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Reactivity of a Bulky Bora-Amidine Ligand with Trimethylaluminum

Harmen S. Zijlstra,^[a,b,c] Alexander Hofmann,^[a] and Sjoerd Harder^{*[a,b]}

Dedicated to Professor Werner Uhl on the Occasion of His 65th Birthday

Abstract. Reaction of Me_3Al with $\text{HB}[\text{N}(\text{H})\text{DIPP}]_2$ ($\text{DIPP} = 2,6\text{-iPr}_2\text{-C}_6\text{H}_3$) in hexane gave a complex mixture of compounds instead of $\text{HB}(\text{N-DIPP})_2\text{AlMe}$. After addition of THF, one of the products could be trapped in trace amounts and was characterized by crystal structure determination: $\text{DIPP-N}(\text{H})\text{B}(\text{H})(\text{N-DIPP})\text{AlMe}_2\cdot\text{THF}$ (**1**). Heating a hexane or fluorobenzene solution of $\text{HB}[\text{N}(\text{H})\text{DIPP}]_2$ and Me_3Al in the absence of THF gave a relatively clean conversion and

allowed for the isolation of $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**), a product that was formed through B/Al ligand exchange. Complex **2** contains protic and hydridic hydrogen atoms in close vicinity. The compound remains intact upon heating, however, it readily releases H_2 when dissolved in THF forming $\text{DIPPN}(\text{AlMe}_2\cdot\text{THF})_2$ (**3**). The latter bimetallic complex contains two THF stabilized Lewis acidic central aluminum atoms in close proximity.

Introduction

The chemistry of aluminum alkyl complexes containing chelating ligands such as β -diketimines^[1] and amidinates^[2] is well-established. A large variety of complexes have been reported and applied in catalysis.^[3] Much less, however, is known about Al-alkyl complexes with the closely related, dianionic, bora-amidinate (bam) ligands, $\text{RB}(\text{NR}')_2^{2-}$, that are formed after double deprotonation of the bora-amidine precursor.^[4] These dianionic ligands are isoelectronic to the corresponding mono-anionic amidinate ligands, $\text{RC}(\text{NR}')_2^-$, through replacement of the CR unit by an isolobal BR^- moiety. Although bam ligands have been reported to stabilize a wide variety of metal complexes, their use in Al chemistry is limited. Chivers et al. reported the reaction of AlCl_3 with $\text{PhB}(\text{NtBu})_2\text{Li}_2$ to give $\text{PhB}(\text{NtBu})_2\text{AlCl}(\text{OEt}_2)$ (see Scheme 1).^[5]

Subsequent addition of a second equivalent of the dilithio-bam precursor gave a Li-aluminate complex, which after oxidation by iodine is transformed into the spirocyclic radical species $[\text{PhB}(\text{NtBu})_2]_2\text{Al}$. The two bam ligands in the latter display a similar arrangement and Al coordination, indicating a

Scheme 1. Formation of $[\text{PhB}(\text{NtBu})_2]_2\text{Al}$ from $\text{PhB}(\text{NtBu})_2\text{Li}_2$ and AlCl_3 .^[5] The unpaired electron is delocalized over both ligands.

uniform spin delocalization throughout both ligands. The ligands in this radical complex could be described being between $\text{PhB}(\text{NtBu})_2^{2-}$ and $\text{PhB}(\text{NtBu})_2^{\cdot-}$ in character.

To the best of our knowledge there are no reports on the direct reaction of Al-alkyl complexes with bam- H_2 ligands. Reaction of *tri*-alkyl Al complexes (R_3Al) with $\text{RB}[\text{N}(\text{H})\text{R}']_2$ should result in the release of RH to give complexes of the type (bam)AlR or aggregates thereof. It is anticipated that use of bulky bam ligands may give access to a monomeric Al alkyl complex with a highly Lewis-acidic tri-coordinate central Al atoms, a complex type that may be valuable as a methylalumoxane (MAO) substitute in olefin polymerization catalyst activation.^[6] We have previously reported a simple one-pot synthesis of the bulky bora-amidine $\text{HB}[\text{N}(\text{H})\text{DIPP}]_2$ ($\text{DIPP} =$

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2,6-*i*Pr₂-C₆H₃)^[7] and explored the potential of its dianionic ligand [HB(N-DIPP)₂]²⁻ in alkaline earth and lanthanide metal chemistry.^[8–11] Herein we report on the reactivity of HB[N(H)DIPP]₂ with Me₃Al.

Results and Discussion

Addition of Me₃Al to benzene, toluene, or hexane solutions of HB[N(H)DIPP]₂ at room temperature led to an uncontrolled reaction giving multiple species that could not be isolated or characterized (Scheme 2). When THF was used as a solvent, no reaction took place at all (also not under reflux conditions). Presumably the formation of a Me₃Al·THF adduct prevents any further reactivity. Running the reaction in hexane in the presence of small amounts of THF, however, led in one occasion to the isolation of traces of the complex DIPP-N(H)B(H)(N-DIPP)AlMe₂·THF (**1**) which could be identified by crystal structure determination (Figure 1; Table 1). The reaction leading to formation of **1** is not well-behaved and gave at all times various products, which made reproducible isolation of **1** difficult. Complex **1** was therefore not further characterized but can be seen as identification of one of many products and intermediates.

Scheme 2. Reactivity of HB[N(H)DIPP]₂ with Me₃Al under varying conditions (DIPP = 2,6-*i*Pr₂-C₆H₃).

Complex **1** has no crystallographic symmetry and contains Al in an almost tetrahedral coordination environment. The Al

Figure 1. Crystal structure of DIPP-N(H)B(H)(N-DIPP)AlMe₂·THF (**1**). *i*Pr groups and hydrogen atoms (except N–H and B–H) are omitted for clarity. See Table 1 for selected bond lengths and angles.

Table 1. Selected bond lengths /Å and angles /° in DIPP-N(H)B(H)(N-DIPP)AlMe₂·THF (**1**), [(DIPPNH)AlMe₂(μ-H)AlMe₂]₂ (**2**), and DIPPN(AlMe₂·THF)₂ (**3**).

DIPP-N(H)B(H)(N-DIPP)AlMe ₂ ·THF (1)			
Al–N1	1.850(3)	Al–N1–B	123.7(3)
Al–O	1.934(2)	O–Al–N1	104.5(1)
B–N1	1.417(4)	N1–B–N2	122.5(2)
B–N2	1.416(5)		
[(DIPPNH)AlMe ₂ (μ-H)AlMe ₂] ₂ (2)			
Al1–N1	1.964(2)	Al1–N1–Al2	120.5(1)
Al2–N1	1.961(2)	Al1–H1–Al2'	148.2(2)
Al1–H1	1.73(2)	N–Al1–H1	91.7(8)
Al2–H1'	1.72(2)	N–Al2–H1'	89.2(9)
DIPPN(AlMe ₂ ·THF) ₂ (3)			
Al1–N	1.824(2)	Al1–N–Al2	125.2(1)
Al2–N	1.841(2)	N–Al1–O1	107.5(7)
Al1–O1	1.969(2)	N–Al2–O2	106.4(7)
Al2–O2	1.953(2)		

is bonded to only one of the N atoms and the Me₂Al moiety is oriented away from the ligand backbone and stabilized by a molecule of THF. This product still contains an acidic NH group and can be considered as an intermediate towards the formation of HB(N-DIPP)₂AlMe. Attempts to enforce the release of the second equivalent of CH₄ through subsequent heating were unsuccessful and resulted in decomposition into various unknown products. Variation of reaction conditions and solvent was not successful and defined reaction products could not be obtained.

During our experimental investigations, we observed that the wide range of Al-Me containing species obtained in reactions of HB[N(H)DIPP]₂ with Me₃Al in non-polar solvents such as hexanes can be decreased upon extensive heating. This gave reaction mixtures with only three predominant Al-Me signals (−0.02, −0.30, and −0.63 ppm), from which a small crop of single crystals could be obtained.

The crystal structure (Figure 2; Table 1) revealed a centrosymmetric tetranuclear aggregate (**2**), in which four Me₂Al fragments are bridged by two H[−] and two DIPP(H)N[−] anions resulting in an eight-membered (Al–N–Al–H)₂ ring. The Al atoms and the H[−] ligands are situated more or less in a plane.

The anilido N atoms point to opposite sides of this plane resulting in a conformation that is reminiscent of a cyclohexane chair structure. The distance of the DIPP(H)N moiety to both central Al atoms are within standard deviation equal: Al1–N1 1.964(2) Å and Al2–N1 1.961(2) Å. The bridging hydrogen atoms show a similar symmetrical bridging with Al–H distances of 1.72(2) Å and 1.73(2) Å. The Al–H–Al units are bent [Al1–H1–Al2' 148.2(2)°] to provide short N–H^{δ+}...H^{δ-}–Al interactions of 2.23(4) Å [N–H...H' 101(2)°] that are well below the sum of the van der Waals radii (2.40 Å). Such attractive proton-hydride interactions are well-established in late transition metal-hydride chemistry^[12] and also have been observed in amine-borane complexes,^[13] but hitherto have gone unnoticed in Al hydride chemistry.

Figure 2. (a) Crystal structure of $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**). (b) Partial structure of the core showing the proton-hydride interactions. Hydrogen atoms are omitted for clarity (except for bridging hydrides and N–H protons). See Table 1 for selected bond lengths and angles.

The rather poor yield (<6%) of complex **2** could be improved (up to 50%) by carrying out the reaction in fluorobenzene (PhF) instead of in hexane and by using a slight excess of Me_3Al . Its ^1H NMR spectrum shows two different Al–Me signals (−0.02 and −0.63 ppm) that originate from the two different substituents at N, and a sharp Al–H singlet at $\delta = 4.38$ ppm.

A structurally similar complex, $[(\text{Me}_2\text{N})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$, was reported in the seventies by Schram et al.: treatment of $(\text{Me}_2\text{NBH}_2)_2$ with excess Me_3Al (also mainly present as a dimer) at 80 °C led to the formation of $[(\text{Me}_2\text{N})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$.^[14] Although the structure contains no acidic NH protons it was similarly obtained through ligand scrambling between Al and B. The authors speculate that Al/B ligand exchange leads to formation of $\text{Me}_3\text{B}(\text{g})$, Me_2AlH , $(\text{Me}_2\text{N}-\text{AlMe}_2)_2$, and $[(\text{Me}_2\text{N})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$. Roessky et al. reported a closely related fluoride bridged structure, in which the hydrides in complex **2** are replaced for fluorides, $[(\text{DIPP}(\text{H})\text{N})\text{AlMe}_2(\mu\text{-F})\text{AlMe}_2]_2$.^[15] The latter was obtained from the reaction of DIPP-NH_2 with Me_2AlF . The Al–N dis-

tances in this complex [1.964(2) Å and 1.961(2) Å] compare well to those in **2**.

Hitherto an exact mechanism for the formation of **2** is unknown, however, several observations led to propose a tentative mechanism. In situ ^{11}B NMR monitoring during the reaction showed the appearance of a sharp singlet ($\delta = 85.6$ ppm) characteristic of Me_3B , supporting Al/B ligand exchange reactions.^[16] ^1H NMR analysis of the mother liquor remaining after crystallization showed, among other minor species, one predominant set of signals with a Al–Me singlet at −0.30 ppm which could be assigned to $[\text{Me}_2\text{AlN}(\text{H})\text{DIPP}]_2$.^[17] Based on these results and the findings reported by Schram et al. on a very similar reaction^[14] we propose a pathway for formation that is shown in Scheme 2 (bottom). Ligand distribution between Me_3Al and $\text{HB}[\text{N}(\text{H})\text{DIPP}]_2$ led to the release of gaseous Me_3B (see Figure S5, Supporting Information) and the formation of Me_2AlH and two equivalents of $[\text{Me}_2\text{AlN}(\text{H})\text{DIPP}]_2$. Combination of these two products gave crystallization of the observed complex **2**, leaving the known dimeric species $[\text{Me}_2\text{AlN}(\text{H})\text{DIPP}]_2$ in the mother liquor (see Figure S4, Supporting Information). The latter is the only other major species in the reaction mixture.

Complex $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**) contains a protic N–H and a hydridic Al–H, suggesting that molecular H_2 could be released. Despite the short proton-hydride distance in the crystal structure of **2** (vide supra) no gas formation was observed, even after heating a PhF solution of **2** at 80 °C for 3 days. However, dissolving the complex in THF led to immediate H_2 evolution already at room temperature and a turbid oil was formed. Recrystallization from cold hexane revealed a complex without N–H or Al–H ^1H NMR signals. The complex only shows one set of *i*Pr and Al–Me signals and contains two coordinated THF molecules per DIPP moiety. X-ray analysis showed the formation of the Al imido complex $\text{DIPP-N}(\text{AlMe}_2\cdot\text{THF})_2$ (**3**) (Figure 3; Table 1).

Figure 3. Crystal structure of $\text{DIPP-N}(\text{AlMe}_2\cdot\text{THF})_2$ (**3**). *i*Pr groups and hydrogen atoms are omitted for clarity. See Table 1 for selected bond lengths and angles.

The structure has no crystallographic symmetry and contains two central Al atoms with almost tetrahedral coordination environments. The Al–N bonds are with Al1–N = 1.824(2) Å and Al2–N = 1.841(2) Å significantly shorter than those of 1.962(2) Å in $[\text{Me}_2\text{AlN}(\text{H})\text{DIPP}]_2$, a molecule with a similar Al–N–Al bridging.^[17] The significantly stronger Al–N interac-

tion in **3** can be explained by the formally double negative charge on DIPP-N^{2-} compared to a single negative charge on DIPP(H)N^- and the inherently lower coordination number of three instead of four. The Al–N bonds in $\text{DIPP-N(AlMe}_2\cdot\text{THF)}_2$ (**3**) differ by 0.025(2) Å, which also results in small difference in the Al–O bond lengths of both Al atoms.

Al-imido complexes have been widely explored^[18] and are usually prepared by reaction of the appropriate primary amine and Al^{III} precursors.^[19] Examples include alumazene^[20] and various other Al containing heterocycles^[21] as well as base stabilized monomeric adducts.^[22] The formation of Al-imido complexes through the breakdown of a bulky β -diketiminato ligand has been reported^[23] but its stepwise formation via the breakdown of a bulky bora-amidinate ligand into a novel Al imido complex is unprecedented.

The Al-imido complex **3** is structurally similar to that of $\text{DIPP-N(AlI}_2\cdot\text{NMe}_3)_2$ reported by Schultz et al.^[22] The latter complex displays similar Al–N distances [1.817(3) and 1.823(3) Å] but a much larger Al–N–Al angle: 136.8(2) vs. 125.2(1)°. The large angle in $\text{DIPP-N(AlI}_2\cdot\text{NMe}_3)_2$ is likely due to the fact that the $\text{AlI}_2\cdot\text{NMe}_3$ moieties are bulkier than the $\text{AlMe}_2\cdot\text{THF}$ moieties in **3**.

The formation of complex **3** is stimulated by addition of the polar solvent THF, which most likely splits the dimer $\{[\text{DIPP(H)N}]\text{AlMe}_2(\text{H})\text{AlMe}_2\}_2$ (**2**) into monomeric units that contain a much more reactive terminal Al–H bond. Close proximity of acidic N–H and hydridic Al–H units led to formation of H_2 . The resulting $\text{DIPP-N(AlMe}_2\cdot\text{THF)}_2$ can be described as a bimetallic Al imido complex that contains two THF stabilized central Al atoms in close proximity [Al1–Al2 3.2540(9) Å]. THF removal or replacement with a less Lewis basic substituent should lead to the formation of a complex with two reactive, highly Lewis acid central Al atoms. Previous work has suggested that bidentate Lewis acids can increase catalytic activity making **3** and its derivatives promising bimetallic Lewis acid catalyst candidates.^[24]

Conclusions

Reaction of Me_3Al with the bora-amidine ligand precursor HB[N(H)DIPP]_2 did not give the anticipated bora-amidinate complex $\text{HB(N-DIPP)}_2\text{AlMe}$ but was found to be more complex. A mixture of compounds that could not be individually isolated was formed. Addition of THF to this mixture allowed for trapping of one of the intermediates, the complex $\text{DIPP-N(H)B(H)(N-DIPP)AlMe}_2\cdot\text{THF}$ (**1**) formed after single deprotonation of the bam ligand. Attempts to induce a second deprotonation by heating complex **1** led to decomposition. However, heating a mixture of HB[N(H)DIPP]_2 and Me_3Al in fluorobenzene without the addition of THF gave a relatively clean conversion and allowed for the isolation of $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**). This product has been formed through B/Al ligand exchange and contains protic and hydridic hydrogen atoms in close vicinity. Despite a short $\text{N-H}^{\delta+}\cdots\text{H}^{\delta-}\text{Al}$ contact of 2.23(4) Å, the compound remains intact upon heating. However, it readily releases H_2 when dissolved in THF forming $\text{DIPPN(AlMe}_2\cdot\text{THF)}_2$ (**3**). This complex contains

two THF stabilized central Al atoms in close proximity and can potentially be transformed into a bimetallic Lewis acid making it an interesting candidate for a variety of reactions and catalytic processes. Its chemistry and reactivity are currently under investigation.

Experimental Section

General Considerations: All experiments were performed in a nitrogen atmosphere using standard Schlenk line and glove box techniques. The solvents were dried on alumina columns and degassed by bubbling nitrogen through the solvent reservoir. Fluorobenzene was bought from Sigma Aldrich, dried with molecular sieves and stored inside the glove box prior to use. THF was dried with sodium and distilled prior to use. HB[N(H)DIPP]_2 was prepared from DIPP-NH_2 and $\text{Me}_2\text{S}\cdot\text{BH}_3$ according to its literature procedure.^[7] Me_3Al (97%, 2 M in hexanes) was purchased from Sigma Aldrich and used as received. ^1H and ^{13}C NMR were recorded with Bruker Avance 300, 400, and 600 MHz spectrometers (specified at individual experiments). Crystal structure determinations were carried out with a Bruker Nonius Kappa CCD (Mo) or Agilent Supernova diffractometer (Cu). Single crystals were coated with perfluoro-polyether and immediately mounted in the cold nitrogen stream of the diffractometer. Elemental analysis was carried out using a Eurovector EA 3000 analyzer.

Reaction of HB[N(H)DIPP]_2 with Me_3Al in Hexane/THF: HB[N(H)DIPP]_2 (250 mg, 686 μmol) was dissolved in hexanes (15 mL) and Me_3Al (51.9 mg, 0.360 mL, 2 M in hexanes, 720 μmol) was added dropwise. The reaction was heated at 45 °C and stirred for 40 min, after which THF (1 mL) was added. After stirring the solution at room temperature overnight, all volatiles were removed under reduced pressure. The remaining oil was dissolved in pentane (4 mL) and the solution was placed at –20 °C for 4 d, after which a few crystals of $\text{DIPP-N(H)B(H)(N-DIPP)AlMe}_2\cdot\text{THF}$ (**1**) were formed (20 mg, 41 μmol , 6%). This allowed for identification by crystal structure analysis and elemental analysis but on account of the very low yield and irreproducibility of product crystallization further characterization was not possible. $\text{C}_{30}\text{H}_{50}\text{AlBN}_2\text{O}$ (492.53): calcd. C 73.16, H 10.23, N 5.69%; found C 72.94, H 10.26 N 5.86%.

Synthesis of $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (2**):** HB[N(H)DIPP]_2 (0.270 g, 741 μmol) was dissolved in fluorobenzene (5 mL) and Me_3Al (0.150 g, 0.200 mL, 2.08 mmol) was added dropwise. The reaction was allowed stirred for 1 h until no more gas evolution was observed. The solution was stored at –20 °C overnight to give a crop of colorless crystals. The crystals were isolated by filtration, dried under reduced pressure, and washed with hexanes (3×2 mL) to yield $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**) as a colorless solid (0.104 g, 178 μmol , 48%). In solution, the product is extremely sensitive to hydrolysis and decomposition. ^1H NMR (400 MHz, C_6D_6): δ = 7.01–6.95 (m, 3 H, Ar), 4.38 (s, 1 H, Al-H), 3.88 (s, 1 H, N-H), 3.44 [sept, 1 H, $^3J_{\text{HH}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$], 3.20 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 1.30 [d, $^3J_{\text{HH}}$ = 6.9 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.22 [d, $^3J_{\text{HH}}$ = 6.9 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], –0.02 (s, 6 H, Al-Me), –0.63 (s, 6 H, Al-Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, $\text{C}_6\text{D}_6/\text{C}_6\text{D}_5\text{Br}$): δ = 139.7 (Ar), 139.5 (Ar), 136.5 (Ar), 125.4 (Ar), 125.3 (Ar), 124.7 (Ar), 29.0 [$\text{CH}(\text{CH}_3)_2$], 28.0 [$\text{CH}(\text{CH}_3)_2$], 25.7 [$\text{CH}(\text{CH}_3)_2$], 23.8 [$\text{CH}(\text{CH}_3)_2$], –7.1 (Al-Me), –11.0 (Al-Me) ppm. $\text{C}_{32}\text{H}_{62}\text{Al}_4\text{N}_2$ (582.79): calcd. C 65.95, H 10.72, N 4.81%; found C 66.47, H 10.67 N 5.01%.

Synthesis of $\text{DIPPN(AlMe}_2\cdot\text{THF)}_2$ (3**):** $[(\text{DIPPNH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**) (100 mg, 171 μmol) was dissolved in THF (5 mL). The

reaction was stirred for 1 h until no more gas evolution was observed. All volatiles were removed under reduced pressure to give a colorless oil. Hexanes (2 mL) were added to the oil, which crystallized upon standing. The crystals were isolated by filtration and dried under reduced pressure to give $\text{DIPP-N(H)B(H)(N-DIPP)AlMe}_2\cdot\text{THF}$ (**3**) as a white solid (145 mg, 335 μmol , 98%). $^1\text{H NMR}$ (400 MHz, C_6D_6): δ = 7.22 (d, $^3J_{\text{HH}}$ = 7.4 Hz, 2 H, Ar), 7.05 (t, $^3J_{\text{HH}}$ = 7.6 Hz, 1 H, Ar), 4.22 [sept, $^3J_{\text{HH}}$ = 6.9 Hz, 2 H, $\text{CH}(\text{CH}_3)_2$], 3.59 (br. m, 8 H, THF), 1.40 [d, $^3J_{\text{HH}}$ = 6.9 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$], 1.10 (m, 8 H, THF), -0.47 (s, 12 H, Al-Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ = 152.8 (Ar), 144.7 (Ar), 123.1 (Ar), 119.5 (Ar), 70.7 (THF), 27.5 [$\text{CH}(\text{CH}_3)_2$], 25.6 (THF), 24.9 [$\text{CH}(\text{CH}_3)_2$], -7.6 (Al-Me) ppm. $\text{C}_{24}\text{H}_{45}\text{Al}_2\text{NO}_2$ (433.59): calcd. C 66.48, H 10.46, N 3.23%; found C 66.20, H 10.21 N 3.41%.

Crystal Structure Determination: Crystal data can be found in the Supporting Information (Table S1). The crystal structures were solved using the Olex software package^[25] through Direct Methods (ShelXT)^[26] and refined with SHELXL.^[27] All geometry calculations and graphics were performed with PLATON.^[28] The hydrogen atoms were placed on calculated positions and were refined isotropically in a riding mode. Specific information regarding the refinement of each structure can be found in the Supporting Information.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1846046 for $\text{DIPP-N(H)B(H)(N-DIPP)AlMe}_2\cdot\text{THF}$ (**1**), CCDC-1846047 for $[(\text{DIPP-NH})\text{AlMe}_2(\mu\text{-H})\text{AlMe}_2]_2$ (**2**), and CCDC-1846048 for $\text{DIPP-N(H)B(H)(N-DIPP)AlMe}_2\cdot\text{THF}$ (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Supporting Information (see footnote on the first page of this article): Details for the crystal structure determinations and selected NMR spectra.

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Keywords: Aluminum; Boron; Hydrides; Imido

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