialuminacyclobutene (38) was isolated as the major component (Scheme 8).\textsuperscript{[73a]} 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).\textsuperscript{[72a]} 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.

\textbf{Scheme 8.} Reactions of barrelene type dialumanes 35 with internal alkynes and aromatic compounds.
The Al distance is 2.632(1) Å comparable to the reported dihydroalumane dimer [Mes*HAl(μ-H)]₂ (2.652(2) Å) (Mes* = 2,4,6-(Bu₃C₆H₃)₃) [76] 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 terminal vibrational absorption bands at 1870 cm⁻¹ (45a), 1872 cm⁻¹ (45b) and the corresponding bridging hydride appears at 1356 cm⁻¹ (45a), 1358 cm⁻¹ (45b). These values are in accordance with the calculated values corresponding to the geometry optimised structure of both compounds (ν[Al–Hterminal] = 1922 cm⁻¹, ν[Al–H-Al] = 1420 cm⁻¹).

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

Reaction of diaryldialumene-benzene adduct 35a with the 14 electron transition metal complex Pt(PCy₃)₂ furnished terminal arylalumylene complex of platinum [Bbp-Al-Pt(PCy₃)₂] 46a as dark red compounds (Scheme 11). Alternatively, the alumylene 46a.b complexes could be achieved through the reduction of 1,2-dibromodialumenes (34) Ar(Br)Al–Al(Br)Ar (Ar = Bbp, Tbb) in the presence of [Pt(PCy₃)₂] (Scheme 11). 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(PCy₃)₂] and PCy₃. The ³¹P NMR spectra of compounds 46a and 46b appear at δ = 69.9 ppm (JPPt = 4015 Hz) and δ = 69.8 ppm (JPPt = 4033 Hz) respectively, which are downfield shifted compared to Pt(PCy₃)₂ (δ = 62.3 ppm, JPPt = 4160 Hz). SC-XRD structure confirmed the two coordinate environment around the Al centre with an almost linear C₆–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) Å (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(PCy₃)₂ moieties.

**Scheme 11.** Synthesis of Pt(PCy₃)₂ stabilised two coordinate arylalumylene complexes 46.

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 dihydrodialumene dimers as colourless compounds 45a.b in quantitative yields (Scheme 10). The ¹H NMR spectra for both compounds appear as broad signals which correspond to the Al bound hydrogen atoms (45a: δH = 4.49, 4.88 ppm and 45b: δH = 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 dihydroalumene dimer [Mes*HAl(μ-H)]₂ (2.652(2) Å) (Mes* = 2,4,6-(Bu₃C₆H₃)₃). 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 terminal vibrational absorption bands at 1870 cm⁻¹ (45a), 1872 cm⁻¹ (45b) and the corresponding bridging hydride appears at 1356 cm⁻¹ (45a), 1358 cm⁻¹ (45b). These values are in accordance with the calculated values corresponding to the geometry optimised structure of both compounds (ν[Al–Hterminal] = 1922 cm⁻¹, ν[Al–H-Al] = 1420 cm⁻¹).

**Scheme 9.** Proposed reaction mechanism between internal alkynes and barrelene type dialumenes 35.
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 Al₂H₂ and Al₂Cl₂ could be realised through fulfillment of the octet on each Al centre. 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 IPr₂Me₂ 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, which can be obtained in good yields. Subsequently, the KC₈ 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). SC-XRD structure analysis revealed that the di aluminium 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 di aluminium 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 σ-bond, whereas the HOMO clearly demonstrates the Al–Al π-bond between the two Al atoms (Figure 7).

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). 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.
6. Aluminium heterodiatomic multiple bonds

In terms of Al-E bonding (where E = s- [79] p- [440] d- [80] or f- [81] 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 isosbestic to CO or PR$_3$, 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. 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 complexes of the type (RAE)$_m$. 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.](image)

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). 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 ($H_2O\cdot B(C_6F_3)_3$) 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-diketiminate 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(C6F3)3, 54.](image)

The isolation of this compound was considered to be the first example of a monomeric member of the (RAIO)$_m$ 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) which 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(C6F3)3, 54.](image)

The first reported complex containing a terminal aluminium chalcogenide bond, was reported by our group. 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-yldene) resulting in a dehydrogenative redox process to yield the monotropic 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.
Computational analysis provided a WBI of 1.20 for Al–Te bond in compound 56, indicating 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 π-symmetry at the Te atom and the HOMO-1 showed a π-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.

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 dimerc 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.

The only other report of a terminal aluminium-chalcogen double bond was reported recently by Nikonov and co-workers.\[85\] Utilising Roesky's Al(I) complex (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 β-diketiminato (nacnac) ligand, terminal sulphide and the fourth coordination site occupied by the resulting carbene, with Al in the most stable +3 oxidation state.

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.


Scheme 17. Selected resonance structures of aluminium telluride 56.

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

bond character of these compounds. The double bond character was further supported by examination of Mayer bond orders (AI-S 1.49) and WBI (AI-S 1.20). Consideration of the Al–NHC bonding was also examined through use of Mayer bond orders (AI-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 ρ-τ orbital.

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 β-diketiminate ligands. \( \text{[25]} \) In terms of iminocaraboranes, a few initial attempts reported by Roesky and co-workers implied the existence of aminocaraboranes, however these could not be structurally verified. \( \text{[26]} \) Cui and co-workers reported the first, and only, monomeric iminoalane complex 62 (Scheme 22). \( \text{[89]} \) This was prepared through the reaction of a larger version of Roesky’s Al(I) complex (2\( ^{\text{th}} \)), this compound contains tert-butyl groups in the β-position. Upon reaction with a Lewis basic NHC, the supporting β-diketiminate ligand undergoes a ring contraction to provide a 4-coordinate Al centre.

The X-ray structure revealed a short Al–N bond length of 1.705(2) Å, which is considerably shorter than the average reported Al–N bond lengths which are 1.85 Å for 4-coordinate aluminium amides. In comparison to the calculated value for the parent quasilinear iminoalane (average 1.85 Å) 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\(^2\) hybrid orbital of the Al atom with one of the two lone pairs of the sp\(^2\)-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 σ-bond and additional ionic component.

Scheme 20. Two resonance structures of compound 58.

Using the outlined method by Bridgeman et al.\( ^{[86]} \) the calculated s- and p- components of the Mayer bond order were comparable (L\( _2 \)Al=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\(^\prime \).

Extension of this chemistry to \( \text{Ph}_3\text{P} = \text{S} \) (triphenylphosphine sulphide) reagents also provided oxidative-cleavage reactivity. This required the use of 2 eq. of \( \text{Ph}_3\text{P} = \text{S} \) and resulted in the unexpected formation of L\( _2 \)Al=S(\( \text{SPH}_3 \)) 59 (L = β-diketiminate) however this compound was found to be thermally unstable above −30 °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.

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 PhNH2 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 PhNH2. 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-pnicogen 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 activity. With the advent of the seminal dianionic diaumyne Na₂[ArAl₆Ar] 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 dialumenes 49 and Al(I) anion 4 will likely fuel the growth of low oxidation state Al chemistry. Nonetheless, a lot of long-standing existing multiple-bonded aluminium compounds such as Al₂, Al(IV) (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.

Acknowledgements

Financial support from WACKER Chemie AG, as well as the European Research Council (SILION 637394) and TUM University Foundation (Fellowship C.W.) are gratefully acknowledged. We are also thankful to Dr. Vitaly Nesterov (TU Munich) for helping us to design frontispiece.

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

References


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.

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