PAPER

Synthesis, characterization and reactivity of an imidazolin-2-iminato aluminium dihydride†

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The reaction of bis(2,6-diisopropylphenyl)imidazolin-2-imine (LH, **1**) with $Me_3N \cdot AlH_3$ furnishes $\{\mu\text{-LAlH}_2\}_2$ (**2**). The marked tendency of **2** to release its hydride substituents is ascribed to the strong electron-donor character of the imidazolin-2-iminato ligand. This is supported by its reactivity study and DFT calculations. In fact, compound **2** was further converted with Me_3SiOTf, $Me_2S \cdot BH_3$, $Me_2S \cdot BBr_3$, and BX_3 (with X = Cl, Br, and I) into $\{\mu\text{-LAl(H)OTf}\}_2$ (**3**), $\{\mu\text{-LAl(BH}_4)_2\}_2$ (**4**), and $\{\mu\text{-LAlX}_2\}_2$ (**5**, X = Br; **6**, X = Cl; **7**, X = I), respectively. For all new aluminium complexes the formulation as dimers was evidenced by high resolution mass spectrometry, as well as single-crystal X-ray diffraction analysis. A prominent structural motif of these compounds is the square-planar four-membered Al_2N_2 ring with two bridging bulky imidazolin-2-imino moieties.

Introduction

Aluminium hydrides – versatile reagents with rich chemistry

For many years, chemical synthesis has been gaining immense benefit from the distinct reactivity of the aluminium–hydrogen bond. The strong need for highly selective transformations, increased focus on safety considerations, and efficiency in handling and storage are only some reasons why we find the chemically rogue parent aluminium hydride tamed into more suitable forms today. A variety of hydridoalanes has been tailored and very often reactivity adjustment is realized by steric congestion at the aluminium centre and by attaching strongly electron-donating substituents to the aluminium atom. Furthermore, hydridoalanes are used in a diverse range of applications. For instance, the hydroalumination of carbonyl[1,2] and alkyne[3–7] functionalities is a common application for this class of compounds in organic synthesis. Though the intermediate aluminium species in these reactions are often elusive, the use of aluminium hydrides such as **I**[8] (Fig. 1) that bear highly sophisticated ligands grants access to all types of isolatable and well-defined model complexes. Compound **I** can be categorized as an aluminium dihydride and is related to the parent aluminium trihydride by replacement of one hydride for an anionic ligand. Thus, an ancillary ligand may
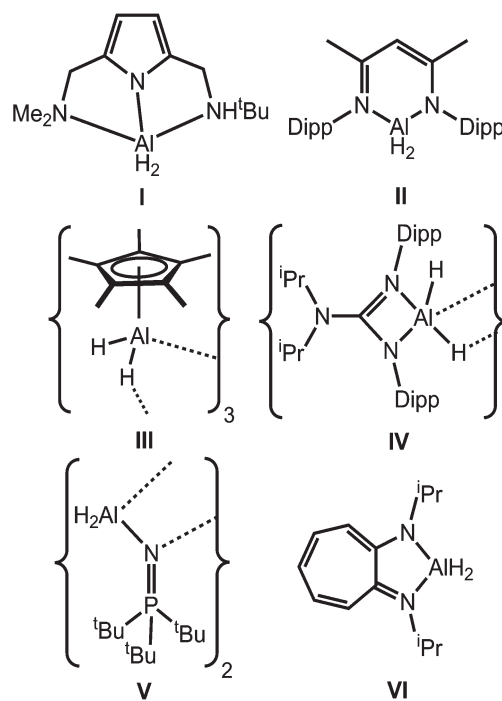

Fig. 1 Selected aluminium dihydride compounds. The pincer complex **I**, the β-diketiminato complex **II**, and the trimeric cyclopentadienide **III**. The guanidinate **IV**, the phosphinimide **V**, as well as the troponimide **VI** (Dipp = 2,6-diisopropylphenyl).

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be introduced, and yet, two reactive functional groups at the metal centre are preserved for the purpose of follow-up chemistry. The β-diketimino group, in particular, has been a key ligand to a rich chemistry of respective aluminium dihydrides.[9–12] A prominent example is **II** (Fig. 1), which can

be used for the activation of non-polar element–element bonds as demonstrated by its conversion with elemental sulphur or selenium.[9,10] In a different field of applied science one finds chemical vapour deposition technology exploiting the thermodynamic properties of molecular aluminium hydrides for the purpose of creating composite materials.[1,13–15]

Aluminium hydrides are considered as fuel storage-materials with reasonable prospects in a hydrogen-based alternate energy-supply concept.[16,17] Moreover, the application of aluminium hydrides in the synthesis of low-valent aluminium compounds has been reported and **III**[18] (Fig. 1) is a very recent example among others[19] of an intriguing nature. Recently, scarce σ-alane complexes of transition metals (*e.g.* Cr, Mo, W, Mn) implementing ligands such as **IV**[19] (Fig. 1) have been described.[20,21] The particular character of the aluminium hydride moiety in transition-metal complexes will most certainly be subject to ongoing profound study.

For advocating the diversity of ligand systems employed in the field we would select the phosphinimide **V**[22] (Fig. 1) as a rare example for the application of this particular electron donating group in aluminium hydride chemistry. A number of non-hydride aluminium complexes with this ligand system have been reported, as well.[22–24] Furthermore, a troponiminato ligand can be used to stabilize the monomeric dihydride species in **VI** (Fig. 1).[25]

The imidazolin-2-iminato ligand – a potent electron donor

The development of a new ligand to control the properties and the reactivity of an aluminium hydride is one indispensable part of this chemistry and hence an important research aim. An imidazolin-2-imino group as an ancillary ligand can be considered a suitable bulky and electron donating group for a novel aluminium dihydride. The imidazolin-2-iminato ligands act as a 2σ- and either a 2π- or a 4π-electron donor and, in consequence, some multiple-bond character in the interaction between the nitrogen atom and the metal centre may result.[26–31] Fine-tuning of this ligand system with respect to its steric and electronic properties can be conveniently accomplished by altering the substituents to the ring.[28,30] Pioneering work related to main group metal complexes of the imidazolin-2-iminato ligand was done by Kuhn and coworkers (**VII**, Fig. 2).[32,33] Contemporary research on transition metal- and rare earth metal complexes of this imino group is mainly carried out by Tamm and coworkers.[28–30,34] For example, striking activity as a catalyst for propylene polymerization is ascribed to the titanium complex **VIII**[30] (Fig. 2) which is representative for the field. Most remarkably, the phosphinonitrene **IX** (Fig. 2) was described by Bertrand and coworkers, thus demonstrating the high potential of this ligand system in main group element chemistry.[35–37] Recently, we have demonstrated the application of the bis(2,6-diisopropylphenyl)imidazolin-2-imino group in the synthesis of the unprecedented silylene **X** (Fig. 2).[31]

Herein we report the synthesis and characterization of the hitherto unknown bis(2,6-diisopropylphenyl)imidazolin-2-
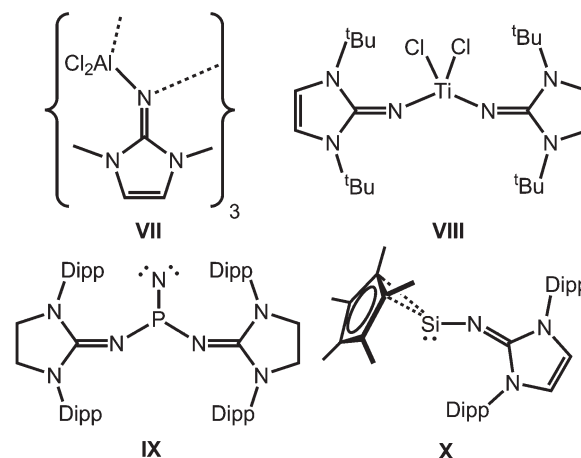

Fig. 2 Imidazolin-2-imino compounds with main group elements (**VII**, **IX**, **X**) and the titanium complex **VIII** (Dipp = 2,6-diisopropylphenyl).

imino aluminium dihydride {μ-LAlH₂}₂ **2** and its reactivity as a hydride transfer reagent.

Results and discussion

Introduction of the bulky imidazolin-2-imino group to the aluminium centre

In order to introduce the bis(2,6-diisopropylphenyl)imidazolin-2-iminato ligand (L⁻) to a hydridoalane moiety we found it reasonable to adopt a procedure[22] reported by Stephan and co-workers for the synthesis of a related phosphinimide. The stoichiometric reaction of LH (**1**)[38] with $Me_3N \cdot AlH_3$ in toluene affords the dimeric aluminium dihydride {μ-LAlH₂}₂ (**2**) in sufficient yield (66%) as confirmed by multinuclear NMR spectroscopy, high resolution mass spectrometry, single-crystal X-ray diffraction data, and elemental analysis (Scheme 1).

In the infrared spectrum the bands at 1830 cm⁻¹ and 1798 cm⁻¹ are assigned to the Al–H bonds in **2**, which is in accordance with the IR absorptions reported for the related
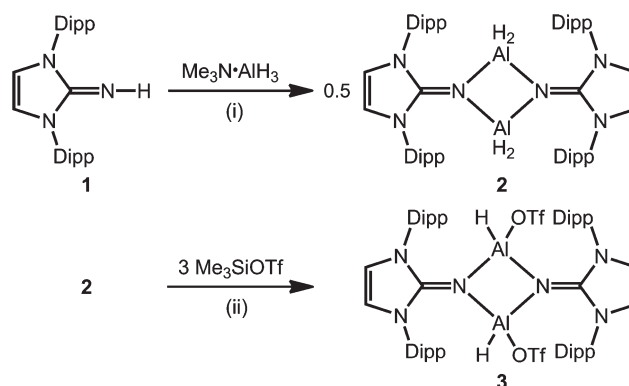

Scheme 1　Formation of the imidazolin-2-imino aluminium hydride **2** *via* conversion of the imine **1** and synthesis of its triflate derivative **3**. (i) Toluene, (1) −78 °C, 2 h, (2) rt, 24 h. (ii) Toluene, (1) 0 °C, 30 min, (2) rt, 24 h. Dipp = 2,6-diisopropylphenyl, Tf = SO₂CF₃.

aluminium dihydride **II**.[10] The resonance pattern observed for the imidazolin-2-iminato moiety in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** resembles the one in related silicon complexes such as LSi(C$_5$Me$_5$)Br$_2$.[31] In the proton NMR spectrum (C$_6$D$_6$), a broad resonance at 2.60 ppm with 4 H intensity is observed that can be assigned to the hydrogen atoms of the AlH$_2$ moieties and is more shielded than those observed for amidino-, β-diketimino-, or 1-azaallyl aluminium dihydrides (4.60 ppm–4.87 ppm)[39–41] and the starting material Me$_3$N·AlH$_3$ (4.08 ppm), as well as [Me$_2$NAlH$_2$]$_3$ (3.8 ppm)[42] but is shifted more downfield than that of aluminium dihydride **VI** (1.08 ppm, Fig. 1).[25] After heating a solution of **2** in toluene to reflux temperature over a period of 12 h the NMR spectroscopic control did not reveal any signs of decomposition which accounts for the thermal stability of this aluminium dihydride. Compound **2** crystallizes from hexane–toluene in the monoclinic space group $P2_1/c$ and the unit cell contains two crystallographically independent centrosymmetric molecules. In one of these molecules, the two equivalent aluminium atoms are disordered over two sites. Since the structural parameters of the two molecules are almost identical, we discuss only the one for which no disordered metal atom is observed. The single-crystal X-ray data of **2** reveals the four-membered Al$_2$N$_2$ ring as the prominent structural motif of the dimer (Fig. 3). The Al–N bond distances of 1.912(1) Å and 1.915(1) Å in **2** are slightly longer than those in compound **V** (Al–N = 1.887(3)–1.905(3) Å).[22] The N(1)–Al(1)–N(1A) and
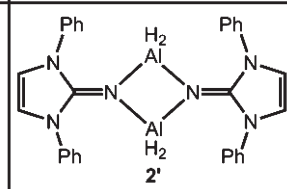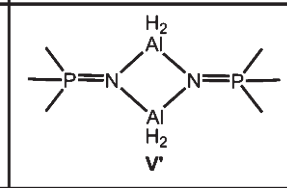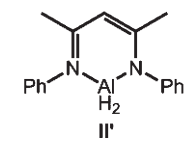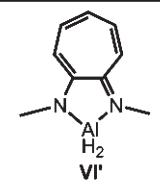
Al(1)–N(1)–Al(1A) angles in **2** are 86.2(1)° and 93.8(1)°, respectively. The dihedral angle N(1A)–Al(1)–N(1)–Al(1A) of 0.0° confirms that these four atoms are all located in one plane. The Al(1)⋯Al(1A) distance in **2** amounts to 2.795(1) Å, which is significantly longer than the metal–metal bond lengths in characteristic donor-stabilized dialanes with four-coordinated aluminium centres.[19,43] The N(1)–C(1) bond length of 1.289(2) Å in **2** only differs slightly from the analogous values in silicon compounds stabilized by imidazolin-2-iminato ligands.[31,38] Furthermore, it is similar to that of the guanidinate {μ-(Me$_2$N)$_2$CNAl(NMe$_2$)$_2$}$_2$.[44] The 5-membered imidazoline ring plane is tilted *versus* the central Al$_2$N$_2$ moiety by 9°. The sum of the bond angles around the nitrogen atom attached to the aluminium centre amounts to 360°, which confirms the trigonal-planar geometry around the nitrogen atom of the imino group.

DFT calculations of related aluminium dihydrides

For obvious reasons, the reactivity of an aluminium dihydride will largely depend on its hydride-donor strength, and one would expect that the tendency for hydride release depends on the electron density at the hydrogen atoms and the nature of the Al–H bonds. Hence, we performed quantum-mechanical calculations on a sterically reduced model compound of **2** (**2′**, Fig. 4) and related model compounds with a four-coordinated
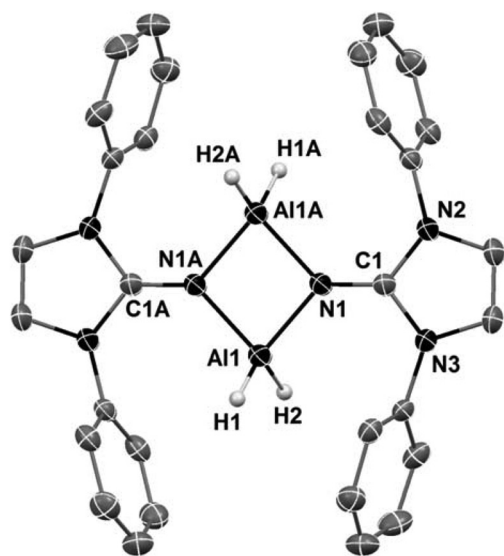
Fig. 3 Molecular structure of **2** in the solid state. The unit cell contains two independent molecules and only one is shown; hydrogen atoms (except on aluminium) and isopropyl groups have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), atom⋯atom distance (Å), bond angles (°), and dihedral angle (°): Al(1)–N(1) 1.915(1), Al(1)–N(1A) 1.912(1), Al(1)–H(1) 1.48(2), Al(1)–H(2) 1.55(2), N(1)–C(1) 1.289(2), N(2)–C(1) 1.389(2), Al(1)⋯Al(1A) 2.795(1); H(1)–Al(1)–H(2) 118(1), N(1)–Al(1)–N(1A) 86.2(1), Al(1)–N(1)–Al(1A) 93.8(1), Al(1)–N(1)–C(1) 131.7(1), Al(1A)–N(1)–C(1) 134.0(1); N(1A)–Al(1)–N(1)–Al(1A) 0.0. Symmetry transformation used to generate equivalent atoms: A: −x + 1, −y + 2, −z + 1.

Entry	Compound	WBI$_{Al-H}$	NBO charge at Al*H*
1	**2′**	0.786	−0.396
2	**V′**	0.788	−0.408
3	**II′**	0.810	−0.385
4	**VI′**	0.809	−0.382

Fig. 4 Calculated Wiberg bond indices of the Al–H bonds and NBO charges at the hydride atoms for the simplified model compounds **2′**, **II′**, **VI′**, and **V′**.

aluminium centre of **II**,[10] **V**,[22] and **VI**[25] (*i.e.* **II′**, **V′**, and **VI′**; Fig. 4) at the B3LYP/6-31G(d) level of theory (*cf.* the ESI† for computational details). The optimized structures of the model compounds matched the experimental data. According to the NBO charges, each H atom at the aluminium centre in **2′** bears a negative net charge (−0.396), which is more negative than those in **II′** (−0.385) and **VI′** (−0.382), but more positive than that in **V′** (−0.408). Interestingly, the calculated WBI values of the Al–H bonds in **2′** (0.786) are smaller than those in **II′** (0.810), **V′** (0.788), and **VI′** (0.809) and the lower bond order implies a higher polarization of the Al–H group. Consequently, reactivity enhancement towards highly polarized electrophiles may coincide. These results suggest that **2** is a strong hydride donor reagent.

Hydride abstraction from {μ-LAlH₂}₂ (2)

Due to the strong electron-donor character of the iminato ligand L⁻ and its steric congestion we had reason to expect a structural motif with discrete LAlH₂ moieties in the solid state instead of the formation of dimers as evidenced by the single crystal X-ray data of {μ-LAlH₂}₂ (**2**) and its high resolution mass spectrum (*vide supra*). Stimulated by a report of Stephan and coworkers about the reaction of **V** with trimethylsilyltriflate to {μ-(ᵗBu)₃PNAl(H)OTf}₂,[22] we treated **2** with three equivalents of Me₃SiOTf (Tf = SO₂CF₃), which resulted in replacement of one hydride substituent per aluminium centre by a triflate group (Scheme 1). Compound **3** {μ-LAl(H)OTf}₂ was obtained in analytically pure form after repeated recrystallization from THF–hexane. It was characterized by multinuclear NMR spectroscopy, high resolution mass spectrometry, single-crystal X-ray study, and elemental analysis. Though the symmetry at the aluminium centre in **3** is lowered in comparison to its precursor, a resonance pattern similar to that of **2** is observed in the ¹H and ¹³C{¹H} NMR spectra of **3** in CD₃CN. Similar to **2**, the molecular structure of **3** in the solid state reveals a dimer with a central Al₂N₂ core (Fig. 5). Two triflate groups are found assuming positions on the same side of the Al₂N₂ ring, thus their configuration is pseudo-*cis* which is reminiscent of the phosphinimide congener {μ-(ᵗBu)₃PNAl(H)OTf}₂.[22] As marked by the dihedral angle N(4)–Al(1)–Al(2)–N(1) = 169.6(2)° the reduced symmetry around the Al₂N₂ ring inflicts slight deviation from its square-planar geometry that is observed for **2** (Fig. 3) in very high approximation. The Al–N bond lengths of **3** are found in a range from 1.849(3) Å to 1.872(3) Å and are notably shorter than those in **2**. This indicates that the triflate substituents in **3** render the aluminium centres more electrophilic, thus strengthening the interaction with the nitrogen atoms of the adjacent ligands.

While the replacement of one hydride at the aluminium atom for OTf⁻ proceeded readily, we were not able to isolate a related species with a ditriflated metal centre even when treating {μ-LAlH₂}₂ (**2**) with a large excess of Me₃SiOTf at an elevated temperature.

As an alternative group of electrophiles that might elucidate the hydride-donating properties of **2**, we conceived boron-centred Lewis acids. The turn from silicon to boron is
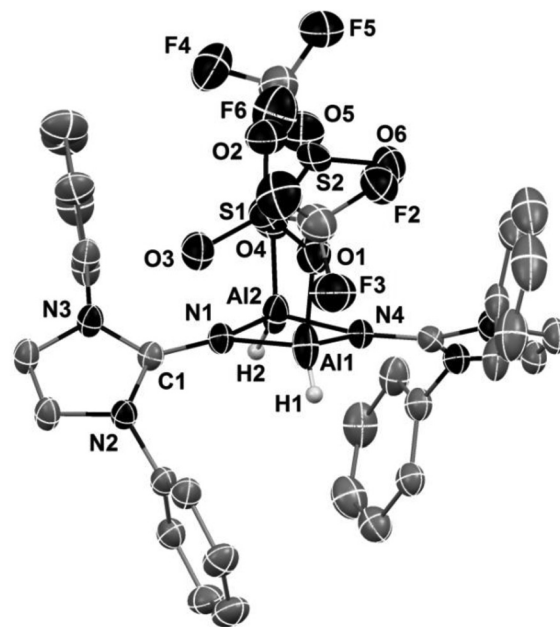

Fig. 5 Molecular structure of **3**(THF)₃ in the solid state. Hydrogen atoms (except on aluminium), isopropyl groups, and THF molecules have been omitted for clarity; only the higher occupied site is shown for atoms disordered over two sites; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), atom⋯atom distance (Å), bond angles (°), and dihedral angle (°): Al(1)–N(4) 1.849(3), Al(2)–N(4) 1.872(3), N(1)–C(1) 1.327(5), N(2)–C(1) 1.376(5), Al(1)⋯Al(2) 2.666(2); N(1)–Al(2)–N(4) 87.7(2), Al(1)–N(1)–Al(2) 91.6(2); N(4)–Al(1)–Al(2)–N(1) 169.6(2).

reasonable because the diagonal relationship between these elements is one of the many verified reactivity patterns emerging from the periodic table.[45] Recently, Harder and Spielmann reported the synthesis of the β-diketiminato-stabilized (Dipp)nacnacAl(BH₄)₂ by reaction of **II** with DippNH₂·BH₃.[46] Inspired by these findings, we set out to react **2** with four equivalents of borane dimethylsulphide complex (Scheme 2). As the outcome of the presumed hydride transfer from the aluminium centre to the boron atom {μ-LAl(BH₄)₂}₂ (**4**) was formed as elucidated by multinuclear NMR spectroscopy, single-crystal X-ray structure determination, elemental analysis, as well as high resolution mass spectrometric analysis.

An early synthesis of the parent Al(BH₄)₃ goes back to Brown and coworkers.[47] Aluminium borohydride is described as a hazardous material, particularly because the vapour of the liquid substance may spontaneously detonate upon contact with air and moisture. In addition, it slowly decomposes at room temperature with the release of dihydrogen.[47] In recent years, Al(BH₄)₃ has gained prominent attention from the field of materials science[16,48] and the transformation into more suitable hydrogen-storage materials as ammine aluminium borohydrides[49–51] and aluminoboranes[52] is explored. Given this background, it is desirable to have access to a room temperature-stable and well-defined model complex such as {μ-LAl(BH₄)₂}₂ (**4**) in which the relevant aluminium centres and borohydride moieties are unified.
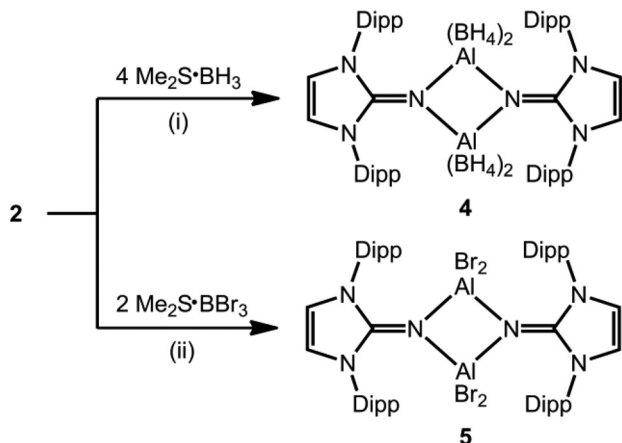
Scheme 2 Conversion of the aluminium dihydride **2** with the dimethylsulphide complexes of borane (top) or boron tribromide (bottom) yielding **4** and **5**, respectively. (i) Toluene, (1) −78 °C, 2 h, (2) rt, 24 h. (ii) Toluene, (1) 0 °C, 20 min, (2) 80 °C, 3 d. Dipp = 2,6-diisopropylphenyl.

In the infrared spectrum of **4** we assign absorptions at 2492 cm^{-1} and 2431 cm^{-1} to be produced by the B–H bonds in **4**. The symmetric and asymmetric BH stretches of $Al(BH_4)_3$ have been reported at a comparable wavenumber.[53] In the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **4** (THF-d$_8$), a deviation from the expected signal pattern for **L** (cf. the NMR data of **2**) is found in that the resonances of the Dipp moieties split into two signal sets of equal intensity. The 16 hydrogen atoms of the BH$_4$ groups give rise to a broad resonance at −0.33 ppm in the ^{1}H NMR spectrum. The chemical shift of the boron nuclei amounts to −37 ppm ($h_{1/2}$ = 270 Hz) as observed in the $^{11}B\{^1H\}$ NMR spectrum (THF-d$_8$). In the proton-coupled ^{11}B NMR spectrum, only a broad singlet at −37 ppm ($h_{1/2}$ = 380 Hz) is observed (cf. (Dipp)nacnacAl(BH$_4$)$_2$: $\delta(^{11}$B) = −36.6 ppm, quintet, J = 85.3 Hz, C$_6$D$_6$).[46] Obviously, the J coupling between boron and hydrogen in **4** is not resolved. However, the signal broadening of 110 Hz in the proton-coupled ^{11}B NMR spectrum suggests the presence of borohydride moieties. After storing a flame-sealed NMR tube with a sample of **4** in THF-d$_8$ at room temperature for two weeks no signs of decomposition were observed. However, upon heating to 60 °C overnight the NMR spectroscopic analysis revealed a new species giving rise to an additional imino ligand signal set in the ^{1}H NMR spectrum, as well as a second singlet in the $^{11}B\{^1H\}$ NMR spectrum at −21.5 ppm. After the sample tube had been exposed to a temperature of 90 °C for 2 d compound **4** had been consumed entirely and the proton NMR spectrum evidenced the formation of several unidentified products, as well as dihydrogen. Crystallization of **4** from toluene–THF–hexane yielded single crystals suitable for X-ray diffraction analysis which contained 1.5 equivalents of toluene in the lattice. The X-ray study confirms the dimeric formulation of compound **4** (Fig. 6) and the structural parameters of the Al$_2$N$_2$ ring and of the attached iminato ligands resemble the geometry of the corresponding groups in **2**. The Al–N bond lengths in **4** lie in a range from 1.873(2) Å to 1.889(2) Å, which marks a slight decrease in
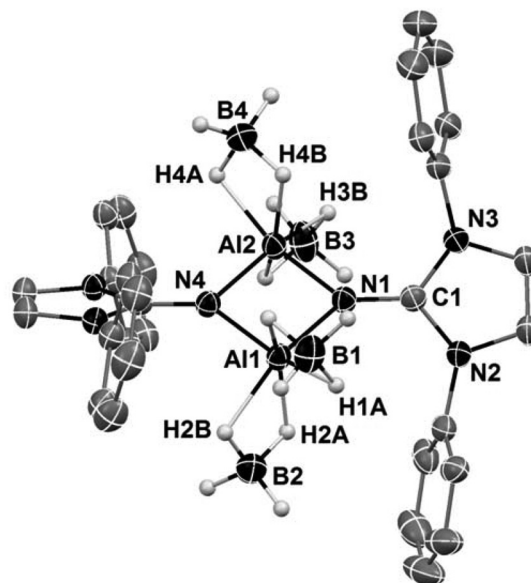
Fig. 6 Molecular structure of **4**(toluene)$_{1.5}$ in the solid state. Hydrogen atoms (except on boron), isopropyl groups, and toluene molecules have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), atom⋯atom distances (Å), and bond angles (°): Al(1)–H(2A) 1.69(2), Al(1)–H(2B) 1.82(2), Al(2)–N(1) 1.873(2), Al(2)–N(4) 1.889(2), N(1)–C(1) 1.319(2), Al(1)⋯Al(2) 2.728(1), Al(1)⋯B(1) 2.229(3), Al(1)⋯B(2) 2.220(3); N(1)–Al(1)–N(4) 87.0(1), N(1)–Al(2)–N(4) 87.1(1), Al(1)–N(1)–Al(2) 93.2(1), Al(1)–N(4)–Al(2) 92.7(1), Al(1)–N(1)–C(1) 134.0(1).

comparison to the respective distances in **2** (Al–N = 1.912(1) Å and 1.915(1) Å; vide supra). The shorter Al–N bond lengths coincide with marginally more acute Al–N–Al′ bond angles (92.7(1)° and 93.2(1)°) in **4** as compared to 93.8(1)° in **2**. Accordingly, the Al(1)⋯Al(2) distance is shortened to 2.728(1) Å with respect to 2.795(1) Å for the corresponding distance in **2**. Concomitantly, the decrease in the Al–N distances leads to an increase in the exocyclic imino groups' bond lengths as exemplified by N(1)–C(1) = 1.319(2) Å in **4** compared to N(1)–C(1) = 1.289(2) Å in **2**. When taking a look at how the Al–N bond lengths in **II** (Fig. 1) are affected by the transformation into Dipp(nacnac)Al(BH$_4$)$_2$ one finds the Al–N distance of 1.899(1) Å in **II**[54] essentially unaltered upon conversion into its aluminium borohydride congener (Al–N = 1.898(3) Å).[46] In this case, the bidentate β-diketiminato ligand appears to be more rigid, allowing for less structural flexibility in its resulting aluminium complexes than the non-chelate-fashioned imino group in **2** and **4**, respectively. The plane of the Al$_2$N$_2$ ring in **4** intersects the planes of its adjacent imidazoline rings with dihedral angles of 34° and 35°, respectively. This is notably more obscure than that in **2** (9°) and presumably due to the steric hindrance of the BH$_4$ moieties in comparison to the hydrides in **2**. With values between 1.07(3) Å and 1.19(2) Å the similarity of all B–H bond lengths as a strong indicator for the formation of BH$_4$ groups underlines the hydride transfer from the aluminium to the boron centre. Each aluminium atom can be described as coordinated by two BH$_4^-$ groups in an η^2 fashion,

which is marked by the eight Al–H distances (1.69(2)–1.82(2) Å). Considering that the coordination number of each aluminium atom is increased, it is a notable observation that the Al–N distances are only slightly affected (*vide supra*). The smallest Al···B distance in **4** amounts to 2.220(3) Å and the largest is determined to be 2.229(3) Å. This is in good agreement with the respective values in (Dipp)nacnacAl(BH$_4$)$_2$ for which an η^2 coordination mode of the BH$_4$ moieties to the aluminium atom has also been described.[46] Accordingly, this type of bonding is also found for {μ-Me$_3$SiOAl(BH$_4$)$_2$}$_2$ (Al···B = 2.156(5) Å, 2.143(4) Å),[55] the parent Al(BH$_4$)$_3$ (Al···B = 2.143(3) Å),[56] and related aluminium borohydrides.[57,58]

Hydride–halide exchange between aluminium and boron

The hydride transfer from {μ-LAlH$_2$}$_2$ (**2**) to Me$_2$S·BH$_3$ yielding {μ-LAl(BH$_4$)$_2$}$_2$ (**4**) prompted us to investigate the reactivity of **2** towards other boron-centred electrophiles. A hydride–halide exchange reaction between a Lewis base complex of a boron trihalide and **2** might equilibrate a haloalane product due to the comparably high stability of many hydridoborane adducts.[59,60] One would expect the degree of hydrogenation at the boron atom to reflect the halogenation of the aluminium centre which would allow monitoring of the reaction progress by proton-coupled ^{11}B NMR spectroscopy. We chose the boron tribromide dimethylsulphide complex[61,62] as a suitable bromide-transfer reagent because it can be conveniently stored and handled as a solid under an inert atmosphere, yet, it readily undergoes bromide–hydride exchange reactions in solution.[62] First, we examined the conversion of **2** with two equivalents of Me$_2$S·BBr$_3$ in C$_6$D$_6$ by preparing an experiment in the NMR tube. It turned out that an initial reaction took place at room temperature as marked in the ^{11}B NMR spectrum by a doublet at −7.8 ppm (*J* = 160 Hz, assigned to Me$_2$S·BHBr$_2$)[62] and a triplet of weaker intensity at −10.8 ppm (*J* = 130 Hz, assigned to Me$_2$S·BH$_2$Br)[62] that superimposed with the resonance caused by the residual starting material (Me$_2$S·BBr$_3$: δ(^{11}B) was observed at −10.7 ppm in C$_6$D$_6$). We stored the flame-sealed NMR tube at elevated temperature until the ^{1}H and ^{11}B NMR spectra indicated the conversion to be complete. Accordingly, the reaction on a preparative scale in toluene granted the analytically pure aluminium dibromide {μ-LAlBr$_2$}$_2$ (**5**) in 57% yield (Scheme 2). The formulation as a dimeric compound is evidenced by the high resolution mass spectrometric analysis, as well as single-crystal X-ray study (Fig. 7).

The ^{1}H and ^{13}C{^{1}H} NMR spectra (C$_6$D$_6$) of **5** differ only insignificantly with respect to **2**, taking aside the expected disappearance of the broad resonance at 2.60 ppm caused by the hydrogen atoms of the AlH$_2$ moieties in **2**. The single-crystal diffraction analysis of **5** shows that, as in **4**, 1.5 equivalents of toluene are incorporated into the crystal lattice. The structural parameters of the planar Al$_2$N$_2$ ring and the adjacent imidazoline rings in **5** are very similar to **4**. The Al–N bond lengths in **5** lie in a range from 1.858(3) Å to 1.871(3) Å and are slightly shorter in comparison to those in **4**. Though rather marginal with respect to **4** the difference from the analogous bond
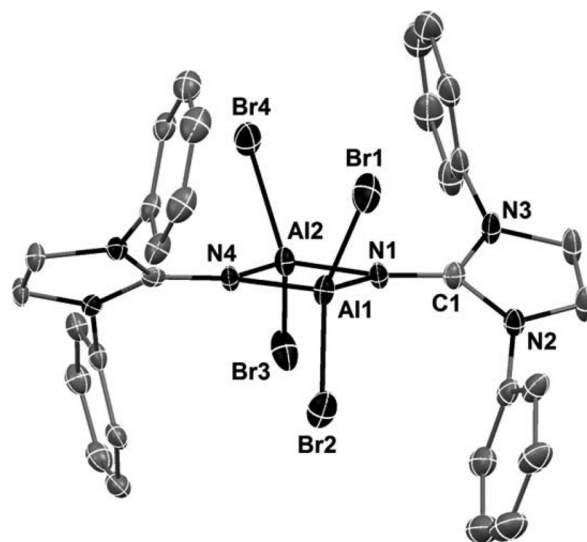
Fig. 7 Molecular structure of **5**(toluene)$_{1.5}$ in the solid state. Hydrogen atoms, isopropyl groups, and toluene molecules have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), atom···atom distance (Å), and bond angles (°): Br(2)–Al(1) 2.282(1), Br(4)–Al(2) 2.298(1), Al(1)–N(4) 1.871(3), Al(2)–N(1) 1.858(3), N(1)–C(1) 1.318(4), Al(1)···Al(2) 2.687(1); Br(1)–Al(1)–Br(2) 110.29(4), N(1)–Al(1)–N(4) 87.7(1), N(1)–Al(2)–N(4) 88.1(1), Al(1)–N(1)–Al(2) 92.3(1), Al(1)–N(4)–Al(2) 91.9(1), Al(1)–N(1)–C(1) 134.0(2).

lengths in **2** (Al–N = 1.912(1) Å, 1.915(1) Å) is now marked and one would assume that it correlates to the stronger electron-withdrawing nature of the bromide substituents in **5** as compared to the hydrides in **2**. In consequence, the electrophilicity of the aluminium centres is increased and the interaction with the nitrogen atoms of the imino ligands is strengthened. In accordance with the observed trend in the bond lengths comparing **2**, **4**, and **5**, the N–Al–N′ bond angles in **5** have yet again slightly sharpened to 91.9(1)° and 92.3(1)°, respectively. The interesting consequence of the aforementioned marginal changes in the geometry of the Al$_2$N$_2$ core is revealed if one notes the Al(1)···Al(2) distance in **5** to amount to 2.687(1) Å. This value is close to the range of metal–metal bond lengths in prominent dialanes with four-coordinated metal centres.[19,43] However, we would not suggest that a bonding interaction between the Al atoms in **5** exists.

Motivated by the prospective results of the conversion of **2** with Me$_2$S·BBr$_3$ we decided to explore the general applicability of the hydride–halide exchange concept. The conversion of **2** with two equivalents of boron trichloride yielded the aluminium dichloride {μ-LAlCl$_2$}$_2$ (**6**) (Scheme 3, *cf.* the ESI† for experimental details). However, the ^{1}H NMR spectrum of the reaction mixture (CDCl$_3$) revealed signal sets induced by yet unassigned additional species of L, presumably intermediate forms in the path of the reaction from **2** to **6**. This came as a surprise as we would have ascribed high reactivity to the uncomplexed form of BCl$_3$. However, treating **2** with another two equivalents of this haloborane significantly improved the yield of **6**. Alternatively, compound **6** was synthesized by
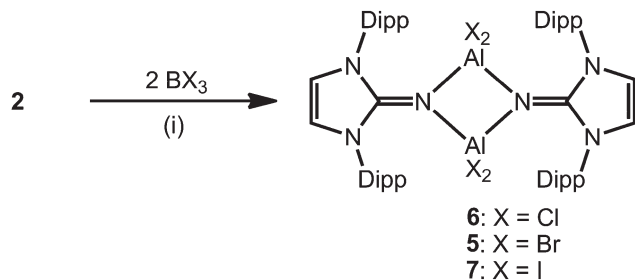
Scheme 3 Syntheses of the imino aluminium dihalides **5**, **6**, and **7** *via* conversion of the aluminium dihydride **2** with boron trihalides. (i) Toluene, −78 °C → rt, 12 h. Dipp = 2,6-diisopropylphenyl.

reaction of bis(2,6-diisopropylphenyl)imidazolin-2-imino lithium[34] {LLi}$_2$ (**8**) with aluminium trichloride (*cf.* the ESI for details on our synthesis of **8** and its molecular structure in the solid state, Fig. S3†). The formation of **6** was evidenced by high resolution mass spectrometry, NMR spectroscopy, as well as X-ray crystallographic analysis. The essential structural characteristics of **6** strongly resemble the heavier halide congener **5** (*cf.* the ESI for the molecular structure of **6** in the solid state, Fig. S1†). Furthermore, parallels exist to the bulky phosphinimide {μ-(ᵗBu)$_3$PNAlCl$_2$}$_2$ reported by Stephan and coworkers.[23] Interestingly, 2,6-dimethylimidazolin-2-imino aluminium dichloride **VII**, a less sterically congested derivative of **6**, forms a six-membered Al$_3$N$_3$ ring in the solid state in which most Al-centred bond angles nearly fit the ideal value of a tetrahedron (109.5°).[32] Thus, the square-planar geometry of the Al$_2$N$_2$ core in **6** must result from the bulkiness of L in that it imposes smaller Al–N–Al′ angles than the iminato ligand in **VII**.

On the other hand, when we reacted **2** with two equivalents of BBr$_3$, quantitative conversion to **5** was observed (NMR spectroscopic control, Scheme 3). Obviously, the reactivity of the heavier haloborane towards **2** is higher which is in line with the general trend in the Lewis acidity of boron trihalides that increases with rising atom number.[63,64] It has to be pointed out that no elevated temperature is required for the reaction with boron tribromide to proceed which contrasts the conversion of **2** with Me$_2$S·BBr$_3$ and, yet again, underlines the correlation between formation of the imino-substituted aluminium halide and the Lewis acidity of the haloborane employed.

To conclude our study on the hydride–halide exchange, we reacted **2** with two equivalents of boron triiodide (Scheme 3). It turned out that the reaction readily proceeded to give the aluminium diiodide {μ-LAlI$_2$}$_2$ (**7**) which we isolated in nearly quantitative yield (92%). In accordance with our previous results, the high Lewis acidity of the boron triiodide promoted the reaction.[63,64] Similar to its lower halide congeners **5** and **6**, the single crystal X-ray data (Fig. S2, *cf.* the ESI†) and the high resolution mass spectrum of **7** support its dimeric formulation. From a mixture of THF–hexane, compound **7** crystallizes with three equivalents of THF incorporated into the lattice. The ¹H NMR spectrum (C$_6$D$_6$) of **7** shows the expected singlet for the four protons of the imidazoline ring of the imino ligands. Notably, in contrast to **2**, **5**, and **6** and similar

to **4** splitting of the resonances induced by the Dipp moieties (Dipp = 2,6-ⁱPr$_2$C$_6$H$_3$) into two signal sets of equal intensity occurs. In consequence, two doublets are observed for the hydrogen atoms in positions 3 and 5 of the 2,6-ⁱPr$_2$C$_6$H$_3$ groups (7.27 ppm, 7.20 ppm, *J* = 8 Hz each) and two septets (3.61 ppm, 3.44 ppm, *J* = 7 Hz each), as well as two doublets of doublets result. Very likely, the splitting in **7** results from hindered rotation of the Dipp moieties due to the comparably large atom radius of iodine. As for **4**, the characteristic deviation of the ¹H and ¹³C{¹H} NMR spectra of **7** (*vide supra*) is not reflected in its molecular structure in the solid state and, accordingly, strong similarities exist to the lower halide congeners **5** and **6**.

Precedence for the transformation of Al–H groups into Al–X functionalities (with X = Cl, Br or I) using BX$_3$ or Lewis base adducts thereof is scarcely found in the literature. To the best of our knowledge, the only related examples refer to the halogenation of Al–H moieties in carbaalane clusters employing the higher haloboranes.[65,66] Obviously, the direct conversion of an aluminium hydride complex with X$_2$ offers an alternative methodology for halogenation at the metal centre. For this procedure we found few reports in the literature merely reporting on respective iodinations.[19,67–69] These comprise only one example[68] in which an aluminium hydride bearing a monodentate N-donor ligand is subject to conversion with I$_2$ and, thus, is strongly related to our report of a non-chelate-fashioned iminato system. Notably, a mixture of products is obtained in this report and we interpret this in terms of an endorsement of our halogenation approach with BX$_3$ as an alternative option to X$_2$. Furthermore, it should be pointed out that our conversions of imidazolin-2-iminato lithium {LLi}$_2$ (**8**) with AlBr$_3$ or AlI$_3$ did not result in the formation of **5** and **7**, respectively. Hence, our investigation of the hydride–halide exchange between aluminium and boron contributes to modern inorganic chemistry in that it may provide access to aluminium halide complexes where standard halogenation and salt metathesis protocols fail.

Conclusions

We have described the synthesis of the dimeric bis(2,6-diisopropylphenyl)imidazolin-2-imino aluminium dihydride {μ-LAlH$_2$}$_2$ (**2**). The strong electron-donating properties of the iminato ligand result in the ability of **2** to act as a potent hydride-transfer reagent. This was demonstrated by the synthesis of {μ-LAl(H)OTf}$_2$ (**3**), {μ-LAl(BH$_4$)$_2$}$_2$ (**4**), {μ-LAlBr$_2$}$_2$ (**5**), {μ-LAlCl$_2$}$_2$ (**6**), and {μ-LAlI$_2$}$_2$ (**7**) *via* conversion of **2** with several Lewis acids (*i.e.* Me$_3$SiOTf, Me$_2$S·BH$_3$, Me$_2$S·BBr$_3$, BCl$_3$, BBr$_3$, and BI$_3$). All new imidazolin-2-iminato aluminium compounds reported in this paper form dimers with a prominent square-planar Al$_2$N$_2$ structural motif and the essential characteristics of the molecular structure in the solid state stay largely untouched when replacing the hydride substituents for halides or tetrahydridoborates.

Importantly, aluminium dihydride **2** possesses potential for applications such as hydroalumination and activation of unpolarized element–element bonds (*e.g.* S–S, Se–Se bonds), as well as in the field of hydrogen-storage materials. We are currently exploring the reactivity of **2** in this regard. In addition, we will target cationic, as well as low-valent aluminium compounds by applying halide abstraction- and reductive dehalogenation protocols, respectively, using **5**, **6**, and **7**.

Experimental

General considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun drybox containing an atmosphere of purified nitrogen. Glass junctions were coated with the PTFE-based grease Merkel Triboflon III. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded on Bruker Avance II 200 or Avance III 500 spectrometers. Chemical shift values are referenced to (residual) solvent signals (^{1}H and ^{13}C{^{1}H} NMR),[70] to external $Et_2O \cdot BF_3$ (^{11}B and ^{11}B{^{1}H} NMR) or to external $CFCl_3$ (^{19}F NMR). *J* coupling values are reported in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, sept = septet, br = broad, n.o. = not observed, n.r. = not resolved, Dipp = 2,6-diisopropylphenyl, L = bis(2,6-diisopropylphenyl)imidazolin-2-imino. High resolution mass spectra were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL using an APCI ion source and providing the analyte dissolved in toluene, C_6D_6, or THF. Elemental analyses were performed by the microanalytical laboratory of the Institut für Chemie, Technische Universität Berlin. Reagents purchased from commercial sources were used as received if not stated otherwise. Boron tribromide was stored over mercury. Boron triiodide (95% grade) was supplied by Sigma-Aldrich Corporation. Borane dimethylsulphide complex (5–6% excess dimethylsulphide) was purchased from abcr GmbH & Co. KG. LH,[38] $Me_3N \cdot AlH_3$,[71] and $Me_2S \cdot BBr_3$ [61] were synthesized according to the reported procedures. *Cf.* the ESI† for the synthesis of {LLi}$_2$ (**8**).

Synthetic procedures

Synthesis of {μ-L(AlH$_2$)}$_2$ (2). A solid mixture of LH (**1**, 5.12 g, 12.7 mmol) and $Me_3N \cdot AlH_3$ (1.13 g, 12.7 mmol) was cooled to −78 °C. Under stirring, toluene (40 mL) was added *via* a syringe and the reaction was allowed to proceed for 2 h with the cooling applied followed by a period of 24 h at room temperature (*caution: gas evolution!*). From the resulting solution the volatiles were evaporated under reduced pressure and the residue was recrystallized from a hot mixture of hexane–toluene (60 mL/10 mL). After crystal formation had been completed at room temperature the supernatant was decanted and stored at low temperature (4 °C and −30 °C consecutively) for 3 d yielding a second crop. By this method, single crystals suitable for X-ray diffraction analysis could be obtained. The crystal fractions were combined and dried *in vacuo*. Yield:

3.63 g, 66% (Found: C, 75.11; H, 8.82; N, 9.67%. Calc. for $C_{54}H_{76}Al_2N_6$ [863.18]: C, 75.14; H, 8.87; N, 9.74%). Decomp.: >260 °C.

IR: $\tilde{v}/cm^{-1}$ = 1830, 1798 (AlH). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.29 (t, *J* = 8, 4 H, DippH-4), 7.11 (d, *J* = 8, 8 H, DippH-3,5), 5.85 (s, 4 H, NC*H*), 3.02 (sept, *J* = 7, 8 H, C*H*(CH$_3$)$_2$), 2.60 (br, 4 H, Al*H$_2$*), 1.45 (d, *J* = 7, 24 H, CH(C*H$_3$*)$_2$), 1.12 (d, *J* = 7, 24 H, CH(C*H$_3$*)$_2$); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 149.9 (N*C*N), 148.8 (DippC-1), 133.0 (DippC-2,6), 130.3 (DippC-4), 124.2 (DippC-3,5), 115.7 (N*C*H), 29.1 (*C*H(CH$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$).

HRMS: *m/z* found (calc.): 895.5728 [M + H + 2O]$^{+}$ (100%), (895.5733); 861.5676 [M − H]$^{+}$ (33), (861.5679); 877.5627 [M + O]$^{+}$ (27), (877.5628).

Synthesis of {μ-LAl(H)OTf}$_2$ (3). Under ice-cooling, Me_3SiOTf (3.07 g, 2.50 mL, 13.8 mmol) was gradually added *via* a syringe to a stirred solution of **2** (3.63 g, 4.2 mmol) in toluene (20 mL). After 30 min, the ice-bath was removed and the reaction continued at room temperature for 24 h. The volatiles were removed under reduced pressure, the residue washed with hexane (30 mL) and subjected to recrystallization from hexane–THF (70 mL/70 mL). The solid material that formed at −30 °C was isolated and dried *in vacuo* yielding 1.96 g of the product with sufficient purity for further conversions (NMR spectroscopic control). In order to obtain analytically pure **3** the crude product was dissolved in hexane–THF (15 mL/35 mL) and a slight amount of insoluble material was removed from the resulting solution by filtration through a frit. The crystallization commenced after storage at 4 °C for 1 d and was allowed to complete at −30 °C over a period of 3 d. A solid fraction produced by this method provided X-ray quality single crystals. The crystalline material was separated from the mother liquor and dried *in vacuo*. Yield: 1.05 g, 22% (Found: C, 58.62; H, 6.52; N, 6.96; S, 5.23%. Calc. for $C_{56}H_{74}Al_2F_6N_6O_6S_2$ [1159.31]: C, 58.02; H, 6.43; N, 7.25; S, 5.53%). Decomp.: 235–245 °C.

^{1}H NMR (200.1 MHz, CD_3CN): δ = 7.46 (t, *J* = 8, 4 H, DippH-4), 7.24 (d, *J* = 8, 8 H, DippH-3,5), 6.74 (s, 4 H, NC*H*), 2.59 (n.r., 8 H, C*H*(CH$_3$)$_2$), 1.21 (n.r., 24 H, CH(C*H$_3$*)$_2$), 1.05 (d, *J* = 7, 24 H, CH(C*H$_3$*)$_2$, n.o. (Al*H*); ^{13}C{^{1}H} NMR (50.3 MHz, CD_3CN): δ = 152.5 (N*C*N), 148.6 (DippC-1), 132.6 (DippC-2,6), 132.5 (DippC-4), 126.0 (DippC-3,5), 119.4 (N*C*H), 29.7 (*C*H(CH$_3$)$_2$), 25.7 (CH(*C*H$_3$)$_2$), 22.8 (br, CH(*C*H$_3$)$_2$), n.o. (*C*F$_3$); ^{19}F NMR (188.3 MHz, CD_3CN): δ = −78.3, −79.3 (C*F$_3$*).

HRMS: *m/z* found (calc.): 1009.5107 [M − C − 3F − 3O − S]$^{+}$ (100%), (1009.5126); 1157.4551 [M − H]$^{+}$ (8), (1157.4568); 1159.4712 [M + H]$^{+}$ (5), (1159.4724).

Synthesis of {μ-L(Al(BH$_4$)$_2$)}$_2$ (4). In a Schlenk tube equipped with a PTFE-coated magnetic stirrer bar and a rubber septum **2** (0.366 g, 0.42 mmol) was dissolved in toluene (5 mL) and the resulting mixture was cooled to −78 °C. Under stirring, a freshly prepared solution (0.5 M) of borane dimethylsulphide complex in toluene (3.5 mL, 1.8 mmol) was added dropwise *via* a syringe over a period of 5 min. The reaction mixture was slowly warmed to room temperature overnight. A colourless suspension formed that was stirred for an

additional 6 h, after which the precipitation was completed by gradual addition of hexane (9 mL). The septum was replaced by a glass stopper, and the solid was allowed to sediment overnight. *Via* a syringe, the supernatant was withdrawn (16 mL) and the residual solvent was evaporated under reduced pressure. The remaining colourless powder was dried *in vacuo* (3 h, 9×10^{-2} mbar), and stored under nitrogen for 2 d before a sample was subjected to elemental analysis. Yield: 0.27 g, 67% (Found: C, 71.43; H, 9.40; N, 8.94%. Calc. for $C_{54}H_{88}Al_2B_4N_6$ [918.52] × 0.5 C_7H_8 [92.14]: C, 71.60; H, 9.61; N, 8.71%). Decomp.: >260 °C.

IR: $\tilde{\nu}/cm^{-1}$ = 2492, 2431 (BH). ^1H NMR (500.1 MHz, THF-d_8): δ = 7.33 (t, J = 8, 4 H, DippH-4), 7.20 (d, J = 8, 4 H, DippH-3,5), 7.16 (d, J = 8, 4 H, DippH-3,5), 6.58 (s, 4 H, NC*H*), 3.18 (sept, J = 7, 4 H, C*H*(CH_3)_2), 2.97 (sept, J = 7, 4 H, C*H*(CH_3)_2), 1.29 (d, J = 7, 12 H, CH(C*H*_3)_2), 1.23 (d, J = 7, 12 H, CH(C*H*_3)_2), 1.11 (d, J = 7, 12 H, CH(C*H*_3)_2), 0.89 (d, J = 7, 12 H, CH(C*H*_3)_2), −0.34 (br, $h_{1/2}$ = 170 Hz, 16 H, B*H*); $^{13}C\{^1H\}$ NMR (125.8 MHz, THF-d_8): δ = 151.5 (N*C*N), 148.2 (Ar*C*), 147.6 (Ar*C*), 135.0 (Ar*C*), 131.4 (Ar*C*), 125.8 (Ar*C*), 124.8 (Ar*C*), 119.9 (N*C*H), 29.4 (*C*H(CH_3)_2), 28.8 (*C*H(CH_3)_2), 27.2 (*C*H(CH_3)_2), 24.4 (CH(*C*H_3)_2), 23.7 (CH(*C*H_3)_2), 23.4 (CH(*C*H_3)_2); ^{11}B NMR (64.2 MHz, THF-d_8): δ = −37 (n.r., $h_{1/2}$ = 380 Hz); $^{11}B\{^1H\}$ NMR (64.2 MHz, THF-d_8): δ = −37 ($h_{1/2}$ = 270 Hz).

HRMS: *m/z* found (calc.): 875.6002 [M − 10 H − 3B]$^+$ (11%), (875.6012).

Synthesis of {μ-LAlBr$_2$}$_2$ (5). A Schlenk tube equipped with a PTFE-coated magnetic stirrer bar and a glass stopper was charged with **2** (0.223 g, 0.26 mmol) and Me$_2$S·BBr$_3$ (0.175 g, 0.56 mmol) in the dry box. Under Schlenk conditions, the solid mixture was cooled to 0 °C and, with stirring, toluene (4.5 mL) was gradually added *via* a syringe. Stirring was continued at 0 °C for 20 min followed by replacement of the cooling for an oil-bath which was heated to 80 °C. After a short induction period, the Schlenk vessel was isolated from the inert-gas system by closing the tap and the reaction proceeded at this temperature for 3 d. Using a frit, the warm reaction mixture was filtered in order to separate a slight amount of insoluble material. From the filtrate, crystals formed upon standing at room temperature overnight. In order to complete the crystallization process it was stored at 4 °C and at −30 °C for a period of 24 h each time. By this method, crystals suitable for X-ray diffraction analysis were obtained. After decantation of the cold supernatant the solid residue was dried *in vacuo* for 3 h and stored for 1 d under nitrogen before it was subjected to elemental analysis. Yield: 0.19 g, 57% (Found: C, 58.05; H, 6.63; N, 6.62%. Calc. for $C_{54}H_{72}Al_2Br_4N_6$ [1178.77] × C_7H_8 [92.14]: C, 57.65; H, 6.34; N, 6.61%).

^1H NMR (500.1 MHz, C$_6$D$_6$): δ = 7.31 (t, J = 8, 4 H, DippH-4), 7.22 (d, J = 8, 8 H, DippH-3,5), 5.84 (s, 4 H, NC*H*), 3.31 (sept, J = 7, 8 H, C*H*(CH_3)_2), 1.57 (d, J = 7, 24 H, CH(C*H*_3)_2), 0.99 (d, J = 7, 24 H, CH(C*H*_3)_2); $^{13}C\{^1H\}$ NMR (125.8 MHz, C$_6$D$_6$): δ = 151.5 (N*C*N), 147.6 (Dipp*C*-1), 134.3 (Dipp*C*-2,6), 131.3 (Dipp*C*-4), 125.3 (Dipp*C*-3,5), 119.1 (N*C*H), 28.9 (*C*H(CH_3)_2), 24.3 (CH(*C*H_3)_2), 20.8 (CH(*C*H_3)_2).

HRMS: *m/z* found (calc.): 1178.2132 [M]$^+$ (100%), (1178.2142).

Synthesis of {μ-LAlCl$_2$}$_2$ (6). A stirring suspension of freshly sublimed AlCl$_3$ (0.38 g, 2.8 mmol) in toluene (8 mL) was cooled to 0 °C and treated dropwise with a solution of {LLi}$_2$ (**8**, 1.11 g, 1.4 mmol) in toluene (19 mL) over a period of 10 min. The resulting reaction mixture was stirred at 0 °C for 30 min, then the cooling was removed and the reaction continued for 12 h at room temperature. After filtration *via* a canula (glass fiber-coated inlet) the solvent was evaporated from the pale yellow solution under reduced pressure, the residue was washed with hexane (two portions of 15 mL, removed 13 mL of supernatant each time), and the crude product was dried *in vacuo*. Yield: 0.74 g, 54% (*cf.* the ESI† for depiction of the NMR spectra of the crude product in CDCl$_3$). Single crystals suitable for X-ray diffraction analysis were obtained after dilution of the filtered reaction mixture with hexane (10 mL) and storage at 4 °C for 1 d.

^1H NMR (500.1 MHz, C$_6$D$_6$): δ = 7.30 (t, J = 8, 4 H, DippH-4), 7.22 (d, J = 8, 8 H, DippH-3,5), 5.87 (s, 4 H, NC*H*), 3.17 (sept, J = 7, 8 H, C*H*(CH_3)_2), 1.54 (d, J = 7, 24 H, CH(C*H*_3)_2), 1.00 (d, J = 7, 24 H, CH(C*H*_3)_2); $^{13}C\{^1H\}$ NMR (125.8 MHz, C$_6$D$_6$): δ = 151.8 (N*C*N), 147.6 (Dipp*C*-1), 133.5 (Dipp*C*-2,6), 131.1 (Dipp*C*-4), 125.0 (Dipp*C*-3,5), 118.3 (N*C*H), 28.9 (*C*H(CH_3)_2), 26.0 (CH(*C*H_3)_2), 23.8 (CH(*C*H_3)_2).

HRMS: *m/z* found (calc.): 1001.4233 [M + H]$^+$ (28%), (1001.4252); 981.4605 [M − Cl + 2 H + O]$^+$ (26), (981.4620).

Synthesis of {μ-LAlI$_2$}$_2$ (7). In the drybox, a solid mixture of **2** (0.511 g, 0.59 mmol) and boron triiodide (0.488 g, 1.25 mmol) was prepared in a Schlenk vessel equipped with a PTFE-coated magnetic stirrer bar and a rubber septum. Under Schlenk conditions, it was cooled to −78 °C and, with stirring, toluene (8 mL) was gradually added *via* a syringe along the inner glass wall of the cold reaction vessel. The resulting reaction mixture was slowly allowed to warm to room temperature overnight. After 18 h the solvent was evaporated under reduced pressure and the colourless solid residue was dried *in vacuo*. It was redissolved in a mixture of hexane–THF (6 mL/12 mL) and, using a frit, a slight amount of insoluble material was removed by filtration. The filtrate was stored at 4 °C for 24 h. Separation of the crystalline product had commenced and was completed at −30 °C for a period of 2 d. The fraction, thus obtained, contained single crystals suitable for X-ray diffraction analysis. The cold supernatant was decanted and the solid was dried *in vacuo*. Yield: 0.74 g, 92% (Found: C, 47.81; H, 5.63; N, 5.87%. Calc. for $C_{54}H_{72}Al_2I_4N_6$ [1366.77]: C, 47.45; H, 5.31; N, 6.15%).

^1H NMR (500.1 MHz, C$_6$D$_6$): δ = 7.32 (t, J = 8, 4 H, DippH-4), 7.27 (d, J = 8, 4 H, DippH-3,5), 7.20 (d, J = 8, 4 H, DippH-3,5), 5.76 (s, 4 H, NC*H*), 3.61 (sept, J = 7, 4 H, C*H*(CH_3)_2), 3.44 (sept, J = 7, 4 H, C*H*(CH_3)_2), 1.63 (d, J = 7, 12 H, CH(C*H*_3)_2), 1.60 (d, J = 7, 12 H, CH(C*H*_3)_2), 1.03 (d, J = 7, 12 H, CH(C*H*_3)_2), 0.93 (d, J = 7, 12 H, CH(C*H*_3)_2); $^{13}C\{^1H\}$ NMR (125.8 MHz, C$_6$D$_6$): δ = 151.2 (N*C*N), 147.6 (Ar*C*), 147.4 (Ar*C*), 136.0 (Ar*C*), 131.6 (Ar*C*), 126.2 (Ar*C*), 125.5 (Ar*C*), 120.4 (N*C*H), 28.9 (*C*H(CH_3)_2), 28.8 (*C*H(CH_3)_2), 26.5 (CH(*C*H_3)_2), 25.9 (CH(*C*H_3)_2), 24.4 (n.r., 2 × CH(*C*H_3)_2).

HRMS: m/z found (calc.): 1239.2567 $[M − I]^+$ (100%), (1239.2583); 1257.2661 $[M − I + 2 H + O]^+$ (75), (1257.2689); 1367.1680 $[M + H]^+$ (6), (1367.1706).

Single crystal structure determination

Data for the single-crystal structure determination of **2**, **3**, **4**, and **7** were collected on an Agilent SuperNova diffractometer equipped with a CCD area Atlas detector and a mirror mono-chromator utilizing CuK$_\alpha$ radiation (λ = 1.5418 Å). Data for the single-crystal structure determination of **5**, **6**, and **8** were collected on an Oxford-Diffraction Xcalibur diffractometer equipped with a CCD area detector Sapphire S and a graphite monochromator utilizing MoK$_\alpha$ radiation (λ = 0.71073 Å).

The crystal structures were solved by direct methods and refined on F^2 using full-matrix least squares with SHELXL-97.[72] The positions of the H atoms of the carbon atoms were calculated and considered isotropically according to a riding model. The positions of the H atoms attached to the aluminium or the boron atoms at the compounds **2**, **3**, and **4** were found in the electron-density map and were refined without restraints of the interatomic distances.

Acknowledgements

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