Anion stabilised hypercloso-hexaalane Al₆H₆

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Boron hydride clusters are an extremely diverse compound class, which are of enormous importance to many areas of chemistry. Despite this, stable aluminium hydride analogues of these species have remained staunchly elusive to synthetic chemists. Here, we report that reductions of an amidinato-aluminium(III) hydride complex with magnesium(I) dimers lead to unprecedented examples of stable aluminium(I) hydride complexes, [<(ArNacnac)Mg]{Al₆H₆(Fiso)}₂, (ArNacnac = [HC(MeCNAr)₂]⁻, Ar = C₆H₂Me₃-2,4,6 Mes; C₆H₃Et₂-2,6 Dep or C₆H₃Me₂-2,6 Xyl; Fiso = [HC(NDip)₂]⁻, Dip = C₆H₃Pr₂-2,6), which crystallographic and computational studies show to possess near neutral, octahedral hypercloso-hexaalane, Al₆H₆, cluster cores. The electronically delocalised skeletal bonding in these species is compared to that in the classical borane, [B₆H₆]²⁻. Thus, the chemistry of classical polyhedral boranes is extended to stable aluminium hydride clusters for the first time.

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The binary hydrides of boron, i.e. boranes (typically $[\text{B}_{x}\text{H}_{y}]_{z}^z$, $x \leq y$, $z = 0$–2), are of enormous importance to chemistry from both fundamental and applications standpoints. The vast majority of these species are low oxidation state boron cluster compounds, which exhibit an enormous array of structural types1. The understanding of the structures of such clusters required the early development of revolutionary theories on chemical bonding (e.g. Wade–Mingos rules for electron counting)2,3, which ultimately led to boranes finding applications in areas as diverse as synthesis4, rocket fuel technology5 and medical science6.

It is remarkable that aluminum, boron’s neighbour in group 13, does not form any isolable hydride cluster compounds, or indeed many binary hydride compounds at all, e.g. $\text{AlH}_{x}$, $\text{H}_{x}\text{Al} (\mu-H)_2\text{AlH}_2$ and $[\text{AlH}_4]$7–7. With that said, a handful of transient, low oxidation state alane cluster compounds have been studied in the gas phase, and some, e.g. $\text{Al}_2\text{H}_6$, have been shown to have fleeting stability8–11. Given that numerous ligand substituted, metalloid aluminium cluster compounds, e.g. $[\text{Al}_{i-1}p(N(SiMe)_3)]_n$12–14, have been reported to be stable at, or close to, room temperature12,13, it seemed that related low-valent aluminium hydride clusters might be ultimately accessible under the right preparative conditions. As a prelude to realising this goal, we have synthesised the first stable binary low oxidation state aluminium hydride fragments, viz. $[\text{Al}_2\text{H}_6]^2$ and Lewis base stabilised $\text{Al}_x\text{H}_y$, by reduction of aluminium(III) hydride precursors with magnesium(I) dimers14,15.

Here, we report that related reductions of an amidinoaluminium(III) hydride complex lead to unprecedented examples of stable aluminium(I) hydride complexes, $[[\text{Nacnac} \text{Mg}][\text{AlH}_6(\text{Fiso})_2]]_2$, $\text{Nacnac} = [\text{HC(MeCNAr)}_2]$, Ar = C$_6$H$_2$Me$_3$-2,4,6 Mes; C$_6$H$_3$Et$_2$-2,6 Dep or C$_6$H$_3$Me$_2$-2,6 Xyl; $\text{Fiso} = [\text{HC(NDip)}_2]$, Dip = C$_6$H$_3$Pr$_2$-2,6), which have weakly bridging or interstitial hydrides within the cluster core (see Supplementary Methods and Supplementary Figs. 15, 16). The hydride ligands of each cluster were identified by $\nu$-D stretching band for $[\text{AlH}_6(\text{Fiso})_2]^-$ completely absent in the infrared spectroscopic data, which exhibits such bands over lower wavenumber (e.g. $1a$, $\nu$ = 1648 cm$^{-1}$) that possibly arise from a weakly bridging $\text{Al}--\text{Mg}$ stretching mode, though these bands overlap with ligand stretching absorptions (see below). Noteworthy is the fact that the band at $\nu$ = 1798 cm$^{-1}$ observed for $1a$ is completely absent in the infrared spectrum of its hexa-deuteride analogue, $1a$-$\text{D}$, which was prepared by magnesium(I) reduction of $[[\mu-N,N$-Fiso$] \text{Al(D)} (\mu-D)]_2$, the Al-D stretching band for $1a$-$\text{D}$ should occur at ca. 1270 cm$^{-1}$, but this is likely masked by strong ligand stretching modes in that region (Supplementary Fig. 12).

Results

Synthetic and spectroscopic studies. Treatment of benzene, toluene, cyclohexane or hexane solutions of the formamidinato-$
\text{ArNacnac}$, $[\text{ArNacnac}]_2$ and $[\text{ArNacnac}]_2$) at elevated temperatures (typically 60–80 °C) reproducibly afforded low yields (ca. 5–20%) of the deep red crystalline aluminium(I) hydride cluster compounds $1$ (Fig. 1), upon cooling the reaction solutions to ambient temperature. On several occasions, a number of low yielding colourless crystalline by-products were isolated from the reaction mixtures, including [(Fiso)Mg(\text{Nacnac})][\text{AlH}(6\text{H}-\text{Fiso})_2]$ and the dialanate salt, $[[\text{MesNacnac}]_2\text{Mg}(\mu-H)]_2[[\text{H}_3\text{Al-\text{AlH}_3}]^2$(see Supplementary Methods and Supplementary Figs. 6–9). The nature of these by-products suggests that the reductive mechanism for the formation of $1$ could involve several intermediates and/or could compete with side reactions. In order to assess these possibilities, reactions that gave $1$ at 70 °C were followed by $^1$H NMR spectroscopy. This revealed complex mixtures of products after several minutes heating, of which $[[\text{Fiso}]\text{Mg}(\text{Nacnac})]$ was identified in significant quantities (Supplementary Fig. 10). Definitive identification of products, other than those which were later isolated as crystalline solids, was not possible, and the mechanism of formation of $1$ is not certain at this time.

To the best of our knowledge compounds $1$ represent the first examples of isolated aluminium(I) hydride complexes, though mononuclear examples have recently been tentatively proposed as unstable intermediates in solution-based reactions19,20. The cluster compounds have negligible solubility in common deuterated solvents, so no meaningful solid state spectroscopic data could be acquired for them. The most relevant solid state spectroscopic data (Supplementary Figs. 11, 12) for the compounds come from their infrared spectra, which exhibit single bands in the characteristic region for terminal Al–H stretching modes7 (e.g. $1a$, $\nu$ = 1798 cm$^{-1}$). In addition, stronger bands are seen at lower wavenumber (e.g. $1a$, $\nu$ = 1648 cm$^{-1}$) that possibly arise from a weakly bridging Al–H–Mg stretching mode, though these bands overlap with ligand stretching absorptions (see below). Noteworthy is the fact that the band at $\nu$ = 1798 cm$^{-1}$ observed for $1a$ is completely absent in the infrared spectrum of its hexa-deuteride analogue, $1a$-$\text{D}$, which was prepared by magnesium(I) reduction of $[[\mu-N,N$-Fiso$] \text{Al(D)} (\mu-D)]_2$, the Al-D stretching band for $1a$-$\text{D}$ should occur at ca. 1270 cm$^{-1}$, but this is likely masked by strong ligand stretching modes in that region (Supplementary Fig. 12).

Crystallographic studies. All complexes $1$ were crystallographically characterised and found to be isostructural, so only the molecular structure of $1a$ is depicted in Fig. 2 (see Supplementary Methods, Supplementary Table 1 and Supplementary Figures 13 and 14). The hydride ligands of each cluster were located from difference maps and freely refined. A neutron diffraction study was also carried out on compound $1a$, which unambiguously confirmed the presence and connectivity of the six hydride ligands, and the absence of any other terminal, bridging or interstitial hydrides within the cluster core (see Supplementary Methods and Supplementary Figs. 15, 16). The compounds can be considered as having near neutral, distorted octahedral $\text{Al}_x\text{H}_y$ cores, opposing equatorial sides of which are coordinated by bridging, electronically delocalised formamidinate ligands. The remaining equatorial sides of the octahedron are bridged by $[[\text{MesNacnac}]\text{Mg}]+$ cations, which have weak interactions with the two hydride ligands that project from each side. Terminal hydride ligands coordinate to the apical aluminium centres of the cluster core, though these are slightly offset from the vector passing through the two aluminium centres to which they are coordinated, presumably for steric reasons. All of the Al–Al distances within the $\text{Al}_x$ core lie in the known range for such bonds (mean: 2.72(12) Å, search of the Cambridge Crystallographic Database, February 2018), though the equatorial Al–Al distances (2.701(2) Å and 2.826(2) Å) are significantly longer than those between all axial and equatorial aluminium centres (2.631(2)–2.691(2) Å). The shorter of the equatorial Al–Al interactions are, not surprisingly, those which are bridged by the formamidinate ligands.

**Fig. 1** Formation of compounds $1$ ($\text{Mes} = \text{C}_6\text{H}_2\text{Me}_3$-2,4,6; $\text{Dep} = \text{C}_6\text{H}_2\text{Et}_2$-2,6; $\text{Xyl} = \text{C}_6\text{H}_3\text{Me}_2$-2,6). The compounds $1$ are prepared by reduction of $[[\mu-N,N$-Fiso$] \text{Al(H)} (\mu-H)]_2$ with magnesium(I) dimers.

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The 14 skeletal valence electron (2) bonds are expected to have a more unsymmetrical, capped structure than shorter Al\textsubscript{eq}–Al\textsubscript{eq} bonds (2.650–2.668 Å) at Al\textsubscript{eq}–Al\textsubscript{eq} distances (2.718–2.819 Å). Reassuringly, the calculated infrared spectrum of 1\textsuperscript{′} (Supplementary Table 3) exhibits terminal and bridging Al–H stretching bands (\(\nu = 1797\text{ cm}^{-1}\) (m) and 1649 cm\(^{-1}\) (s) respectively) that are very close to the experimental values for 1a, thus supporting the use of 1\textsuperscript{′} as a model for 1. The charges on the whole Al\textsubscript{eq}H\textsubscript{eq} fragment (−0.67), both \(\text{H}^{3}\) ligan (−1.10) and both \([\text{MeNacnac}]^{2–}\) cations, showed this fragment to be stable, with a geometry similar to that in the full contact ion compound (Supplementary Fig. 17 and Supplementary Table 2). This, combined with the fact that the uncoordinated Al\textsubscript{eq}H\textsubscript{eq} octahedral unit was calculated to be an unstable entity in the electronic singlet state, suggests that the hypercloso-Al\textsubscript{eq}H\textsubscript{eq} moiety of 1\textsuperscript{′} is stabilised by coordination to the \(\text{H}^{3}\) anions.

The electronic structure of the [Al\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}(\text{H}^{3}\text{Fiso})\textsubscript{2}]\textsuperscript{2–} dianion was calculated and found to be similar to that of the full contact ion compound (Supplementary Figs. 19–21), so only the former is displayed in Fig. 3. There are seven Al-based molecular orbitals (MOs) on the dianion, six of which are filled, in line with the view that the cluster is a 12 skeletal valence electron species. None of these MOs are degenerate, but they do closely resemble the seven filled cluster based MOs for closo-[B\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}]\textsuperscript{2–} (triply degenerate \(\text{t}_{2}\) and \(\text{t}_{1}\) orbital sets, and \(\text{a}_{\text{eq}}\) orbital\textsuperscript{2\textsuperscript{3},2\textsuperscript{4}}), and thus display significant electronic delocalisation over the Al\textsubscript{eq} core. The lack of degeneracy of the Al-based MOs of [Al\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}(\text{H}^{3}\text{Fiso})\textsubscript{2}]\textsuperscript{2–} arises from the lower symmetry, and lower skeletal electron count, of the dianion relative to those of closo-[B\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}]\textsuperscript{2–}. Interestingly, the UMO\textsubscript{1} (lower energy empty MOs are ligand based) of [Al\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}(\text{H}^{3}\text{Fiso})\textsubscript{2}]\textsuperscript{2–} resembles the degenerate \(\text{t}_{1}\text{H}^{3}\) HOMO of closo-[B\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}]\textsuperscript{2–} which exhibits the most analogous, quasi-equatorial B–B bonding character. This goes a long way to explaining the weak Al\textsubscript{eq}–Al\textsubscript{eq} interactions in 1\textsuperscript{′}. The HOMO and HOMO-1 of [Al\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}(\text{H}^{3}\text{Fiso})\textsubscript{2}]\textsuperscript{2–} are reminiscent of the other two \(\text{t}_{2}\) orbitals of closo-[B\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}]\textsuperscript{2–}, while the HOMO-2, HOMO-3 and HOMO-4 show similarities with the \(\text{t}_{1}\) orbitals of the borane. At lower energy is the HOMO-9 which corresponds to the \(\text{a}_{\text{eq}}\) orbital of closo-[B\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}]\textsuperscript{2–}. No Al-based MO exhibits significant contributions from the \(\text{H}^{3}\) anions, the lone pairs of which are polarised towards their N-centres, and should therefore not be included in the counting of electrons contributing to Al–Al bonding within the cluster core. This view is supported by results of an energy decomposition analysis of the intrinsic interactions between the Al\textsubscript{eq}H\textsubscript{eq} core and the amidinate ligands in [Al\textsubscript{1}\textsubscript{eq}H\textsubscript{eq}(\text{H}^{3}\text{Fiso})\textsubscript{2}]\textsuperscript{2–} (Supplementary Fig. 22 and Supplementary Table 6). Calculations of the NICS values of 1\textsuperscript{′} at the centre of the Al\textsubscript{eq}H\textsubscript{eq} core suggest that the cluster exhibits significant 3-dimensional aromaticity (NICS\textsubscript{30} = −12.49 ppm, NICS\textsubscript{z} = −45.74 ppm) (Supplementary Table 7), as is common for polyhedral boranes\textsuperscript{1}.

**Methods**

**General.** Experiments were carried out under a dry, oxygen-free dinitrogen atmosphere using Schlenk-Line and glove-box techniques. All solvents and reagents were rigorously dried and deoxygenated before use. Compounds were variously characterised by elemental analyses, NMR, FTIR, and Raman spectroscopies, single crystal X-ray diffraction studies, and DFT calculations. Further details are available in Supplementary Methods.
Preparation of \([\{\text{XylNacnac}\}	ext{Mg}(\text{OEt}_2)]\). A freshly prepared solution of MeMgI (28.4 mmol) in diethyl ether (80 mL) was added over 20 min to a stirred solution of 85% Nacnach (8.08 g, 26.4 mmol) in diethyl ether (100 mL) at −30 °C, yielding a colourless precipitate. The suspension was warmed to room temperature and stirred for 1 h after which time the precipitate of the title compound was collected by filtration. The supernatant solution was concentrated to ca. 40 mL and cooled to −30 °C to afford a second crop (12.86 g, 90%). M.P. 195 °C to afford a second crop (12.86 g, 90%). M.P. 195 °C (decomp.); 1H NMR (100 MHz, 298 K, C6D6), 1.54 (s, 6H; NCCCH3), 3.11 (br, 4H; OCH2CH3), 4.86 (s, 1H; CH), 6.75–7.15 (m, 6H; Ar-), 13.0 (NCCCH3), 18.7 (ortho-CH3), 21.1 (ortho-CH3), 23.4 (OCH2CH3), 65.9 (OCH2CH3), 95.3 (CH), 124.7, 129.6, 131.5, 147.7 (Ar-C), 168.8 (NCCCH3); MS (EI 70 eV), m/z (%): 457.1 (MH+ -OEt2, 5), 306.4 (XylNacnacH+), 100; IR (Nujol) ν (cm−1): 1518s, 1262m, 1215w, 1197m, 1185m, 1148m, 1092m, 1021m, 996m, 857m, 848w, 775s, 758m, 636m. Note: A satisfactory reproducible microanalysis of the compound could not be obtained due to co-crystallisation of the product with small amounts (ca. 5%) of the iodide bridged magnesium(II) dimer, \([\{\text{XylNacnac}\}	ext{Mg}(\text{I})]\), which could not be removed after several recrystallisations. The constitution of this co-crystallised mixture was confirmed by a poor quality crystal structure determination of \([\{\text{XylNacnac}\}	ext{Mg}]_2\), details of which are not reported here due to the low quality of the diffraction data.

Preparation of \([\{\text{MesNacnac}\}	ext{Mg}(\text{OEt}_2)]\). Toluene (80 mL) and diethyl ether (ca. 2 mL) were added to \([\{\text{MesNacnac}\}	ext{Mg}(\text{OEt}_2)]\) (1.58 g, 2.40 mmol). The resultant solution was rapidly stirred over a sodium mirror (0.70 g, 30.4 mmol) for 5 days to yield a yellow/green suspension. This was filtered, the yellow filtrate concentrated to ca. 20 mL and placed at −30 °C overnight to give yellow crystals of the title compound. A second crop was isolated after further concentration and cooling of the supernatant solution (0.28 g, 29%). M.P. 159–161 °C (decomp.); 1H NMR (400 MHz, 298 K, C6D6), δ = 1.48 (s, 12H; NCCCH3), 1.90 (br, s, 24H; ortho-CH3), 4.76 (s, 2H; CH), 6.85–7.10 (m, 12H; Ar-H); 13C{1H} NMR (100 MHz, 298 K, C6D6), δ = 19.2 (NCCCH3), 23.1 (ortho-CH3), 95.3 (CH), 124.1, 128.4, 131.8, 148.0 (Ar-C), 166.3 (NCCCH3); MS (EI 70 eV), m/z (%): 659.5 (MH+ +, 10); IR (Nujol) ν (cm−1): 1555s, 1520w, 1278m, 1262m, 1197m, 1176m, 1148m, 1148m, 1092m, 1012m, 996m, 857m, 848m, 775s, 758s, 636m. Note: A satisfactory reproducible microanalysis of the compound could not be obtained due to co-crystallisation of the product with small amounts (ca. 3%) of the β-diketimine, 85% Nacnach, which could not be removed after several recrystallisations.
allow spectroscopic characterisation, but it is noteworthy that the 2,6-dihydropyridine substituted analogue of the compound, \([15^\text{N}]\text{Nacnac}\text{Mg}[\mu-\text{H}]](\text{H-Al-AlH})\), has been previously isolated and fully characterised.15 (ii) Reproducible low-T preparation of 1a (typically 5–20%) were achieved under a number of reaction conditions. For example, toluene, hexane, cyclohexane or benzene could be used as the reaction solvent, the reaction temperature was varied from ca. 60–80 °C, the reaction pressure was monitored from 1.2 to 2.1 (\([15^\text{N}]\text{Nacnac}\text{Mg}[\mu-\text{H}])\); \((\mu-\text{N-N-Fiso})\text{Al}(\mu-\text{H}))\), and the time the reaction mixture was kept at elevated temperature varied from 5 to 25 min. The time required for the reaction depended strongly on the diameter of the reaction flask. (iii) Compound 1a (and 1b-c) have negligible solubility in common deuterated solvents once crystallised, so no meaningful kinetic data could be acquired for these. Attempts to dissolve 1a in d6-THF led to decomposition of the compound. (iv) Attempts were made to obtain solution state spectroscopic data on 1a from red reaction solutions before it crystallised from those solutions. NMR spectroscopic data on those solutions showed complex product mixtures (Supplementary Figure 10), while ESI mass spectroscopic analyses of the reaction solutions showed no ion that could be assigned to 1a or its fragmentation products.

**Preparation of \(((\text{DepNacnac})\text{Mg})_2[\text{AlH}_3\text{Fiso}_2]_3\) (1b).** \((\mu-\text{N-N-Fiso})\text{Al}(\mu-\text{H}))\)19 (200 mg, 0.26 mmol) was added to a suspension of \(((\text{DepNacnac})\text{Mg})_2\) (200 mg, 0.26 mmol) in benzene (2 mL) in a grease-free Schlenk (20 mm diameter). The mixture was heated to 65 °C for 5 min or until a bright red solution formed. Allowing the solution to stand at room temperature for 4 days resulted in the deposition of deep red crystals of 1b (10 mg, 5% based on aluminium). M.P. > 150 °C (decomp.); IR (Nujol) ν (cm–1): 1834m (Al–H str.), 1363s, 1320s, 1258s, 1187s, 1023s, 809m. No solution state spectroscopic data could be obtained for the compound due to its negligible solubility in common organic solvents. A reproducible microanalysis of the compound could be obtained due to its low yield and the fact that it co-crystallised with the known dialanate salt, \(((\text{DepNacnac})\text{Mg})_2(\mu-\text{H})\)\text{[H}_3\text{Al}(\text{H})\text{Al}(\text{H})]\text{[H}_3\text{Al}(\text{H})\text{H]}_2\text{N,N-Fiso})\text{Al}(\text{H})\); IR (Nujol) ν (cm–1): 1829m (Al–H), 1623m (br incl. Al–H str.), 1593m, 1543v, 1336v, 1322v, 1265m, 1257m, 1233m, 1185m, 1096m, 1031m, 951m, 843m, 802m, 762, 698s. No solution state spectroscopic data could be obtained for the compound due to its negligible solubility in common organic solvents. A reproducible microanalysis of the compound could not be obtained due to the low yield and the fact that it co-crystallised with colourless crystalline compounds from which it could not be completely separated.

**Preparation of \([(\text{DepNacnac})\text{Mg})_2[\text{AlD}_3\text{Fiso}_2]_3\) (1c).** \((\mu-\text{N-N-Fiso})\text{Al}(\mu-\text{D}))\)19 (165 mg, 0.21 mmol) was prepared as the procedure for \((\mu-\text{N-N-Fiso})\text{Al}(\mu-\text{H}))\)19 (see Supplementary Methods), was added to a suspension of \(((\text{DepNacnac})\text{Mg})_2\) (200 mg, 0.42 mmol) in benzene (5 mL) in a grease-free Schlenk flask (20 mm diameter). The mixture was heated to 65 °C for 5 min or until a bright red solution formed. Allowing the solution to stand at room temperature for 4 days resulted in the deposition of deep red crystals of 1c (10 mg, 4% based on aluminium). M.P. > 150 °C (decomp.); IR (Nujol) ν (cm–1): 1829m (Al–H), 1623m (br incl. Al–H str.), 1593m, 1543v, 1336v, 1322m, 1265m, 1257m, 1233m, 1185m, 1096m, 1031m, 951m, 843m, 802m, 762, 698s. No solution state spectroscopic data could be obtained for the compound due to its negligible solubility in common organic solvents. A reproducible microanalysis of the compound could not be obtained due to the low yield and the fact that it co-crystallised with colourless crystalline compounds from which it could not be completely separated.
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Author contributions

C.J. and A.S. contributed to conception and design of experiments, data collection, analysis and interpretation; G.F., A.J.E., S.J.B., D.C. and N.H. contributed to data collection, analysis and interpretation; R.O.P. extracted the neutron single-crystal data from the Laue diffraction images; C.J. wrote the manuscript with input from all authors.

Additional information

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