

Tripodal Amido Boron and Aluminum Complexes

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Received November 1, 2006

The synthesis and structural elucidations of novel boron and aluminum complexes incorporating the tripodal triamido $[N_3]^{3-}$ ligand framework that is hypothesized to promote the preorganized pyramidal geometry for high Lewis acidity are reported. Salt metathesis between the in situ-generated trianionic lithium complexes of the tripodal amido ligands with BCl_3 leads to boranes $HC[SiMe_2N(4-MeC_6H_4)]_3B$ (**1**) and $MeSi[SiMe_2N(4-MeC_6H_4)]_3B$ (**2**); however, substitution of the *N*-Ar group with the bulky ^tBu affords the unexpected non-boron-containing LiCl adduct $\{[HC-(SiMe_2N^tBu)_2(SiMeN^tBu)]Li_3(Et_2O)Cl\}_2$ (**3**) via apparent elimination of $MeBCl_2$. The products derived from the salt metathesis reaction with $AlCl_3$ are determined by the reaction medium: while the reaction in a hexanes–ether mixture or toluene affords solvated salt adduct $HC[SiMe_2N(4-MeC_6H_4)]_3Al \cdot ClLi(Et_2O)_2$ (**4**) or salt adduct $HC[SiMe_2N(4-MeC_6H_4)]_3Al \cdot ClLi$ (**5**), respectively; the addition of a small amount of THF produces a mixture of complexes $HC[SiMe_2N(4-MeC_6H_4)]_3Al \cdot (THF)$ (**6**, major) and $HC[SiMe_2N(4-MeC_6H_4)]_3Al(OCH=CH_2) \cdot Li(THF)_2$ (**7**, minor). The desired complex **6** can be exclusively formed using $HC[SiMe_2N(4-MeC_6H_4)]_3Li_3 \cdot (THF)_3$ and the hexanes–ether mixture solvent. The molecular structures of complexes **1**, **3**, **5**, **6**, and **7** have been elucidated by X-ray diffraction studies. The structure of **1** shows an approximately trigonal pyramidal geometry at B with no significant N–B π - π interactions. The strong salt adduct and solvate formation of the tripodal amido Al complex, as well as its similarity to the strong Lewis acid $Al(C_6F_5)_3$ in the THF adduct and enolaluminate formation and structure, indicate the desired core structure $[N_3]Al$ is indeed highly Lewis acidic.

Introduction

Organo-boron and -aluminum Lewis acids (LAs) are important reagents widely employed in organic synthesis,¹ olefin polymerization catalysis,² and polymerization of polar monomers.³ In particular, strong organo-LAs $E(C_6F_5)_3$ ($E = B, Al$) and methylalumoxanes (MAO) are being extensively used in academic and industrial laboratories as critical components, catalysts, cocatalysts, stabilizers, scavengers, etc., for various types of catalytic processes.² Their high Lewis acidity is rendered by either the inclusion of the three

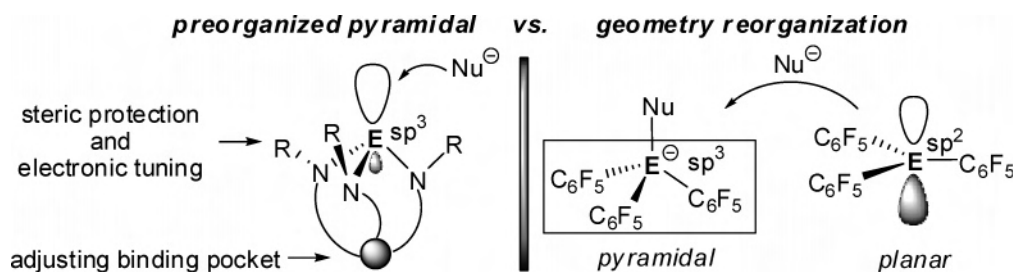
strong electron-withdrawing perfluoroaryl ligands in the case of $E(C_6F_5)_3$ or the still not fully understood cluster structures in the case of MAO that must be used in large excess to be effective in catalysis. Because of the need of the expensive perfluoroaryl ligands in $E(C_6F_5)_3$ or use in large excess of MAO, such reagents contribute significantly to the overall cost of a given catalytic system.

In efforts toward the design and synthesis of alternative strong Lewis acidic boron and aluminum structures that neither contain strong electron-withdrawing ligands such as C_6F_5 nor require their use in excess, we reasoned that, for three-coordinate B and Al complexes to be effective LA catalysts, especially cocatalysts for metal-mediated olefin polymerization catalysis, they require (a) a *preorganized pyramidal geometry* which not only provides a vacant sp^3 orbital disposed ideally to accept a fourth donor ligand but also needs to pay no (or minimal) energy penalty for geometry reorganization (e.g., going from trigonal planar LAs to pyramidal activated species) during LA-mediated chemical processes, and (b) an adequate steric protection of the E center against potential ligand redistribution reactions with a substrate or within the activated species (Chart 1). A

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Chart 1



potentially suitable ligand platform for supporting such sterically protected pyramidal B and Al centers is Gade's tripod-like triamido $[N_3]^{3-}$ ligands having neopentane and trisilylmethane (or trisilylsilane) backbones.⁴ These and analogous tripod-like triamido ligands provide adjustable binding pockets for different metal ions, while variation in the peripheral N-substituents adds additional tools for the fine-tuning of sterics and electronics, as well as introduction of chirality at the typical tetravalent metal centers including those of group 4 metals.⁵ However, to the best of our knowledge, there were no prior reports on such tripod-like triamido complexes of trivalent boron and aluminum,⁶ although main-group (e.g., Verkade's boron and aluminum azatranes⁷) and transition-metal complexes bearing the related *tetradentate* triamido-amine type ligand have been extensively studied by Verkade⁸ and Schrock,⁹ respectively. Reported here are the first syntheses and structural elucidations of a series of boron and aluminum complexes incorporating *tridentate* tripod-like amido ligands.

Experimental Section

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon- or nitrogen-filled glovebox. HPLC grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for THF, Et₂O, and CH₂Cl₂), followed by passage through Q-5-supported copper-catalyst (for toluene and hexanes) stainless steel columns. Benzene-*d*₆ and toluene-*d*₈ were degassed, dried over sodium/potassium alloy, and filtered before use, whereas CDCl₃ and CD₂Cl₂ were degassed and dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, ¹H; 96 MHz, ¹¹B; 75 MHz, ¹³C; 282 MHz, ¹⁹F). Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and reported as parts per million relative to SiMe₄, whereas ¹⁹F spectra were referenced

to external CFCl₃ and ¹¹B spectra to BF₃·Et₂O. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Commercial reagents were purchased from Aldrich Chemical Co., and literature procedures were employed for the preparation of the following neutral tripod-like amido ligands and their corresponding lithium salts (unsolvated or solvated with 2Et₂O): HC[SiMe₂NH(Ar)]₃ (Ar = 4-MeC₆H₄, HC[N₃H₃] and HC[N₃Li₃],¹⁰ MeSi[N₃H₃] and MeSi[N₃Li₃],¹¹ as well as HC[SiMe₂NH(*t*Bu)]₃ and HC[SiMe₂N(*t*Bu)]₃Li₃.¹²

Synthesis of HC[SiMe₂N(4-MeC₆H₄)]₃B (1). ⁿBuLi (5.63 mL, 1.6 M in hexanes, 9.00 mmol) was added to a stirred solution of HC[N₃H₃] (1.52 g, 3.00 mmol) in a solvent mixture (60 mL of hexanes and 10 mL of ether) precooled to -50 °C. The mixture was warmed gradually to ambient temperature and stirred for an additional 5 h. The resulting HC[N₃Li₃·(Et₂O)₂] solution was cooled to -78 °C, and BCl₃ (3.00 mL, 1.0 M in hexanes, 3.0 mmol) was quickly added. This mixture was warmed gradually to ambient temperature while stirring overnight, after which the resulting suspension was filtered. The filtrate was concentrated to ~10 mL and kept at -30 °C. Colorless crystals were obtained after 3 d, which were collected and dried under vacuum affording 0.58 g (38% yield) of the pure complex HC[N₃]B (1). Concentration of the mother liquor followed by crystallization gave 0.20 g (10% recovery yield) of the unreacted [N₃]Li₃·(Et₂O)₂ as colorless crystals. When the same reaction was carried out in toluene, complex 1 was also produced but in a much lower yield of only 11%. ¹H NMR (C₆D₆, 23 °C): δ 7.14 (d, ³J_{HH} = 8.4 Hz, 6 H), 6.89 (d, ³J_{HH} = 8.4 Hz, 6 H) (4-MeC₆H₄), 2.09 (s, 9 H, 4-MeC₆H₄), 0.33 (s, 18 H, SiMe₂), -0.23 (s, 1 H, HC). ¹³C NMR (C₆D₆, 23 °C): δ 145.4, 130.7, 129.5, 120.4 (4-MeC₆H₄), 21.0 (4-MeC₆H₄), 13.9 (HC), 5.0 (SiMe₂). ¹¹B NMR (C₆D₆, 23 °C): δ 39.11 (br). Anal. Calcd for C₂₈H₄₀BN₃Si₃: C, 65.47; H, 7.85; N, 8.18. Found: C, 65.18; H, 7.83; N, 7.96.

Synthesis of MeSi[SiMe₂N(4-MeC₆H₄)]₃B (2). Complex 2 was synthesized using similar procedures to those for 1. MeSi[N₃H₃] (0.86 g, 1.6 mmol), a solvent mixture (20 mL of hexanes and 10 mL of ether), ⁿBuLi (3.0 mL, 1.6 M hexanes solution, 4.8 mmol), and BCl₃ (1.6 mL, 1.0 M hexanes solution, 1.6 mmol) were used. The concentrated filtrate (~15 mL) was kept at -30 °C for 2 d to give 0.25 g (22% recovery yield) of the unreacted MeSi[N₃]Li₃·(Et₂O)₂. The filtrate was further concentrated to ~3 mL and kept at -30 °C for 2 weeks to afford 0.08 g (9% yield) of the pure complex MeSi[N₃]B (2) as colorless crystals. ¹H NMR (C₆D₆, 23 °C): δ 7.24 (d, ³J_{HH} = 8.4 Hz, 6 H), 6.89 (d, ³J_{HH} = 8.4 Hz, 6 H) (4-MeC₆H₄), 2.07 (s, 9 H, 4-MeC₆H₄), 0.51 (s, 18 H, SiMe₂), 0.16 (s, 3 H, MeSi). Anal. Calcd for C₂₈H₄₂BN₃Si₄: C, 61.84; H, 7.78; N, 7.73. Found: C, 61.85; H, 8.07; N, 7.75.

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Synthesis of $\{[\text{HC}(\text{SiMe}_2\text{N}^i\text{Bu})_2(\text{SiMe}^i\text{Bu})]\text{Li}_3(\text{Et}_2\text{O})\text{Cl}\}_2$ (3**).** BCl_3 (0.97 mL, 1.0 M hexanes solution, 0.97 mmol) was quickly added to a stirred solution of $\text{HC}[\text{SiMe}_2\text{N}(\text{Bu})]_3\text{Li}_3$ (0.41 g, 0.97 mmol) in a solvent mixture (30 mL of toluene and 5 mL of Et_2O) precooled to -78°C . This mixture was warmed gradually to ambient temperature while stirring overnight, after which the resulting suspension was evaporated to dryness in vacuo. The residue was extracted with hexanes (40 mL), and the hexanes extract was concentrated to ~ 5 mL and then kept at -30°C for 2 d, affording 0.15 g (29% yield) of the pure complex **3** as colorless crystals after filtration and drying under vacuum. ^1H NMR (C_6D_6 , 23°C): δ 3.39 (q, $^3J_{\text{HH}} = 6.9$ Hz, 4 H, OCH_2CH_3), 1.49 (s, 18 H), 1.28 (s, 9 H, *t*Bu), 1.03 (t, $^3J_{\text{HH}} = 6.9$ Hz, 6 H, OCH_2CH_3), 0.71 (s, 3 H), 0.57 (s, 6 H), 0.40 (s, 3 H), 0.32 (s, 3 H) (*SiMe*, *SiMe*₂), -0.17 (s, 1 H, *HC*). Anal. Calcd for $[\text{C}_{22}\text{H}_{53}\text{Li}_3\text{N}_3\text{OSi}_3\text{Cl}]_2$: C, 51.19; H, 10.35; N, 8.14. Found: C, 50.41; H, 10.29; N, 8.26.

Synthesis of $\text{HC}[\text{SiMe}_2\text{N}(4\text{-MeC}_6\text{H}_4)]_3\text{Al}\cdot\text{ClLi}(\text{Et}_2\text{O})_2$ (4**) and $\text{HC}[\text{SiMe}_2\text{N}(4\text{-MeC}_6\text{H}_4)]_3\text{Al}\cdot\text{ClLi}$ (**5**).** The synthesis of complex **4** was similar to that of **1**, employing the following reagents: $\text{HC}[\text{N}_3]\text{H}_3$ (1.62 g, 3.2 mmol), a solvent mixture (20 mL of hexanes and 20 mL of ether), $^i\text{BuLi}$ (9.6 mmol), and a solution of AlCl_3 (0.43 g, 3.2 mmol) in 20 mL of Et_2O . The pure complex $\text{HC}[\text{N}_3]\text{-Al}\cdot\text{ClLi}(\text{Et}_2\text{O})_2$ (**4**) (0.82 g, 70% yield) was obtained as a colorless crystalline solid. ^1H NMR (C_6D_6 , 23°C): δ 7.24 (d, $^3J_{\text{HH}} = 8.4$ Hz, 6 H), 7.01 (d, $^3J_{\text{HH}} = 8.4$ Hz, 6 H) (*4-MeC}_6\text{H}_4*), 3.03 (q, $^3J_{\text{HH}} = 6.9$ Hz, 8 H, OCH_2CH_3), 2.18 (s, 9 H, *4-MeC}_6\text{H}_4*), 0.83 (t, $^3J_{\text{HH}} = 6.9$ Hz, 12 H, OCH_2CH_3), 0.45 (s, 18 H, *SiMe}_2*), -0.46 (s, 1 H, *HC*). ^{13}C NMR (C_6D_6 , 23°C): δ 149.8, 130.1, 129.1, 126.4 (*4-MeC}_6\text{H}_4*), 65.9 (OCH_2CH_3), 21.0 (*4-MeC}_6\text{H}_4*), 14.9 (OCH_2CH_3), 8.5 (*HC*), 5.9 (*SiMe}_2*). The ether-free complex $\text{HC}[\text{N}_3]\text{Al}\cdot\text{ClLi}$ (**5**) was prepared in a 91% yield by heating **4** at 165°C under vacuum (0.5 Torr) for 2 h. Alternatively, complex **5** was prepared in toluene starting from the neutral ligand, affording an overall yield of 51%. ^1H NMR (C_6D_6 , 23°C): δ 6.96 (q_{AB}, $^3J_{\text{HH}} = 6.0$ Hz, 12 H, *4-MeC}_6\text{H}_4*), 2.13 (s, 9 H, *4-MeC}_6\text{H}_4*), 0.34 (s, 18 H, *SiMe}_2*), -0.54 (s, 1 H, *HC*). Anal. Calcd for $[\text{C}_{28}\text{H}_{40}\text{AlLiN}_3\text{Si}_3\text{Cl}]_2$: C, 58.77; H, 7.05; N, 7.34. Found: C, 58.37; H, 7.58; N, 6.60.

Synthesis of $\text{HC}[\text{SiMe}_2\text{N}(4\text{-MeC}_6\text{H}_4)]_3\text{Al}\cdot(\text{THF})$ (6**) and $\text{HC}[\text{SiMe}_2\text{N}(4\text{-MeC}_6\text{H}_4)]_3\text{Al}(\text{OCH}=\text{CH}_2)\cdot\text{Li}(\text{THF})_2$ (**7**).** $^i\text{BuLi}$ (4.8 mmol) was added to a stirred solution of $\text{HC}[\text{N}_3]\text{H}_3$ (0.81 g, 1.6 mmol) in a solvent mixture (10 mL of hexanes and 20 mL of ether) precooled to -50°C . The mixture was warmed gradually to ambient temperature and stirred for an additional 5 h. The resulting $\text{HC}[\text{N}_3]\text{Li}_3\cdot(\text{Et}_2\text{O})_2$ solution was cooled to -78°C , and AlCl_3 (0.21 g, 1.6 mmol) in a solvent mixture (20 mL of Et_2O and 2 mL of THF) was added. This mixture was warmed gradually to ambient temperature while stirring overnight, after which the resulting mixture was evaporated to dryness under vacuum. The residue was extracted with Et_2O (40 mL) and filtered to remove LiCl salt; the ether solution was evaporated to dryness, and the residue was further extracted with hexanes (20 mL). The hexanes extract was concentrated to ~ 8 mL and kept at -30°C for 3 d. Colorless crystals obtained by recrystallization from hexanes were manually separated, depending on the size and shape of the crystals, into complexes $\text{HC}[\text{N}_3]\text{Al}\cdot(\text{THF})$ (**6**) (large block, 0.18 g, 19% yield) and $\text{HC}[\text{N}_3]\text{-Al}(\text{OCH}=\text{CH}_2)\cdot\text{Li}(\text{THF})_2$ (**7**) (small rhombic, 0.02 g, 2% yield). When more THF was used in the reaction, the yield of **6** was lowered. On the other hand, when $\text{HC}[\text{N}_3]\text{Li}_3\cdot(\text{THF})_3$ (0.83, 1.12 mmol) and AlCl_3 (0.15 g, 1.12 mmol) were used in a solvent mixture of hexanes (10 mL) and ether (25 mL), only complex **6** was formed and isolated in high yield (0.58 g, 86%).

^1H NMR for **6** (C_6D_6 , 23°C): δ 7.15 (d, $^3J_{\text{HH}} = 8.4$ Hz, 6 H), 7.01 (d, $^3J_{\text{HH}} = 8.4$ Hz, 6 H) (*4-MeC}_6\text{H}_4*), 3.41 (t, $^3J_{\text{HH}} = 6.6$ Hz, 4

H, OCH_2CH_2), 2.21 (s, 9 H, *4-MeC}_6\text{H}_4*), 0.55 (s, 18 H, *SiMe}_2*), 0.42 (t, $^3J_{\text{HH}} = 6.6$ Hz, 4 H, OCH_2CH_2), -0.26 (s, 1 H, *HC*). ^{13}C NMR (C_6D_6 , 23°C): δ 150.6, 130.3, 128.8, 126.3 (*4-MeC}_6\text{H}_4*), 74.9 (OCH_2CH_2), 24.5 (OCH_2CH_2), 21.2 (*4-MeC}_6\text{H}_4*), 9.2 (*HC*), 5.7 (*SiMe}_2*). Anal. Calcd for $\text{C}_{32}\text{H}_{48}\text{AlN}_3\text{OSi}_3$: C, 63.85; H, 8.04; N, 6.98. Found: C, 63.41; H, 8.09; N, 6.86.

^1H NMR for **7** (C_6D_6 , 23°C): δ 7.09 (d, $^3J_{\text{HH}} = 8.4$ Hz, 6 H), 6.95 (d, $^3J_{\text{HH}} = 8.4$ Hz, 6 H) (*4-MeC}_6\text{H}_4*), 6.69 (dd, $^3J_{\text{HH}} = 6.0$, 14.1 Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.60 (q_{AB}, $^3J_{\text{HH}} = 6.0$, 14.1, $^2J_{\text{HH}} = 0.9$ Hz, 2 H, $\text{OCH}=\text{CH}_2$), 3.04 (t, $^3J_{\text{HH}} = 6.6$ Hz, 8 H, OCH_2CH_2), 2.19 (s, 9 H, *4-MeC}_6\text{H}_4*), 1.17 (t, $^3J_{\text{HH}} = 6.6$ Hz, 8 H, OCH_2CH_2), 0.61 (s, 18 H, *SiMe}_2*), -0.09 (s, 1 H, *HC*). Anal. Calcd for $\text{C}_{38}\text{H}_{59}\text{AlLiN}_3\text{O}_3\text{-Si}_3$: C, 63.04; H, 8.21; N, 5.80. Found: C, 63.08; H, 7.90; N, 6.11.

X-ray Crystallographic Analyses of **1, **3**, **5**, **6**, and **7**.** Single crystals of all complexes suitable for X-ray diffraction were grown from hexanes at -30°C inside the freezer of a glovebox. The crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at $120^\circ\text{C}/10^{-6}$ Torr for 24 h) after the mother liquors were decanted, mounted on thin glass fibers, and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least-squares on F^2 for all reflections.¹³ Unless otherwise indicated, all non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. In **3**, the hexane solvent carbon atoms were located by difference Fourier synthesis but were refined isotropically. One whole hexane solvent is disordered viewing a cyclic structure when symmetrically operated. Thus, the occupation of carbon atoms C(52), C(54), C(56), and C(57) was set as 0.75, and that of C(51), C(53), C(55) and C(58) was set as 0.375. This gives the rational U_{eq} of these atoms; however, the corresponding hydrogen atoms were geometrically included only to 12. In another half hexane solvent molecule, although the occupation of the whole molecule was set as 0.25, the U_{eq} of some atoms was still large because of the thermal vibration of this free solvent molecule in the crystal lattice. In **5**, the hexane solvent atoms were located by difference Fourier synthesis, with the whole molecule disordered into two positions (the respective occupation of 0.308 and 0.192), and refined isotropically. The subsequent symmetric operation generated the adjacent hexane molecules, and this did not allow the inclusion of the hydrogen atoms in the hexane. In **6**, two independent molecules were found, of which the two coordinated THF [O(1)C(41)C(42)C(43)C(44) 0.70], [O(1A)C(41A)C(42A)C(43A)C(44A) 0.30], [O(2)C(91)C(92)C(93)C(94) 0.85], [O(2A)C(91A)C(92A)C(93A)C(94A) 0.15], and one *p*-tolyl group [C(31)C(32)C(33)C(34)C(35)C(36)C(37) 0.85], [C(31A)C(32A)C(33A)C(34A)C(35A)C(36A)C(37A) 0.15] were disordered and treated in part, respectively. Thus, average metric parameters were given as follows: $\text{Al}(1)\text{-O}_{\text{THF}} = 1.8612(45)$ Å (av), $\text{Al}(2)\text{-O}_{\text{THF}} = 1.8564(54)$ Å (av), $\text{O}_{\text{THF}}\text{-Al}(1)\text{-N}(1) = 109.03(16)^\circ$ (av), $\text{O}_{\text{THF}}\text{-Al}(1)\text{-N}(2) = 105.88(16)^\circ$ (av), $\text{O}_{\text{THF}}\text{-Al}(1)\text{-N}(3) = 112.00(13)^\circ$ (av), $\text{O}_{\text{THF}}\text{-Al}(2)\text{-N}(6) = 106.39(21)^\circ$ (av), $\text{O}_{\text{THF}}\text{-Al}(2)\text{-N}(7) = 114.01(18)^\circ$ (av), $\text{O}_{\text{THF}}\text{-Al}(2)\text{-N}(8) = 106.20(19)^\circ$ (av). In **7**, one carbon atom in the disordered *4-MeC}_6\text{H}_4* group and four carbon atoms in the disordered THF molecule were located and treated in part into two positions [C(11)C(12)C(13)C(14)-C(15)C(16)C(17) 0.54], [C(11A)C(12A)C(13A)C(14A)C(15A)C(16A)C(17A) 0.46], [O(3)C(55)C(56)C(57)C(58) 0.50], [O(3A)C(55A)C(56A)C(57A)C(58A) 0.50], and the related carbon atoms

(13) SHELXTL, version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001.

Table 1. Crystal Data and Structure Refinements for **1**, **3**·2C₆H₁₄, **5**·C₆H₁₄, **6**, and **7**^a

	1	3 ·2C ₆ H ₁₄	5 ·C ₆ H ₁₄	6	7
formula	C ₂₈ H ₄₀ BN ₃ Si ₃	C ₅₆ H ₁₃₁ Cl ₂ Li ₆ N ₆ O ₂ Si ₆	C ₆₂ H ₉₄ Al ₂ Cl ₂ Li ₂ N ₆ Si ₆	C ₃₂ H ₄₈ AlN ₃ O ₃ Si ₃	C ₃₈ H ₅₉ AlLi ₃ O ₃ Si ₃
fw	513.71	1201.75	1230.71	601.98	724.07
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 1	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	7.6940(4)	10.5785(3)	28.8457(11)	14.7157(6)	11.9203(7)
<i>b</i> (Å)	26.1454(13)	21.6592(7)	13.0329(6)	14.7551(6)	26.6447(14)
<i>c</i> (Å)	14.5059(7)	17.0059(5)	23.9200(9)	18.0703(8)	13.5389(7)
α (deg)				90.799(2)	
β (deg)	94.895(2)	91.549(2)	126.888(1)	101.923(2)	99.636(3)
γ (deg)				118.783(2)	
<i>V</i> (Å ³)	2907.4(3)	3895.0(2)	7192.3(5)	3335.1(2)	4239.9(4)
<i>Z</i>	4	2	4	4 ^b	4
ρ _{calcd} (g cm ⁻³)	1.174	1.025	1.137	1.199	1.134
μ (mm ⁻¹)	0.185	0.212	0.254	0.198	0.169
<i>F</i> (000)	1104	1322	2632	1296	1560
cryst size (mm ³)	0.49 × 0.34 × 0.15	0.58 × 0.39 × 0.13	0.26 × 0.26 × 0.16	0.37 × 0.33 × 0.28	0.44 × 0.27 × 0.21
θ range (deg)	2.77–32.59	1.52–33.24	3.08–30.62	1.16–35.04	1.53–33.19
index ranges	−11 ≤ <i>h</i> ≤ 11 −39 ≤ <i>k</i> ≤ 39 −21 ≤ <i>l</i> ≤ 21	−15 ≤ <i>h</i> ≤ 16 −33 ≤ <i>k</i> ≤ 33 −26 ≤ <i>l</i> ≤ 26	−41 ≤ <i>h</i> ≤ 41 −18 ≤ <i>k</i> ≤ 18 −34 ≤ <i>l</i> ≤ 34	−22 ≤ <i>h</i> ≤ 23 −23 ≤ <i>k</i> ≤ 23 −29 ≤ <i>l</i> ≤ 28	−15 ≤ <i>h</i> ≤ 18 −40 ≤ <i>k</i> ≤ 40 −20 ≤ <i>l</i> ≤ 20
collected data	95 108	66 125	87 853	127 598	78 983
unique data	10 551 (<i>R</i> _{int} = 0.0365)	14 904 (<i>R</i> _{int} = 0.0617)	11 031 (<i>R</i> _{int} = 0.0370)	29 278 (<i>R</i> _{int} = 0.0315)	16 105 (<i>R</i> _{int} = 0.0514)
completeness to θ	99.6%	99.4%	99.5%	99.4%	99.2%
data/restraints/params	10 551/0/325	14 904/13/369	11 031/13/392	29 278/414/887	16 105/0/512
GOF on <i>F</i> ²	1.073	1.033	1.066	1.002	1.018
final <i>R</i> indices	<i>R</i> 1 = 0.0398	<i>R</i> 1 = 0.0535	<i>R</i> 1 = 0.0466	<i>R</i> 1 = 0.0421	<i>R</i> 1 = 0.0568
[<i>I</i> > 2σ(<i>I</i>)]	w <i>R</i> 2 = 0.0972	w <i>R</i> 2 = 0.1422	w <i>R</i> 2 = 0.1300	w <i>R</i> 2 = 0.1083	w <i>R</i> 2 = 0.1462
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0596 w <i>R</i> 2 = 0.1094	<i>R</i> 1 = 0.0858 w <i>R</i> 2 = 0.1663	<i>R</i> 1 = 0.0558 w <i>R</i> 2 = 0.1386	<i>R</i> 1 = 0.0631 w <i>R</i> 2 = 0.1216	<i>R</i> 1 = 0.0921 w <i>R</i> 2 = 0.1683

^a All data were collected at 173(2) K using Mo Kα ($\lambda = 0.71073$ Å) radiation. ^b Two independent molecules.

[C(17), C(17A), C(55), C(56), C(57), C(58), C(55A), C(56A), C(57A), C(58A)] were refined isotropically.

Selected crystal data and structural refinement parameters are collected in Table 1.

Results and Discussion

Synthesis and Structural Studies of Tripodal Amido Boron Complexes. The metathesis reaction of the in situ-generated trianionic lithium salt HC[N₃]Li₃·(Et₂O)₂ (or in its unsolvated form when generated in toluene) with BCl₃ in a hexanes/ether solvent mixture (or in toluene) produces the desired tripodal triamido borane HC[N₃]B (**1**), which was isolated as colorless crystals in a 38% yield (or 11% yield). The donor solvent promotes higher yield, but in both cases significant quantities (10%) of the unreacted HC[N₃]Li₃ (with or without 2Et₂O) was recovered during the workup, even when an excess of BCl₃ was employed. Noteworthy in the ¹H NMR spectra on going from the neutral ligand to **1** is a significant upfield shift by 1.1 ppm for the apical CH upon complex formation of the time-average C_{3v}-symmetric borane **1**. The molecular structure of **1** (Figure 1) reveals that the B atom is located above the N₃-basal plane by 0.1785 Å, and the sum of the angles about B is 355.7°. The geometry at each of the three N atoms deviates somewhat from planarity, with the sums of the angles around them ranging from 352.8 to 355.0°. There appears to be no significant N–B p–p π -interactions as evidenced by the N–B bond lengths (from 1.459(2) to 1.469(2) Å) for typical N–B single bonds and large twist angles (67.3–76.9°) between the N₃-basal plane and the B–N–Si planes. The absence of any significant N–Ar p– π interactions is also implicated by the same

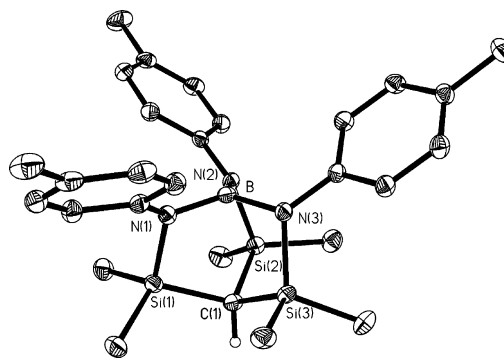
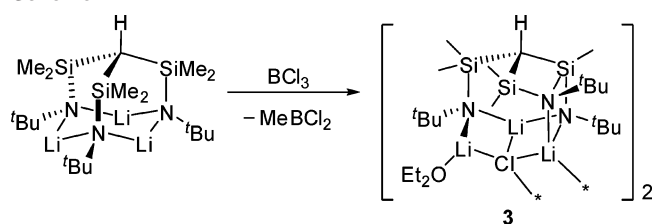


Figure 1. X-ray crystal structure of **1** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): B–N(1) = 1.459(2), B–N(2) = 1.466(2), B–N(3) = 1.469(2), Si(1)–N(1) = 1.786(1), Si(2)–N(2) = 1.778(1), Si(3)–N(3) = 1.784(1), Si(1)–C(1) = 1.899(1), Si(2)–C(1) = 1.902(1), Si(3)–C(1) = 1.901(1); N(1)–B–N(2) = 118.5(1), N(1)–B–N(3) = 119.0(1), N(2)–B–N(3) = 118.2(1).

N–C(ipso) bond length (within 2σ; av 1.421(2) Å) and large torsion angles (46.1–52.2°) of Ar relative to the plane defined by Si, N, and C(ipso). As a whole, all crystallographic evidence is consistent with a trigonal pyramidal geometry at B in the tripodal borane structure **1**, although the degree of pyramidalization is not significant in this complex.

Subsequently, we set out to prepare two different classes of tripodal amido borane derivatives: backbone (HC[N₃] → MeSi[N₃]) and N-substitution (4-MeC₆H₄ → 'Bu). Specifically, the tripodal amido borane bearing the all-silicon (i.e., trisilylsilane) backbone, MeSi[N₃]B (**2**) was successfully synthesized via the salt metathesis route employing the corresponding trianionic lithium salt MeSi[N₃]Li₃·(Et₂O)₂;

Scheme 1



however, it was isolated in low yield (9%), and a significant amount (22%) of the unreacted $\text{MeSi}[\text{N}_3]\text{Li}_3 \cdot (\text{Et}_2\text{O})_2$ was recovered after the reaction and workup. On the other hand, when the *N*-Ar group was substituted with the bulky *t*Bu, the reaction of the lithium salt $\text{HC}[\text{Si}(\text{Me}_2)\text{N}(\text{tBu})]\text{Li}_3$ with BCl_3 did not yield the desired tripodal triamido borane; instead, the reaction afforded non-boron-containing LiCl adduct $\{[\text{HC}(\text{SiMe}_2\text{N}^t\text{Bu})_2(\text{SiMeN}^t\text{Bu})]\text{Li}_3(\text{Et}_2\text{O})\text{Cl}\}_2$ (**3**) via apparent elimination of MeBCl_2 , with the chloride deriving from BCl_3 and the Me from a $\text{Me}_2\text{Si} <$ group in the tripodal ligand giving rise to the new $\text{Me}(\text{tBuN})\text{Si} <$ moiety (Scheme 1).

The solution ^1H NMR spectrum of **3** shows two types of the *t*Bu groups (18H at 1.49 ppm and 9H at 1.28 ppm) and four types of the *SiMe* groups at 0.71 (3H), 0.57 (6H), 0.40 (3H), and 0.32 (3H) ppm, respectively, and its molecular structure was confirmed by X-ray diffraction (Figure 2), featuring a centrosymmetric dimeric structure. The two derived tripodal ligand moieties after the MeBCl_2 elimination are connected by tetracoordinate Li and Cl centers forming a parallelogram linkage with alternating short and long Li–Cl bonds that differ by only 0.086 Å; each ligand moiety comprises 4 unique fused four-membered rings involving all the mainframe atoms, except for Si(2), with 2 of them being planar [ring 1, C(1)–Si(1)–N(1)–Si(3), $\Delta = 0.0128$ Å; ring 2, N(1)–Si(3)–Li(2)–N(3), $\Delta = 0.0293$ Å] and the other two being quasiplanar [ring 3, Li(2)–N(3)–Cl(1)–Li(3), $\Delta = 0.0662$ Å; ring 4, Cl(1)–Li(3)–N(2)–Li(1), $\Delta = 0.0726$ Å]. The dihedral angles are 113.6° (rings 1 and 2), 68.8° (rings 2 and 3), and 135.1° (rings 3 and 4). All Li–N (amido) bonds have comparable lengths [Li(1)–N(2) = 1.951(3) Å, Li(2)–N(3) = 1.991(3) Å, Li(3)–N(2) = 1.976(3) Å, Li(3)–N(3) = 1.982(3) Å], except for the Li–N (amino) bond which is significantly longer [Li(2)–N(1) = 2.393(3) Å]. The structure clearly shows the new connection of the *SiMe* group to another adjacent *N**t*Bu nitrogen atom through Si, thus making that nitrogen a neutral amino N donor which resets the whole ligand in divalent state.

Synthesis and Structural Studies of Tripodal Amido Aluminum Complexes. The ionic radius of Al^{3+} is approximately double that of its cogeneric B^{3+} , which should render more pyramidalized geometry for the similar tripodal triamido Al complexes. In this context, the $\text{HC}[\text{N}_3]\text{H}_3$ ligand was selected for the synthesis of its tripodal aluminum complexes using the salt metathesis approach, but they were isolated either in its solvated form or as a LiCl adduct. Specifically, the reaction of $\text{HC}[\text{N}_3]\text{Li}_3 \cdot (\text{Et}_2\text{O})_2$ with AlCl_3 in a hexanes/ether solvent mixture led to formation of the tripodal triamido aluminum complex $\text{HC}[\text{N}_3]\text{Al} \cdot \text{ClLi}(\text{Et}_2\text{O})_2$

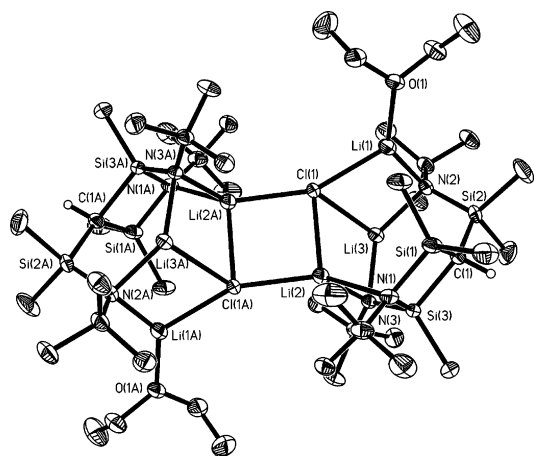
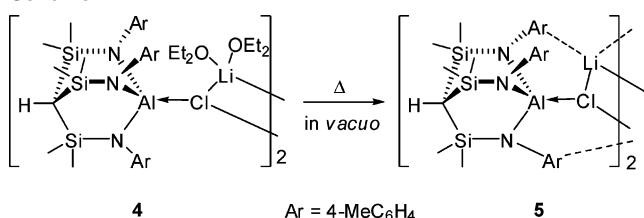


Figure 2. X-ray crystal structure of **3** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)–Si(1) = 1.867(2), C(1)–Si(2) = 1.877(2), C(1)–Si(3) = 1.906(2), Si(1)–N(1) = 1.760(1), Si(2)–N(2) = 1.704(1), Si(3)–N(3) = 1.683(1), Si(3)–N(1) = 1.797(1), Cl(1)–Li(1) = 2.378(3), Cl(1)–Li(2) = 2.477(3), Cl(1)–Li(3) = 2.439(3), Cl(1)–Li(2A) = 2.391(3); Li(2)–Cl(1)–Li(2A) = $88.16(9)$, Cl(1)–Li(2)–Cl(1A) = $91.84(9)$.

Scheme 2



(**4**) in a 70% yield, likely existing as a dimer (Scheme 2). In an effort to remove the coordinated LiCl and its solvated Et_2O , complex **4** was subjected to heat (165°C) under vacuum (0.5 Torr) or to treatment with AgBPh_4 , affording the Et_2O -free complex $\text{HC}[\text{N}_3]\text{Al} \cdot \text{ClLi}$ (**5**) that can also be produced directly from the reaction of $\text{HC}[\text{N}_3]\text{Li}_3$ with AlCl_3 in a hexanes/toluene solvent mixture. In solution, complex **5** has a time-average C_{3v} symmetry on the NMR time scale at room temperature; however, the interaction between Li and Ar is shown by an AB spin splitting pattern of the Ar protons in **5** versus the typical AX(M) spin patterns for those without such coordination (e.g., **1**, $\text{HC}[\text{N}_3]\text{Li}_3$, and **4**).

The molecular structure of tripodal aluminum complex **5** derived from X-ray diffraction (Figure 3) reveals a unique centrosymmetric dimeric structure in which each tetracoordinate Li center is bound to two *N*-aryl rings from two separate $[\text{N}_3]$ ligand moieties, with two three-coordinate Cl atoms completing its coordination sphere. One of the aryl rings is coordinated to Li in a best-described η^2 -fashion [Li(1)–C(15) = 2.387(3) Å, Li(1)–C(16) = 2.345(3) Å; the other Li(1)–C(Ar) distances are in the range of 2.698(3)–3.052 Å with a Li(1)–C(Ar-ring centroid) distance of 2.339 Å], whereas the other is in a best-described η^1 -fashion [Li(1)–C(22A) = 2.397(3) Å; the other Li(1)–C(Ar) distances are in the range of 2.802–4.005 Å with the Li(1)–C(Ar-ring centroid) distance of 2.997 Å]. Such $\text{N} \cdots \text{Ar} \cdots \text{Li}$ interactions noticeably lengthen the distances of Al to such amido nitrogens; thus, the two same Al–N bonds (within 2σ ; av 1.8466(14) Å) exhibiting the $\text{Ar} \cdots \text{Li}$ interactions are longer

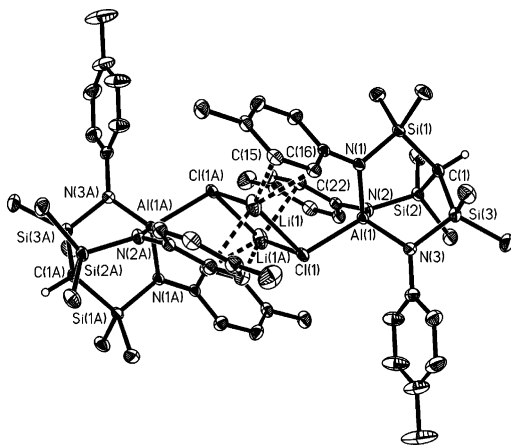
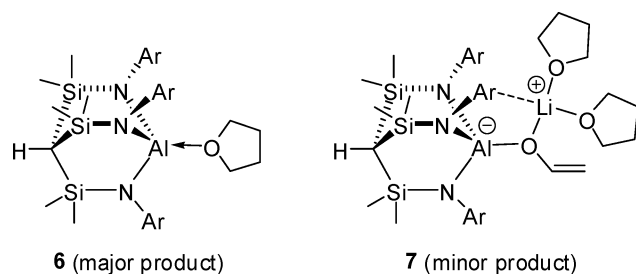


Figure 3. X-ray crystal structure of **5** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) = 1.847(1), Al(1)–N(2) = 1.846(1), Al(1)–N(3) = 1.829(1), Al(1)–Cl(1) = 2.2272(5), Cl(1)–Li(1A) = 2.390(3), Cl(1)–Li(1) = 2.527(3); N(1)–Al(1)–N(2) = 109.00(6), N(1)–Al(1)–N(3) = 111.50(6), N(2)–Al(1)–N(3) = 108.79(6), Cl(1)–Li(1)–Cl(1A) = 90.9(1), Li(1)–Cl(1)–Li(1A) = 89.2(1).

Chart 2



than the third Al–N bond, absent of such interactions, by ~ 0.02 Å. The two tripodal ligand moieties are further connected by two bridging Cl atoms that form a nearly rectangular linkage with two Li atoms exhibiting alternating short and long Li–Cl bonds that differ by 0.137 Å. The geometry at Al is that of a slightly distorted tetrahedron with the sum of the N–Al–N angles being 329.3° , while the adduct $\text{HC}[\text{N}_3]\text{Al}\cdot\text{ClLi}$ nature of complex **5** is recognized by the observed relatively long Al–Cl bond length of 2.2272(5) Å and the normal Cl–Li bond length of 2.390(3) Å.

When a small amount of THF was added to the same salt metathesis reaction in a hexanes/ether mixture, two products, neutral alane-THF adduct $\text{HC}[\text{N}_3]\text{Al}\cdot(\text{THF})$ (**6**, 19% yield) and ionic lithium aluminate complex $\text{HC}[\text{N}_3]\text{Al}(\text{OCH}=\text{CH}_2)\cdot\text{Li}(\text{THF})_2$ (**7**, 2% yield), were isolated (Chart 2), both of which were structurally characterized by X-ray diffraction (Figures 4 and 5). Depending on the acceptor metal (Al vs Li), the coordinated THF molecules exhibit distinctly different chemical shifts in ^1H NMR: 3.41 (t) and 0.42 (t) when bound to Al and 3.04 (t) and 1.17 (t) when bound to Li. The coordinated THF in **6** was not removed by vacuum or heat treatment, indicative of the strongly Lewis acidic nature of the transient tripodal amido alane species, “[N_3]Al”. The solid-state structure of the complex **6** (Figure 4) consists of two independent molecules with similar metric parameters, only one of which is shown and discussed here. The Al center adopts a slightly distorted tetrahedral geometry with the sum of the N–Al–N angles being 329.8° , while the Al atom sits

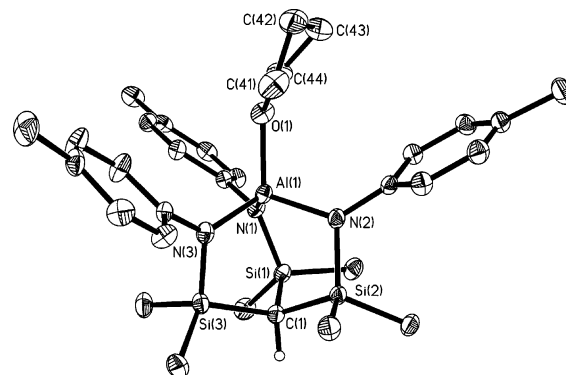


Figure 4. X-ray crystal structure of **6** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) = 1.8458(9), Al(1)–N(2) = 1.8300(9), Al(1)–N(3) = 1.835(1), Si(1)–N(1) = 1.7457(9), Si(2)–N(2) = 1.735(1), Si(3)–N(3) = 1.734(1), Al(1)–O(1) = 1.861(5) (av for the disordered THF); N(1)–Al(1)–N(2) = 110.15(4), N(1)–Al(1)–N(3) = 110.38(4), N(2)–Al(1)–N(3) = 109.30(4).

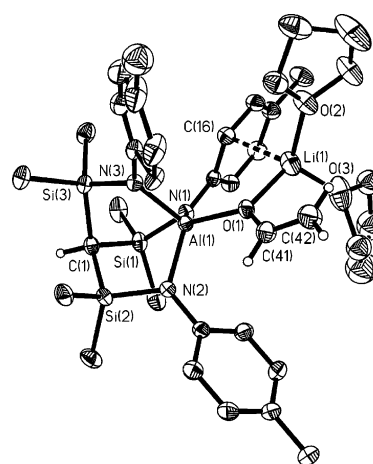


Figure 5. X-ray crystal structure of **7** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) = 1.867(1), Al(1)–N(2) = 1.844(1), Al(1)–N(3) = 1.851(1), Al(1)–O(1) = 1.790(1), Li(1)–O(1) = 1.924(4), Li(1)–O(2) = 1.910(4), Li(1)–O(3) = 1.90(1) (av for the disordered THF), Li(1)–C(16) = 2.466(4), C(41)–C(42) = 1.318(3); N(1)–Al(1)–N(2) = 107.69(6), N(1)–Al(1)–N(3) = 105.90(6), N(2)–Al(1)–N(3) = 108.15(6).

above the N_3 -basal plane by 0.5979 Å. The three Al–N single-bond lengths slightly differ from one another with an average Al–N length of 1.837(1) Å, which is longer than the average Al–N (amido) distances of 1.809(6) and 1.802(2) Å observed for the tetracoordinate triamido aluminum complexes $\text{N}[\text{CH}_2\text{CH}_2(\text{Me}_3\text{Si})\text{N}]_3\text{Al}^{14}$ and $[\text{Al}(\text{NMe}_2)_3]_2^{15}$ for the equatorial Al–N and terminal Al–N bonds, respectively. The amido nitrogens are nearly planar with the average of the sum of angles around them being 359.3° , which can be attributed to partial π -bonding between long pairs of N and d orbitals of the neighboring Si.¹⁴ The Al–O bond length of 1.861(5) Å in **6** is identical to that observed in $(\text{C}_6\text{F}_5)_3\text{Al}\cdot(\text{THF})$ (1.860(2) Å),¹⁶ further indicating high Lewis acidity of the tripodal amido alane species $[\text{N}_3]\text{Al}$.

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(15) Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257–263.

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The details about the formation of the unanticipated complex **7** are currently unknown, although it is clear that its formation is directly related to the presence of free THF in solution, suggesting a plausible pathway through the ring-opening of THF followed by the C–C bond cleavage. Accordingly, this side product can be either substantially suppressed using a minimal amount of THF in the reaction solvent mixture or completely avoided using $\text{HC}[\text{N}_3]\text{Li}_3 \cdot (\text{THF})_3$ for its reaction with AlCl_3 in a hexanes–ether solvent mixture. By the latter approach, the pure complex **6** was isolated in an 85% yield. The enolate moiety ($\text{OCH}=\text{CH}_2$) within complex **7** is readily characterized by its ^1H NMR resonances at 6.69 (dd, 1H) and 3.60 ppm (q_{AB} , 2H), as well as by the X-ray structure showing the C(41)–C(42) bond length of 1.318(3) Å (Figure 5) for a C=C double bond. The tetracoordinate Li is bound to three O atoms (1 from the enolate and 2 from the two coordinated THF) and an aryl C(ortho) in a best-described η^1 -fashion [$\text{Li}(1)\text{--C}(16) = 2.466(4)$ Å; the other $\text{Li}(1)\text{--C}(\text{Ar})$ distances are in the range of 2.927 to 4.247 Å with the $\text{Li}(1)\text{--C}(\text{Ar-ring centroid})$ distance of 3.181 Å]. Because of such $\text{N--Ar}\cdots\text{Li}$ interactions, the bond length of Al to this amido N [$\text{Al}(1)\text{--N}(1) = 1.867(1)$ Å] is noticeably longer than the other two Al–N bonds that are essentially the same (within 2σ ; av 1.847(1) Å). The geometry around the four-coordinate Al center is that of a distorted tetrahedron with the sum of the N–Al–N angles being 321.7° ; for the same reason described above, the N(2) and N(3) adopt a nearly planar geometry with the average of the sum of angles around them being 359.6° . The overall structure of **7** somewhat resembles those of lithium ester enolaluminate complexes $\text{Li}[\text{Me}_2\text{C}=\text{C}(\text{O}^i\text{Pr})\text{OAlMe}(\text{BHT})_2]$ and $\text{Li}(\text{THF})_2[\text{Me}_2\text{C}=\text{C}(\text{O}^i\text{Pr})\text{OAl}(\text{C}_6\text{F}_5)_3]$.¹⁷

Conclusions

In summary, motivated by the hypothesis that preorganized trigonal pyramidal boranes and alanes with an adequate steric

protection provided by a class of tripodal triamido ligands should be strong LAs, we have synthesized several such novel B and Al tripodal triamido complexes, the structures of five of which have been elucidated by X-ray diffraction studies. The trigonal pyramidal geometry at B in the tripodal triamido borane structure **1**, as a consequence of the lack of significant N–B p–p π -interactions, suggests significant Lewis acidity imposed by the geometry within the tripodal triamido binding pocket.¹⁸ Furthermore, the strong adduct and solvate formations of the tripodal amido Al complexes, as shown in **4**, **5**, and **6**, as well as their similarity to the exceptionally strong Lewis acid $\text{Al}(\text{C}_6\text{F}_5)_3$ in the THF adduct and enolaluminate formation and structure, as shown in **6** and **7**, indicate the desired core structure $[\text{N}_3]\text{Al}$ is indeed highly Lewis acidic. Our ongoing efforts are directed at the synthesis of highly pyramidalized tripodal boranes and salt- or donor-solvent-free tripodal amido alanes, as well as catalytic applications of these preorganized pyramidal B and Al complexes as LA catalysts or cocatalysts.

Acknowledgment. This work was supported by an unrestricted research fund provided by Sumitomo Chemical Co. Ltd. We thank Masayuki Fujita, Tatsuya Miyatake, and Kazuo Takaoki for helpful discussions, as well as Susie Miller for the X-ray diffraction data collections.

Supporting Information Available: Crystallographic data for complexes **1**, **3**, **5**, **6**, and **7** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data for the five structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers CCDC-624044 (**1**), 624045 ($3 \cdot 2\text{C}_6\text{H}_{14}$), 624046 ($5 \cdot \text{C}_6\text{H}_{14}$), 624047 (**6**), and 624048 (**7**). These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax (+44) 1223–336-033; e-mail deposit@ccdc.cam.ac.uk).

IC0620889

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(18) Preliminary experiments showed facile reaction between **1** and a metallocene complex, Cp_2ZrMe_2 or *rac*- $\text{C}_2\text{H}_4(\text{Ind})_2\text{ZrMe}_2$.