

**Main Group Elements**

# Magnesium(I) Reduction of Aluminum(III) Hydride Complexes: Generation of Mixed Valence Aluminum (Al<sup>I</sup>/Al<sup>0</sup>) Hydride Cluster Compounds, [Al<sub>6</sub>H<sub>8</sub>(NR<sub>3</sub>)<sub>2</sub>{Mg(β-diketiminato)}<sub>4</sub>]\*\*

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**Abstract:** Reduction of a range of amido- and aryloxy-aluminum dihydride complexes, e.g. [AlH<sub>2</sub>(NR<sub>3</sub>){N-(SiMe<sub>3</sub>)<sub>2</sub>}] (NR<sub>3</sub>=NMe<sub>3</sub> or N-methylpiperidine (NMP)), with β-diketiminato dimagnesium(I) reagents, [(<sup>Ar</sup>Nacnac)Mg]<sub>2</sub> (<sup>Ar</sup>Nacnac=[HC(MeCNAr)<sub>2</sub>]<sup>-</sup>, Ar=mesityl (Mes) or 2,6-xylyl (Xyl)), have afforded deep red mixed valence aluminum hydride cluster compounds, [Al<sub>6</sub>H<sub>8</sub>(NR<sub>3</sub>)<sub>2</sub>{Mg(<sup>Ar</sup>Nacnac)}<sub>4</sub>], which have an average Al oxidation state of +0.66, the lowest for any well-defined aluminum hydride compound. In the solid-state, the clusters are shown to have distorted octahedral Al<sub>6</sub> cores, having zero-valent Al axial sites and monovalent AlH<sub>2</sub><sup>-</sup> equatorial units. Several novel by-products were isolated from the reactions that gave the clusters, including the Mg–Al bonded magnesio-aluminate complexes, [(<sup>Ar</sup>Nacnac)(Me<sub>3</sub>N)Mg–Al(μ-H)<sub>3</sub>{Mg(<sup>Ar</sup>Nacnac)}<sub>2</sub>(μ-H)]. Computational analyses of one aluminum hydride cluster revealed its Al<sub>6</sub> core to be electronically delocalized, and to possess one unoccupied, and six occupied, skeletal molecular orbitals.

The chemistry of aluminum hydride compounds has rapidly developed since Wiberg's synthesis of polymeric alane, (AlH<sub>3</sub>)<sub>n</sub>, in 1942.<sup>[1–4]</sup> Compounds containing Al–H bonds have since found innumerable applications in inorganic and organic synthesis, catalysis, materials science, hydrogen storage, and rocket science, to name but a few.<sup>[1–6]</sup> Despite this, it is curious that almost all known aluminium hydride compounds contain the metal in the formal +3 oxidation state. This contrasts with aluminum's lighter cousin, boron, low oxidation state hydride oligomers and clusters of which, e.g. [B<sub>6</sub>H<sub>6</sub>]<sup>2-</sup>, are the subjects of numerous review articles and textbooks.<sup>[7]</sup> While there is a dearth of related low oxidation state aluminum hydride clusters, Schnöckel and others syntheses of a multitude of low-valent aluminum metalloid clusters bearing halide, amide, silyl, alkyl or aryl ligands,<sup>[8]</sup> e.g. [Al<sub>22</sub>Br<sub>20</sub>(THF)<sub>10</sub>]<sup>[9]</sup> and [Al<sub>77</sub>{N-(SiMe<sub>3</sub>)<sub>2</sub>]<sub>20</sub>]<sup>2-</sup>,<sup>[10]</sup> gives hope for their eventual development.

Although low-valent, polynuclear aluminum hydrides, e.g. Al<sub>4</sub>H<sub>6</sub>, have been well studied in the gas phase and cryogenic matrices,<sup>[11]</sup> only one room temperature stable dinuclear example was known prior to 2010.<sup>[12]</sup> In that year we reported on the synthesis of a series of well-defined Al<sup>I</sup> hydrides, including the N-heterocyclic carbene (NHC) stabilised parent dialane(4) **I** (Figure 1).<sup>[13]</sup> This was followed in 2017 by the dialanate complex **II**, the [Al<sub>2</sub>H<sub>6</sub>]<sup>2-</sup> core of which is a valence isoelectronic analogue of ethane.<sup>[14]</sup> The next year, magnesium(I) reduction of a formamidinato-aluminum(III) hydride gave the remarkable aluminum(I) cluster complex, **III**.<sup>[15–17]</sup> This can be considered as anion stabilised *hypercloso*-hexaalane, Al<sub>6</sub>H<sub>6</sub>, and represented the first aluminum analogue of classical polyhedral boranes. We were keen to extend the chemistry of low-valent aluminum hydride clusters to systems in which the oxidation state of Al is less than +1. Here, we show that reductions of a range of simple amido- and aryloxy-aluminium dihydrides, with β-diketiminato dimagnesium(I) reagents, lead to mixed valence, metalloid Al hydride clusters, [Al<sub>6</sub>H<sub>8</sub>(NR<sub>3</sub>)<sub>2</sub>{Mg(β-diketiminato)}<sub>4</sub>], the average Al oxidation state of which is +0.66. Several novel aluminum hydride complexes, which are by-products of these reactions, are also described.

Given the success of the synthetic route to clusters **III**,<sup>[15]</sup> the dimagnesium(I) reduction of aluminum(III) hydride complexes bearing mono-dentate anionic ligands was explored. For this purpose, the enantiopure, chiral amido-alane complex, [AlH<sub>2</sub>(NMe<sub>3</sub>)[N(SiMe<sub>2</sub>Ph){Si(OBor)<sub>3</sub>}]

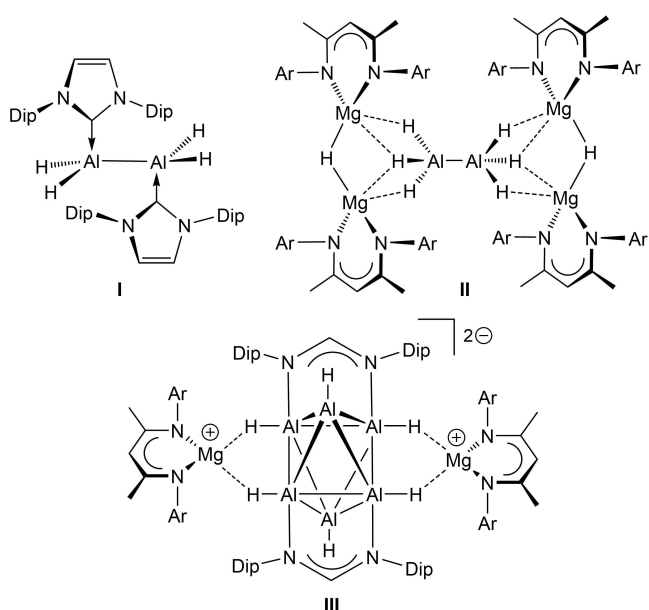
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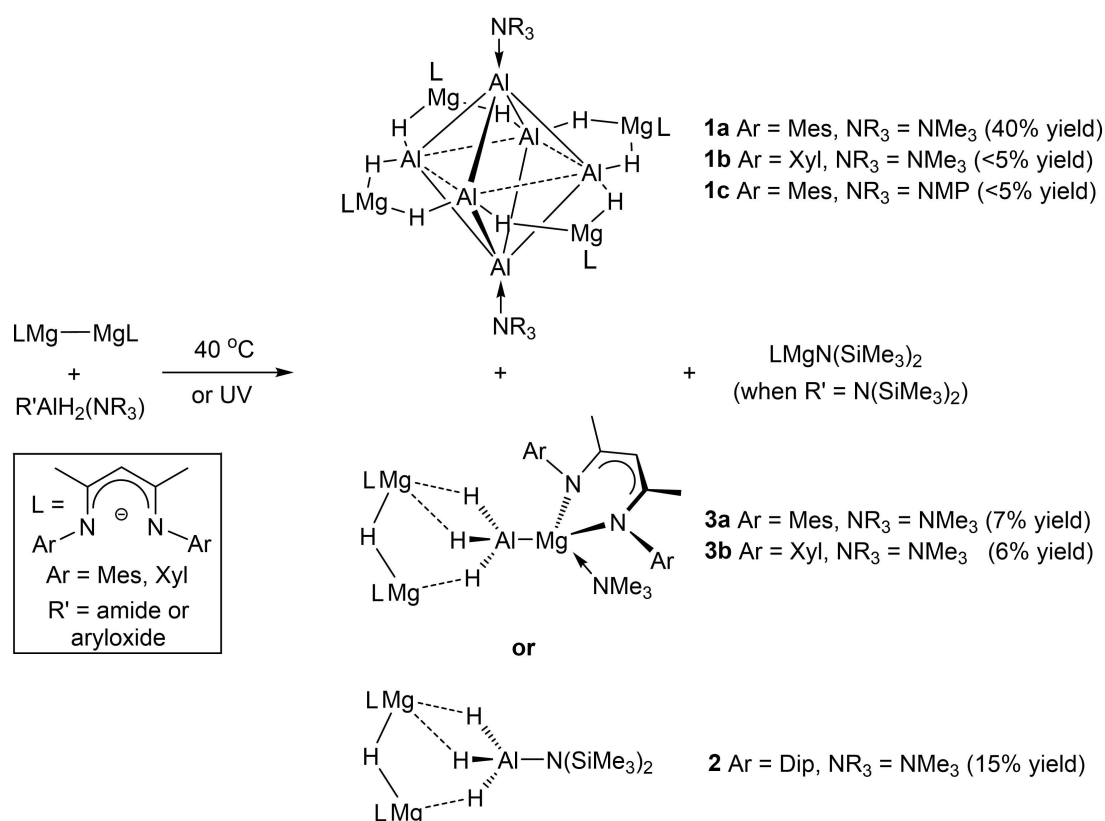


**Figure 1.** Examples of Al<sup>II</sup> and Al<sup>I</sup> hydride complexes formed by reduction of aluminum(III) hydride compounds with dimagnesium(I) reagents (Ar = bulky aryl, Dip = 2,6-diisopropylphenyl).

(OBor = [(1*S*-endo)-(–)-borneoxy], was initially developed, as it was expected that the bulky amide would provide kinetic protection, and potentially synthetically useful chir-

ality, to reduced products, if they incorporated the substituent. However, reduction of the alane with one equivalent of dimagnesium(I) complex,  $[\{(\text{Mes})\text{Nacnac}\}\text{Mg}]_2$  ( $\text{Mes} = \text{mesityl}$ ),<sup>[18]</sup> at 40 °C (or under irradiation with UV light,  $\lambda = 370 \text{ nm}$ ) gave a complex mixture of products, from which a few crystals of the deep red crystalline aluminum hydride cluster compound, **1a**, were isolated (Scheme 1). As the cluster product is amide free, an analogous reduction of the related known, and more easily prepared, alane  $[\text{AlH}_2(\text{NMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$ ,<sup>[19]</sup> was carried out. This also afforded compound **1a** in a low to moderate, but reproducible yield (ca. 40%, based on magnesium), under heating or UV irradiation conditions. Repeating the reaction in 1:2 and 2:1 stoichiometries led to decreased yields of **1a** in both cases, suggesting that the 1:1 reaction stoichiometry is close to optimal. It is noteworthy that the related 1:1 reaction between  $[\{(\text{Mes})\text{Nacnac}\}\text{Mg}]_2$  and the bulky aryloxy-alane,  $[\text{AlH}_2(\text{NMe}_3)\{\text{O}(\text{C}_6\text{H}_3\text{Bu}'_2-2,6)\}]$ , gave cluster **1a** in a similar isolated yield (35%).

So as to investigate the effect the steric bulk of the dimagnesium(I) reagent has on the outcome of reactions with  $[\text{AlH}_2(\text{NMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$ , the alane was treated with one equivalent of less bulky  $[\{(\text{Xyl})\text{Nacnac}\}\text{Mg}]_2$  (Xyl = 2,6-xylyl).<sup>[15]</sup> The reaction afforded a few deep red crystals (yield < 5%) of cluster **1b**, which is analogous to **1a**, save for its less bulky N-aryl substituents. In contrast, no low-valent aluminum cluster was isolated from the reaction of the bulkier dimagnesium(I) compound,  $[\{(\text{Dip})\text{Nacnac}\}\text{Mg}]_2$



**Scheme 1.** Synthesis of low-valent aluminum hydride cluster compounds **1** and magneso-aluminate complexes **3**.

(Dip = 2,6-diisopropylphenyl),<sup>[18]</sup> with the alane. Instead, the colorless crystalline amido–Aluminate,  $[(\text{Me}_3\text{Si})_2\text{N}]\text{Al}(\mu\text{-H})_3[\text{Mg}(\text{DipNacnac})_2(\mu\text{-H})]_2$  **2** was isolated (yield: 15 %) from a mixture of otherwise unidentified products (see Supporting Information for further details). This conceivably forms via reaction of  $[\text{AlH}_2(\text{NMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$  with  $[\{(\text{DipNacnac})\text{Mg}(\mu\text{-H})\}_2]$ , the latter of which is a by-product of the reduction of the former. To verify this as a possibility, compound **2** was rationally prepared in good yield (61 %) by the 1:1 reaction of  $[\text{AlH}_2(\text{NMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$  with  $[\{(\text{DipNacnac})\text{Mg}(\mu\text{-H})\}_2]$ .<sup>[18]</sup>

A further variation of the reduction reactions described above was to alter the Lewis base donor in the alane precursor compound. That is, the amine or NHC coordinated alanes,  $[\text{AlH}_2(\text{L})\{\text{N}(\text{SiMe}_3)_2\}]$  (L = N-methylpiperidine (NMP) or  $:\text{C}(\text{MeNCMe}_2)_2$  (TMC)) were treated with  $[\{(\text{MesNacnac})\text{Mg}\}_2]$ . The former gave a low isolated yield (< 5 %) of the expected cluster compound **1c** (Scheme 1), while no identifiable products could be isolated from the latter.

Considering the low yields of the poorly soluble clusters **1**, it was of interest to explore the identity of other reaction products, as this could shed some light on the mechanism of formation of the clusters. The reactions between  $[\{(\text{Mes}^{\text{Xyl}}\text{Nacnac})\text{Mg}\}_2]$  and  $[\text{AlH}_2(\text{NMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$  were chosen for this phase of the study. <sup>1</sup>H NMR spectroscopic examinations of the reaction mixtures, before **1a** or **1b** crystallized from them, highlighted complex mixtures of products. Once **1a** or **1b** had crystallized from the mixtures, concentration of the mother liquors led to crystallization of low yields (ca. 7 %) of the unusual magnesio-aluminate complex, **3a** and **3b**, which contain rare examples of unsupported Mg–Al bonds (Scheme 1). It is unknown how these form, though they possibly arise from reactions of in situ generated  $(\text{Mes}^{\text{Xyl}}\text{Nacnac})(\text{Me}_3\text{N})\text{MgAlH}_2$  and  $[\{(\text{Mes}^{\text{Xyl}}\text{Nacnac})\text{Mg}(\mu\text{-H})\}_2]$  (cf. the formation of **2**). Whatever the case, subsequent reaction of **3a** or **3b** with  $[\{(\text{Mes}^{\text{Xyl}}\text{Nacnac})\text{Mg}\}_2]$  did not lead to the clusters **1a** or **1b**, which suggests they are not intermediates en route to those clusters. The fate of the  $\text{N}(\text{SiMe}_3)_2$  substituents in the reduction processes was proposed to be incorporation of that group within magnesium amide by-products  $[(\text{ArNacnac})\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}]$  (Ar = Mes or Xyl). <sup>1</sup>H NMR spectroscopy was used to tentatively assign these as significant products in the reaction mixtures. This was later confirmed by comparison with the <sup>1</sup>H NMR spectra of intentionally prepared  $[(\text{ArNacnac})\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}]$ . No similar magnesium aryloxy by-products could be identified from the reaction between  $[(2,6\text{-Bu}_2\text{C}_6\text{H}_3\text{O})\text{AlH}_2(\text{NMe}_3)]$  with  $[\{(\text{MesNacnac})\text{Mg}\}_2]$ . Despite identifying several products from the reactions under study, there is little firm evidence as to the mechanism of formation of cluster compounds **1**, except to say that it clearly involves initial magnesium(I) reduction of the aluminum(III) hydride precursor compounds.

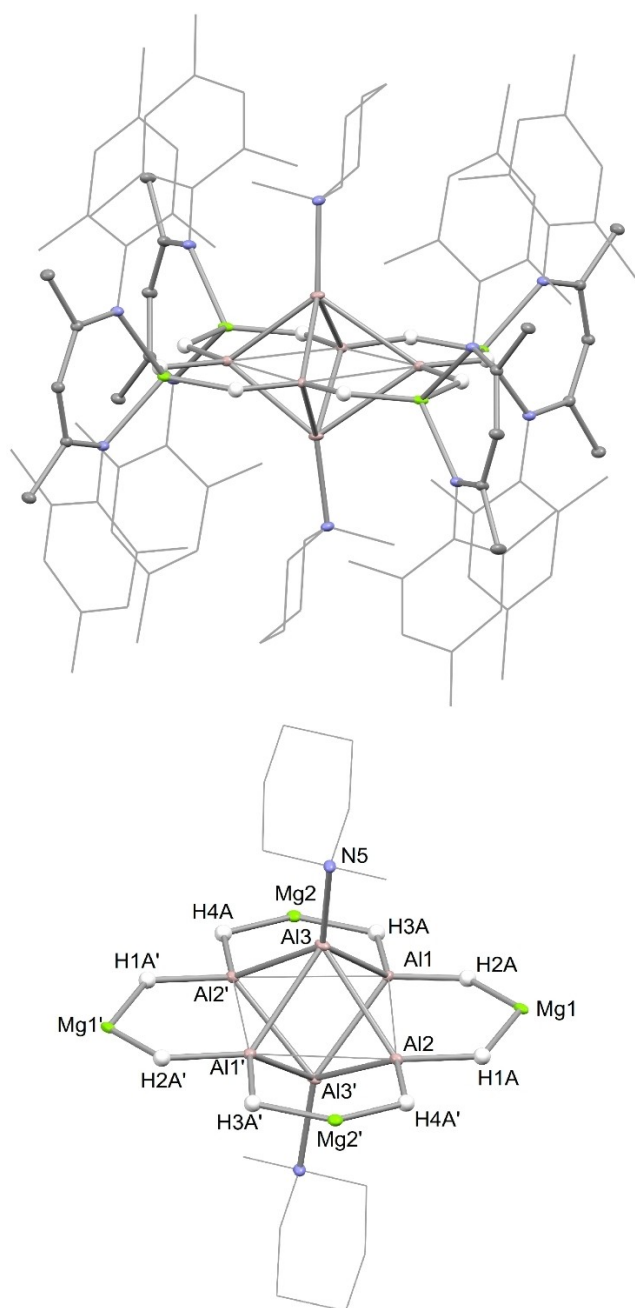
The aluminum hydride clusters **1** are very air sensitive in the solid state, but are thermally quite robust (**1a**: decomp. at ca. 150 °C). Once crystallized, the compounds are essentially insoluble in coordinating and non-coordinating deuterated solvents, and thus solution-state spectroscopic data could not be obtained. The solid-state infrared spec-

trum of **1a** was obtained, though the absorption bands due to metal-hydride stretching modes associated with the Al–H–Mg moieties could not be assigned, as these likely lie in the fingerprint region of the spectrum, as has been reported to be the case for other compounds containing hydride bridged units, Al–H–Mg.<sup>[14,15]</sup> Accordingly, the deuterated analogue of **1a**, viz.  $[\text{Al}_6\text{D}_8(\text{NMe}_3)_2\{\text{Mg}(\text{MesNacnac})\}_4]$  **1a-D**, was prepared and its infrared spectrum acquired. Due to likely overlap with strong ligand absorptions, it was not possible to distinguish between Al–H–Mg and Al–D–Mg stretching bands in the spectra of the compounds. Similarly, Al–H–Mg stretching bands in the solid-state infrared spectrum of the poorly soluble magnesio-aluminate complex **3** are apparently masked by ligand modes, and could not be assigned.

The X-ray crystal structures of the cluster compounds **1** were determined, and found to be essentially isostructural to one another.<sup>[20]</sup> The hydride ligands in all structures were identified from difference maps, and refined isotropically with no positional restraints. In the crystal structures of **1a** and **1b**, the carbon atoms of the  $\text{NMe}_3$  ligands were found to be disordered over two positions. This disorder was successfully modelled. Moreover, although the refinements of all structures converged satisfactorily (see SI), the anisotropic displacement parameters of the Al atoms suggested a degree of unresolved disorder within their  $\text{Al}_6$  cores. This could not be adequately modelled for the structures of **1a** and **1b**. In contrast, disorder within the  $\text{Al}_6$  core of less symmetric **1c** could be modelled, showing the  $\text{Al}_6$  core disordered over two slightly offset sites, each with an atomic occupancy of 50 %. That said, related disorder over the hydride and Nacnac ligand sites could not be resolved. Thus, the metal hydride distances within the structure should not be considered as definitive.

Attempts were made to acquire a neutron single crystal structure for **1a**, and thus accurately locate the hydride nuclear positions. To this end, and although the diffraction data were too weak for a full refinement, neutron diffraction images from two single-crystal specimens of the compound were obtained, and proved suitable for careful difference mapping analyses of the limited low-resolution data sets thus acquired. The presence of the eight hydrides associated with the  $\text{Al}_6$  core, as derived from the X-ray diffraction analysis, is consistent with the available neutron data. Moreover, no additional significant difference density was observed, thus highlighting the absence of any further aluminum bound hydride ligands (see Supporting Information for full details).

Compound **1c** can be considered as having a central, slightly asymmetrical, dianionic  $[\text{Al}_6\text{H}_8(\text{NMP})_2]^{4-}$  core, that is hydride bridged to four  $[\text{Mg}(\text{MesNacnac})]^+$  cations (Figure 2; see Supporting Information for molecular structures of **1a** and **1b**). The axial NMP coordinated Al centers are in the zero-oxidation state, while the equatorial Al atoms are formally in the +1 oxidation state. Consequently, the average Al oxidation state for the compound is +0.66. The cluster is comparable to the only other known sub-valent aluminum hydride cluster type, **III**, but also to the neutral, NHC coordinated, octahedral gallium cluster,  $[(\text{IPriMe})\text{Ga}$

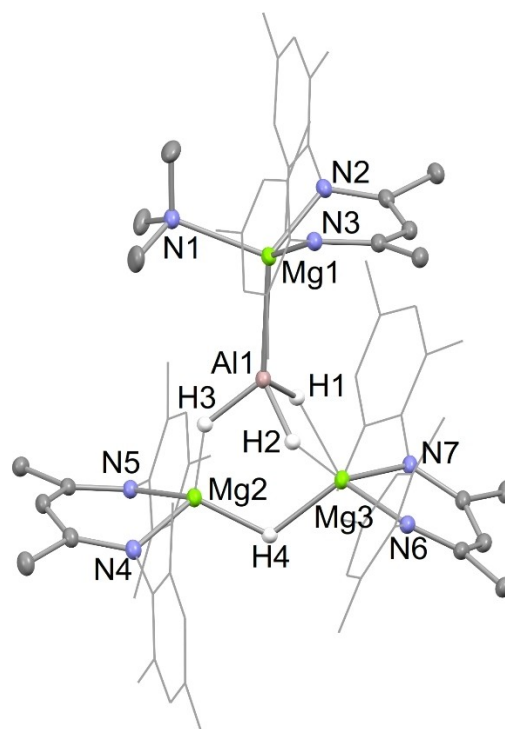


**Figure 2.** Molecular structure of **1c** (top, 20% displacement ellipsoids are shown; hydrogen atoms, except hydrides omitted; mesityl and NMP groups shown as wireframe for clarity). Structure of the core of **1c**, with <sup>Mes</sup>Nacnac ligands deleted (bottom). Selected bond lengths [Å] and angles [°]: Al(3)–N(5) 2.022(3), Al(1)–Al(3) 2.541(9), Al(2)–Al(3) 2.717(3), Al(2)′–Al(3) 2.518(3), Al(3)–Al(1)′ 2.668(4), Al(3)′–Al(1) 2.529(9), Al(3)′–Al(2) 2.657(3), Al(3)′–Al(1)′ 2.671(9), Al(3)′–Al(2)′ 2.546(3), Al(1)–Al(2) 3.100(3), Al(1)–Al(2)′ 3.027(6), Al(2)–Al(1)′ 2.842(9), Al(1)′–Al(2)′ 2.900(9), Al(2)–Al(3)–Al(2)′ 106.39(9), Al(1)–Al(3)–Al(1)′ 107.24(9), Al(3)–Al(1)–Al(3)′ 74.6(1), Al(3)–Al(1)′–Al(3)′ 70.3(1), Al(3)–Al(2)–Al(3)′ 69.8(1), Al(3)–Al(2)′–Al(3)′ 74.8(1).

(GaMes)<sub>4</sub>Ga(IPriMe)] (IPriMe = :C{(Pr<sup>n</sup>NCMe)<sub>2</sub>})<sup>[21]</sup> which similarly has an average Ga oxidation state of +0.66. The Al<sub>6</sub> octahedron of **1c** is heavily tetragonally compressed, in that the axial-axial Al<sub>ax</sub>–Al<sub>ax</sub> distance (3.074(2) Å) is more

that one angstrom less than the transannular equatorial-equatorial Al<sub>eq</sub>–Al<sub>eq</sub> distances (4.195 Å mean). All of the Al<sub>ax</sub>–Al<sub>eq</sub> separations (ca. 2.52–2.72 Å) are within the normal Al–Al single bonding range,<sup>[22]</sup> while the long Al<sub>eq</sub>–Al<sub>eq</sub> equatorial edge distances (ca. 2.84–3.10 Å) are suggestive of little bonding character. Therefore, the equatorial Al atoms are best viewed as having distorted tetrahedral geometries, with two attached hydrides, each of which bridges to a [Mg(<sup>Mes</sup>Nacnac)]<sup>+</sup> cation. It is noteworthy that the closely related neutral cluster, Al<sub>6</sub>H<sub>4</sub> (avge. Al oxidation state = +0.66), has been calculated to have a distorted octahedral structure, with “naked” Al centers in the axial sites, and a terminal hydride at each equatorial site.<sup>[23]</sup>

The magnesio-aluminate complex **3a** is isostructural to its <sup>Xyl</sup>Nacnac coordinated analogue **3b** (Figure 3; see Supporting Information for details of the structure of **3b**), and shows it to consist of a contact ion pair between an unprecedented tetrahedral trihydridomagnesio-aluminate anion and the magnesium hydride cation, [(<sup>Mes</sup>Nacnac)Mg]<sub>2</sub>–(μ-H)<sup>+</sup>. This is similar to the bonding situation in the hexahydrido-dialuminate **II**.<sup>[14]</sup> The unsupported Mg–Al covalent bond in **3a**, 2.7595(16) Å, is in the known range for



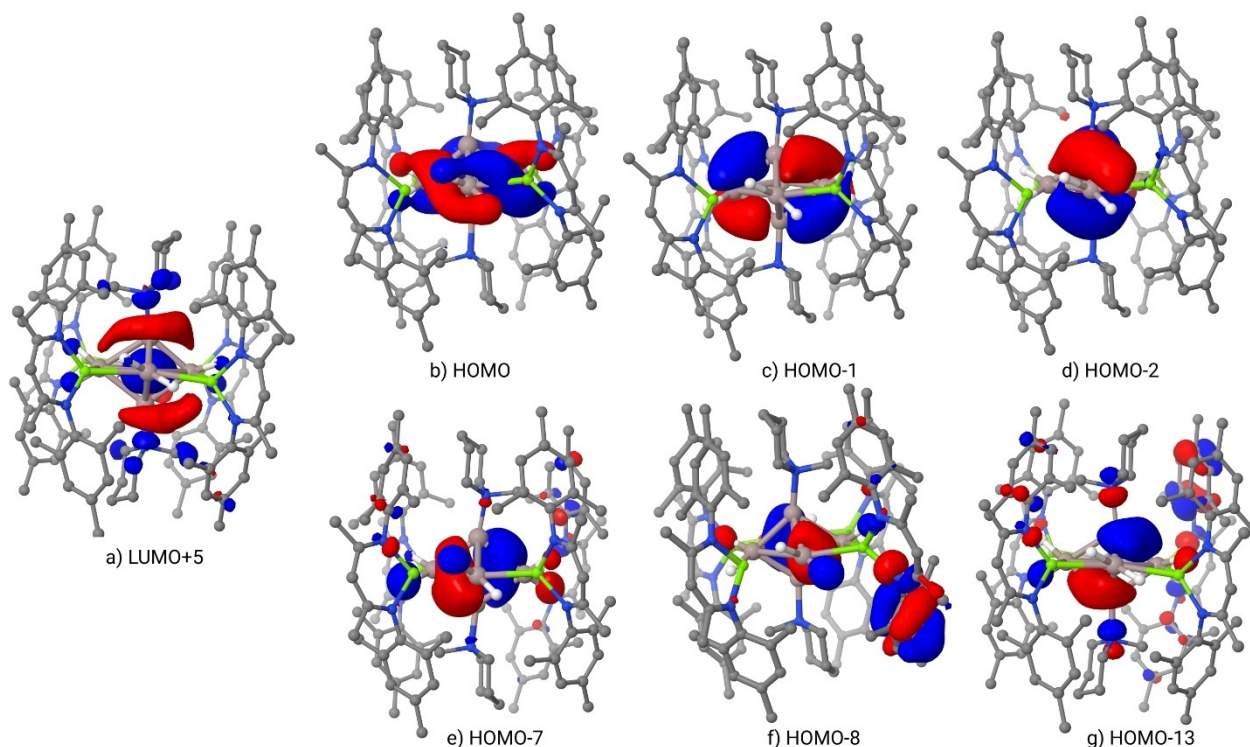
**Figure 3.** Molecular structure of **3a** (20% displacement ellipsoids are shown; hydrogen atoms, except hydrides, omitted; mesityl groups shown as wireframe for clarity). Selected bond lengths [Å] and angles [°]: Al(1)–Mg(1) 2.7595(16), Al(1)–H(1) 1.56(4), Al(1)–H(2) 1.55(4), Al(1)–H(3) 1.57(6), Mg(1)–N(3) 2.059(3), Mg(1)–N(2) 2.063(3), Mg(1)–N(1) 2.176(3), Mg(2)–H(3) 1.75(5), Mg(2)–H(4) 1.81(4), Mg(3)–H(1) 1.99(5), Mg(3)–H(2) 2.03(4), Mg(3)–H(4) 1.97(4), Mg(1)–Al(1)–H(1) 121.9(17), Mg(1)–Al(1)–H(2) 129.9(15), Mg(1)–Al(1)–H(3) 131(2), N(3)–Mg(1)–N(2) 92.37(12), N(3)–Mg(1)–N(1) 108.43(12), N(2)–Mg(1)–N(1) 107.45(12).

such interactions (2.696–2.798 Å; 7 examples<sup>[24]</sup>), while the Mg atom component of that bond has a distorted tetrahedral geometry, being chelated by a <sup>Mes</sup>Nacnac ligand, and  $\kappa^1$ -ligated by NMe<sub>3</sub>. The bridging Al–H distances (1.56 Å mean) in **3a** are considerably shorter than the corresponding three Mg–H separations (1.92 Å mean).

DFT calculations were carried out on cluster **1c** in the gas phase using a series of different functionals, either with or without dispersion corrections applied (see Supporting Information for full details). Whatever the functional used, and with the inclusion of a dispersion correction, two distinct, but energetically very similar (1.8 kcal mol<sup>-1</sup> different), structures were obtained upon geometry optimization. The first has a distorted octahedral structure, while the second one possesses a more open Al<sub>6</sub> core (see Supporting Information for details). A comparison between the experimental and optimized structures of **1c** was achieved by computing their radial distribution functions (rdf, Figure S43). This showed the optimized octahedral structure to be in near perfect agreement with the solid-state structure, while the more open structure is markedly different. That said, the eight hydrides in the calculated octahedral structure lie alternately slightly above and below the Al<sub>4</sub> equatorial plane, which is consistent with the aforementioned unresolved site disorder of the hydrides in the solid-state structure of **1c**, all of which appear to lie in the Al<sub>4</sub> equatorial plane. The possibility that the axial Al centers of **1c** are actually Mg atoms was probed by optimising the structure of [Mg<sub>2</sub>Al<sub>4</sub>H<sub>8</sub>(NMP)<sub>2</sub>][Mg(<sup>Mes</sup>Nacnac)]<sub>4</sub> in the gas

phase. The geometry of this compound was found to be significantly different to that of **1c** (Figure S49).

The distorted octahedral structure of **1c** obtained with the B3PW91 functional (including a dispersion correction), was subsequently probed using Natural Bonding Orbital (NBO) analysis, paying special attention to the Al<sub>6</sub> skeletal molecular orbitals. The study revealed two sets of broadly similar Al–Al Wiberg Bond Indexes (WBI), i.e. those associated with the Al<sub>eq</sub>–Al<sub>eq</sub> interactions (WBI of ca. 0.2 to 0.3), and those for the Al<sub>eq</sub>–Al<sub>ax</sub> bonds (WBI of ca. 0.6 to 0.7, see Figure S45). These results imply that the latter bonding interactions are more covalent and stronger than the former, which is consistent with the variance of Al–Al bond lengths in the solid-state structure. The NPA charge on each (<sup>Mes</sup>Nacnac)Mg fragment (+0.7 avge.) indicate that the molecule is best viewed as consisting of a [Al<sub>4</sub>H<sub>8</sub>(NMP)<sub>2</sub>]<sup>4-</sup> tetra-anion having partially covalent interactions with four [(<sup>Mes</sup>Nacnac)Mg]<sup>+</sup> cations, as also shown from an Atoms in Molecules (AIM) analysis (Figure S48). One may consider that the Al<sub>4</sub>Al<sub>2</sub> core of **1c** should have 14 skeletal electrons, as was proposed for the Ga<sub>4</sub>Ga<sub>2</sub> core of related cluster [(IPriMe)Ga(GaMes)<sub>4</sub>Ga(IPriMe)]<sub>2</sub>.<sup>[21]</sup> Indeed, an analysis of the MO diagram of **1c** revealed 7 delocalized skeletal MOs (Figure 4) necessary for a *closo*-octahedral structure. However, only 6 skeletal orbitals are occupied and one is unoccupied, so the system can be approximated as having 12 skeletal electrons, as was the case for *hypercloso*-aluminum(I) cluster **III**.<sup>[15]</sup> This again is consistent with apparent weakness of the Al<sub>eq</sub>–Al<sub>eq</sub> interactions seen in the solid-state structure of **1c**.



**Figure 4.** 3D-depiction of the seven skeletal orbitals on the Al<sub>6</sub> core of complex **1c** (B3PW91-D3). The iso-contour is set to 0.03.

In summary, reduction of several amido- and aryloxy–Aluminum dihydride complexes with dimagnesium(I) reagents have afforded three discrete isostructural examples of mixed valence aluminum hydride cluster compounds,  $[\text{Al}_6\text{H}_8(\text{NR}_3)_2\{\text{Mg}(\text{A}^{\text{T}}\text{Nacnac})\}_4]$ , in which the average Al oxidation state is +0.66, the lowest for any well-defined aluminum hydride. These represent only the second examples of low oxidation state aluminum hydride clusters, and thus further add to analogies with ubiquitous boron hydride clusters, and the non-hydrido aluminum metalloid clusters of Schnöckel and others. Although the mechanism of formation of  $[\text{Al}_6\text{H}_8(\text{NR}_3)_2\{\text{Mg}(\text{A}^{\text{T}}\text{Nacnac})\}_4]$  could not be determined, several interesting by-products, e.g. metal-metal bonded, anionic magnesio-aluminate complexes,  $[(\text{A}^{\text{T}}\text{Nacnac})(\text{Me}_3\text{N})\text{Mg}-\text{AlH}_3]^-$ , were isolated from reactions that gave the clusters. Computational analyses of  $[\text{Al}_6\text{H}_8(\text{NMP})_2\{\text{Mg}(\text{M}^{\text{es}}\text{Nacnac})\}_4]$  revealed that its distorted octahedral  $\text{Al}_6$  core is electronically unsaturated, in that it exhibits one unoccupied, and six occupied, delocalized skeletal molecular orbitals. This is consistent with the experimentally observed long  $\text{Al}_{\text{eq}}-\text{Al}_{\text{eq}}$  bonds in the cluster. We continue to explore the development of stable metalloid aluminum hydride clusters, and compare their chemistry with that of polyhedral boranes.

### Experimental Section

Full synthetic, spectroscopic and crystallographic details for new compounds; and full details and references for the DFT calculations can be found in the Supporting Information.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Aluminum • Cluster • Hydride • Magnesium(I) • Sub-Valent

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