

Low-Coordinate Aluminum Amides from Silylanilines and Alkylalanes

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The aluminum amides $R_2AlN(Ar)SiMe_3$ [$R = Et$, $Ar = Dipp$, **1** ($Dipp = 2,6-iPr_2C_6H_3-$); $R = iBu$, $Ar = Dipp$, **2**; $R = Et$, $Ar = Mes$, **3** ($Mes = 2,4,6-Me_3C_6H_2-$); $R = iBu$, $Ar = Mes$, **4**] were prepared by ethane or hydrogen elimination reaction between Et_3Al or iBu_2AlH and $ArN(H)SiMe_3$ in refluxing hexane solution. The $LiCl$ salt elimination route resulted in the formation of the monomeric aluminum amide $Et_2AlN(Mes)-SiPh_3$ (**5**) featuring three-coordinate aluminum and nitrogen

centers. In addition, the synthesis and characterization of the dinuclear species $Ph_2Si\{N(Mes)AlEt_2\}_2$ (**6**) and the hydride-bridged eight-membered ring compound $\{MesN(SiMe_3)Al(iBu)(\mu-H)\}_2(\mu-LiH)(\mu-iBu_2AlH)$ (**7**) are reported. All compounds have been characterized by 1H and $^{13}C\{^1H\}$ NMR spectroscopy, and compounds **5**, **6**, and **7** have also been characterized by single-crystal X-ray crystallography.

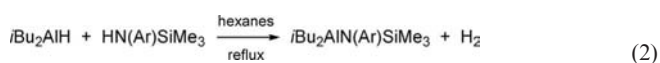
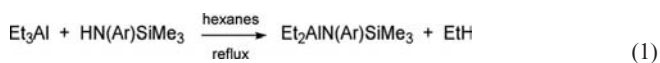
Introduction

Neutral aluminum compounds are widely used as catalysts for Lewis-acid-mediated reactions such as Friedel–Crafts and Diels–Alder reactions, as reagents in alkylation reactions, as initiators for cationic polymerizations, and co-catalysts/activators in transition-metal-catalyzed olefin polymerizations.^[1,2] Bulky substituents have been employed to increase the reactivity by providing a three-coordinate Lewis acidic aluminum center as well as to increase the selectivity by blocking alternative positions in the substrate.^[3] The Lewis acidity of the aluminum center can be further enhanced by the use of electronegative substituents such as amides R_2N- , alkoxides $RO-$ or aryloxides $ArO-$ and by the introduction of a positive charge in combination with a lowering of the coordination number to two as in $[RAIR']^+$ ($R, R' = \text{alkyl, aryl}$). As part of our ongoing investigations of low-coordinate cationic aluminum and gallium compounds^[4] we have become interested in the synthesis of low-coordinate cationic alkylaluminum amides such as $[EtAlN(Ar)SiR_3]^+$. The bulky anilides $-N(Ar)SiR_3$ ($Ar = Mes, Dipp$; $Mes = 2,4,6-C_6H_2-$; $Dipp = 2,6-iPr_2C_6H_3-$; $R = Me, Ph$) are thought to prevent aggregation of the cationic species in addition to limit cation–anion contacts. The precursors for these compounds would be dialkylaluminum amides such as $Et_2AlN(Ar)SiR_3$. While the synthesis of three-coordinate aluminum amides with bulky substituents on both the aluminum and nitrogen center is well documented,^[5] we describe here the preparation of diethyl and diiso-

butylaluminum amides $R_2AlN(Ar)SiR'_3$ with the steric protection being provided by bulky anilides. The monomeric methylaluminum compounds with very bulky disilylamides $Me_2AlN(SiPh_tBu_2)(SiMe_tBu_2)$ ^[6] and $Me(Cl)AlN(SiPh_tBu_2)(SiMe_tBu_2)$ ^[7] have been reported. A series of dimethylaluminum silyl anilides $Me_2AlN(Ar)SiR'_2$ ($Ar = Mes, Dipp$; $R = Me, R' = Me, iPr, tBu, Mes$) has been prepared by the Roesky group, and $\{Me_2AlN(Dipp)SiMe_3\}_2$ was found to be dimeric with bridging methyl substituents.^[8] Contrary to the majority of previously reported aluminum amides the aluminum precursors Et_3Al , Et_2AlCl and iBu_2AlH are commercially available and inexpensive, and the silyl anilines can be prepared in simple one-step procedures from the readily available anilines $ArNH_2$ ($Ar = Mes, Dipp$) and R_3SiCl ($R = Me, Ph$). In addition, we report the synthesis and characterization of the dinuclear $Ph_2Si\{N(Mes)AlEt_2\}_2$ and the hydride-bridged eight-membered-ring compound $\{MesN(SiMe_3)Al(iBu)(\mu-H)\}_2(\mu-LiH)(\mu-iBu_2AlH)$.

Results and Discussion

The aluminum amides $R_2AlN(Ar)SiMe_3$ ($R = Et$, $Ar = Dipp$, **1**; $R = iBu$, $Ar = Dipp$, **2**; $R = Et$, $Ar = Mes$, **3**; $R = iBu$, $Ar = Mes$, **4**) were prepared by the ethane or hydrogen elimination reaction in refluxing hexane according to Equations (1) and (2).



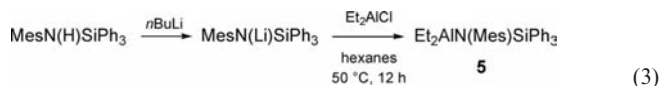
Compounds **1–4** were obtained as pale yellow oils, which could not be purified further. The diethylaluminum amides **1** and **3** were analytically pure, but the diisobutylaluminum

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amides **2** and **4** contained approximately 10% of unreacted silylamines. Based on freezing point depression experiments on **1** and the similarity of their solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in C_6D_6 , compounds **1–4** are most likely monomeric in solution. Typically, aluminum amides are dimeric species with bridging amides such as $\{\text{iBu}_2\text{AlN}(\text{H})\text{Dipp}\}_2$,^[9] $\{\text{Neo}_2\text{AlN}(\text{H})\text{Dipp}\}_2$ [Neo = neopentyl, $-\text{CH}_2\text{C}(\text{CH}_3)_3$],^[10] or $\{\text{Me}_2\text{AlN}(\text{H})\text{Dipp}\}_2$.^[11] Introduction of the bulky Me_3Si group in $\{\text{Me}_2\text{AlN}(\text{Dipp})\text{SiMe}_3\}_2$ prevented amide bridging, but methyl bridging via two-electron-three-center bonds was observed.^[8] The present observation that compounds **1–4** are most likely monomeric in solution may be explained by the lower bridge-forming tendency of alkyl groups other than methyl.^[12]

In order to obtain a crystalline species, the larger and crystalline aniline derivative $\text{MesN}(\text{H})\text{SiPh}_3$ was prepared, lithiated and reacted with Et_2AlCl to give the solid compound $\text{Et}_2\text{AlN}(\text{Mes})\text{SiPh}_3$ (**5**), see Equation (3). Attempts to generate the Dipp analogue were unsuccessful.



The crystal structure of **5** (Figure 1) confirms that it is a monomer with three-coordinate planar aluminum and nitrogen centers [$\Sigma(\text{angles})$: 360° for both centers]. The planes at aluminum and nitrogen are essentially coplanar (angle between normals: 2.1°) allowing for a short Al–N distance of $1.813(4)$ Å as well as potential overlap of the lone pair on the nitrogen into the empty p -orbital on aluminum. The large size of the SiPh_3 group causes a widening of the $\text{N}(1)\text{–Al}(1)\text{–C}(29)$ and $\text{Si}(1)\text{–N}(1)\text{–Al}(1)$ angles to $123.48(19)^\circ$ and $127.6(2)^\circ$, respectively. The Al–N distance is among the shorter ones having been reported for aluminum monoamides, see for example $\text{Trip}_2\text{AlN}(\text{H})\text{Dipp}$ (Trip = 2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$),^[13] $\text{iBu}_2\text{AlNMe}_2$ and $\text{iBu}_2\text{AlN}(\text{Dipp})\text{SiPh}_3$ ^[14] with values of $1.784(3)$, $1.823(4)$, and $1.834(3)$ Å, respectively. Similarly, the angle between the planes at aluminum and nitrogen falls in the lower range of those observed to date for this class of compounds. Most often angles in the

range of $49\text{--}86^\circ$ are observed.^[5] Only those reported for $\text{Trip}_2\text{AlN}(\text{H})\text{Dipp}$ and $\text{iBu}_2\text{AlN}(\text{Dipp})\text{SiPh}_3$ with values of 5.5 and 16.1° come close to the value of 2.1° found in **5**.

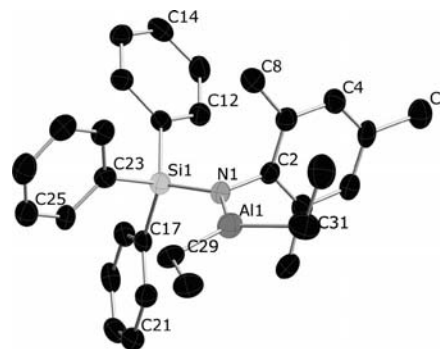
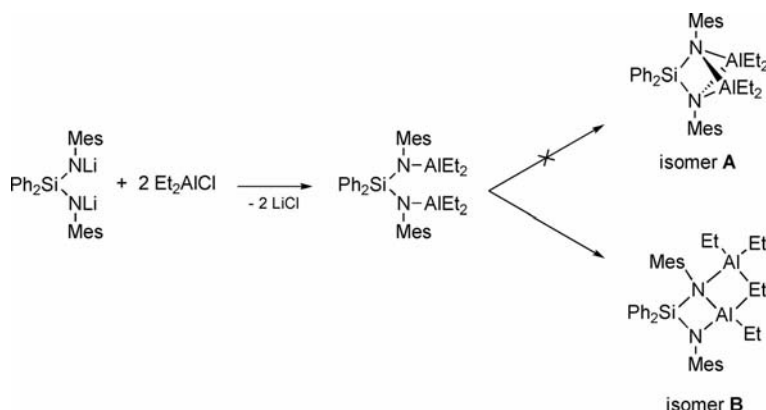


Figure 1. Structure of **5** (50% ellipsoids). H atoms are omitted for clarity. Important bond lengths [Å] and angles [$^\circ$]: $\text{Al}(1)\text{–N}(1)$ $1.813(4)$, $\text{Al}(1)\text{–C}(29)$ $1.950(4)$, $\text{Al}(1)\text{–C}(31)$ $1.969(5)$, $\text{N}(1)\text{–C}(2)$ $1.451(5)$, $\text{Si}(1)\text{–N}(1)$ $1.737(3)$, $\text{N}(1)\text{–Al}(1)\text{–C}(29)$ $123.48(19)$, $\text{N}(1)\text{–Al}(1)\text{–C}(31)$ $116.3(2)$, $\text{C}(29)\text{–Al}(1)\text{–C}(31)$ $120.2(2)$, $\text{Si}(1)\text{–N}(1)\text{–Al}(1)$ $127.6(2)$, $\text{C}(2)\text{–N}(1)\text{–Al}(1)$ $114.5(3)$, $\text{C}(2)\text{–N}(1)\text{–Si}(1)$ $117.9(3)$.

The reaction of the in-situ generated lithiated diamide $\text{Ph}_2\text{Si}\{\text{N}(\text{Mes})\text{Li}\}_2$ with 2 equiv. Et_2AlCl afforded the new compound $\text{Ph}_2\text{Si}\{\text{N}(\text{Mes})\text{AlEt}_2\}_2$, **6**, in moderate yields (Scheme 1). This type of compounds has been previously obtained in two isomers: $(\text{CH}_2)_4\text{Si}\{\text{N}(\text{tBu})\text{AlCl}_2\}_2$ and $(\text{CH}_2)_5\text{Si}\{\text{N}(\text{tBu})\text{AlMe}_2\}_2$ form cage structures in which the equivalent aluminum centers form a symmetric bridge between the amide nitrogen atoms (isomer **A**).^[15] $\text{Me}_2\text{Si}\{\text{N}(\text{tBu})\text{AlPh}_2\}_2$ forms a bicyclic structure consisting of two edge-sharing four-membered rings (isomer **B**).^[16] As solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **6** showed only one set of signals, which were also slightly broadened for the AlCH_2 group indicating a fluxional behavior, the crystal structure of **7** was determined (Figure 2). Compound **6** crystallizes as isomer **B** featuring a bridging ethyl group. The SiN_2Al ring is essentially planar, whereas the NAl_2C ring is puckered. The angle between the ring planes is 118° . Both aluminum centers are four-coordinate with a distorted tetrahedral environment. $\text{Al}(1)$ is connected to two amide nitrogen atoms, one terminal ethyl and one bridging ethyl



Scheme 1.

group, where as Al(2) is connected to one amide nitrogen, two terminal ethyl and one bridging ethyl group. The Al–C distances with average values of 1.966 and 2.166 Å fall in the range observed for terminal and bridging Al–C groups^[12] and are slightly shorter than the values reported for $\text{Me}_2\text{Si}\{\text{N}(\text{tBu})\text{AlPh}_2\}_2$ with average values of 2.019 and 2.176 Å.^[16] The Al–N distances vary with the coordination number of the nitrogen center: The Al(1)–N(1) distance involving a distorted trigonal planar nitrogen [$\Sigma(\text{angles}) = 359.5^\circ$] is 1.833(3) Å and the Al(1)–N(2) and Al(2)–N(2) distances average 1.987 Å.

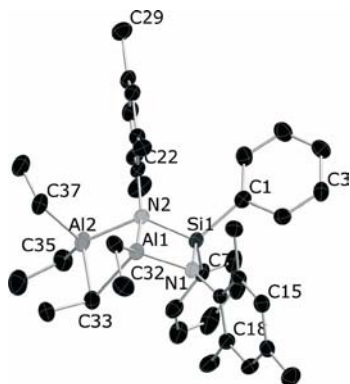


Figure 2. Structure of **6** (50% ellipsoids). H atoms are omitted for clarity. Important bond lengths [Å] and angles [°]: Al(1)–C(31) 1.955(4), Al(1)–C(33) 2.140(4), Al(1)–N(1) 1.833(3), Al(1)–N(2) 1.994(3), Al(2)–C(33) 2.192(4), Al(2)–C(35) 1.980(5), Al(2)–C(37) 1.964(4), Al(2)–N(2) 1.980(3), Si(1)–N(1) 1.714(3), Si(1)–N(2) 1.818(3), N(1)–Al(1)–N(2) 83.95(12), C(31)–Al(1)–C(33) 101.90(15), C(31)–Al(1)–N(2) 139.16(14), N(1)–Al(1)–C(31) 124.00(15), C(37)–Al(2)–C(35) 113.8(3), N(2)–Al(2)–C(33) 95.03(13), Al(2)–N(2)–Al(1) 82.93(11), Si(1)–N(2)–Al(1) 87.26(12), C(13)–N(1)–Si(1) 138.3(2), C(13)–N(1)–Al(1) 125.4(2), Si(1)–N(1)–Al(1) 95.82(14), N(1)–Si(1)–N(2) 92.97(13), Al(1)–C(33)–Al(2) 74.81(12).

On one occasion, a colorless crystalline compound was obtained from the reaction of $i\text{Bu}_2\text{AlH}$ with $\text{MesN}(\text{H})\text{SiMe}_3$. Its crystalline nature, its NMR spectra and the IR absorption at 1754 cm^{-1} clearly showed that it was not the expected compound **4**, and its structure was determined by single-crystal X-ray crystallography (Figure 3) as the unusual cyclic species $\{\text{MesN}(\text{SiMe}_3)\text{Al}(i\text{Bu})(\mu\text{-H})\}_2(\mu\text{-LiH})(\mu\text{-}i\text{Bu}_2\text{AlH})$, **7**. Two $\text{MesN}(\text{SiMe}_3)\text{Al}(i\text{Bu})$ moieties are connected via hydrogen bridges through a $\mu\text{-H-Li-H}$ and a $\mu\text{-H-Al}(i\text{Bu})_2\text{-H}$ unit to form an eight-membered $\text{Al}_3\text{-LiH}_4$ ring. While the formation of $\text{Al}_2\text{Li}_2\text{H}_4$ rings is common for many substituted lithium alanates including $\{\text{TriphAl}(\text{H})(\mu\text{-H})(\mu\text{-LiH})(\text{OEt}_2)_{1.5}\}_2$ (Triph = 2,4,6- $\text{Ph}_3\text{C}_6\text{H}_2$),^[17] $\{(\text{Me}_3\text{Si})_3\text{CAl}(i\text{Bu})(\mu\text{-H})(\mu\text{-LiH})(\text{THF})\}_2$,^[18] and $\{(\text{Me}_3\text{Si})_2\text{CH}(\text{Dipp})\text{NAl}(\text{H})(\mu\text{-H})(\mu\text{-LiH})(\text{THF})\}_2$,^[19] the Al_3LiH_4 ring observed here appears to be the first of its kind. In addition, compound **7** seems to be the only compound of this type in which the lithium cation is not solvated by ethers or amines, but by the π -electron density of two aromatic rings in an η^6 -fashion. The Al–C and Al–N distances average 1.956 and 1.848 Å fall within the normal range for four-coordinate aluminum centers. The Al–H distances are shorter than the Li–H distances [2.08 Å (avg.)]

but they differ significantly from one another. The dialkyl-substituted Al(1C) features two short Al–H bonds with values of 1.46(9) and 1.56(9) Å, whereas each of the amide-substituted Al(1A) and Al(1B) show a short and a long Al–H bond. The short Al–H bonds [Al(1A)–H(1AA) 1.35(9) Å, Al(1B)–H(1BB) 1.44(8) Å] involve the Al–H–Li bridges, and the long Al–H bonds [Al(1A)–H(1AC) 1.87(8) Å, Al(1B)–H(1BC) 1.87(9) Å] involve the Al–H–Al bridges. The Li \cdots C contacts are unsymmetrical and vary from 2.581 to 2.896 Å for the C1A ring and from 2.506 to 2.877 Å for the C1B ring. The nitrogen centers are in a trigonal planar environment [$\Sigma(\text{angles}) = 359.5^\circ$], which is typical for amines with two or more electropositive substituents. The Li–H bond lengths in **7** are almost 0.3 Å longer than those observed for the alanates listed above. This is probably a due to the Li \cdots arene coordination and the constraints resulting from this.

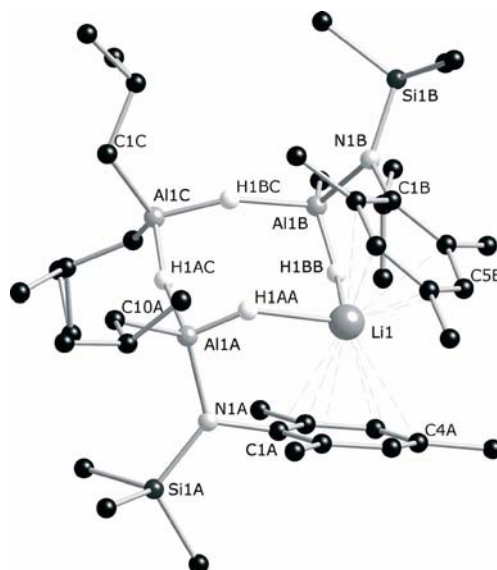


Figure 3. Structure of **7**. Due to disorder problems the ball and stick plot is shown here. H atoms except of those bound to Al and Li are omitted for clarity. Important bond lengths [Å] and angles [°]: Al(1A)–C(10A) 1.958(8), Al(1A)–N(1A) 1.834(6), Al(1A)–H(1AA) 1.35(9), Al(1A)–H(1AC) 1.87(8), Al(1B)–C(10B) 1.974(9), Al(1B)–N(1B) 1.859(7), Al(1B)–H(1BB) 1.44(8), Al(1B)–H(1BC) 1.87(9), Al(1C)–C(1C) 1.967(13), Al(1C)–C(5C) 1.924(12), Al(1C)–H(1AC) 1.46(9), Al(1C)–H(1BC) 1.56(9), Li(1)–H(1AA) 2.11(9), Li(1)–H(1BB) 2.06(9), Li(1) \cdots C(1A–6A) 2.581–2.896, Li(1) \cdots C(1B–6B) 2.506–2.877, N(1A)–Al(1A)–C(10A) 120.2(3), H(1AA)–Al(1A)–H(1AC) 100(5), N(1B)–Al(1B)–C(10B) 118.6(3), H(1BB)–Al(1B)–H(1BC) 103(4), C(5C)–Al(1C)–C(1C) 127.7(6), H(1AC)–Al(1C)–H(1BC) 90(5), H(1AA)–Li(1)–H(1BB) 100(3).

Due to its approximate C_2 symmetry, its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are relatively easy to interpret and also indicate that the cyclic structure is maintained in solution. It is currently not clear how compound **7** formed, but an old batch of $n\text{BuLi}$ that was used to prepare the precursor $\text{MesN}(\text{H})\text{SiMe}_3$ may be to blame. It is known that $n\text{BuLi}$ solutions slowly decompose via β -hydrogen elimination to give LiH and butene.^[2] This LiH can remain soluble by incorporation into various $n\text{BuLi}$ clusters^[20] and may have

been carried over into the reaction with *i*Bu₂AlH. The ¹H NMR spectrum of the precursor did not show any impurities, however.

Summary

Monomeric aluminum amides featuring three-coordinate Al and N centers can be obtained in simple procedures from readily available starting materials. Compounds **1–4** were prepared via ethane or hydrogen elimination reactions, where as compounds **5** and **6** were obtained using salt elimination metathesis. The crystalline species **5** is a rare example in which the planes at Al and N are almost coplanar. The dinuclear compound **6** adopts a ladder structure with an Al–Et–Al bridge, and the unusual compound **7**, which possesses an eight-membered Al₃LiH₄ ring core, was isolated in one instance probably due to impurities in one of the starting materials. Conversions of compounds **1–5** into the corresponding cationic species [R₂AlN(Ar)SiR'₃]⁺ are currently underway and will be reported in a future contribution.

Experimental Section

General Procedures: All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres dry box unless otherwise noted. Dry, oxygen-free solvents were used unless otherwise indicated. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ¹H NMR chemical shift values were determined relative to the residual protons in C₆D₆ as internal reference (δ = 7.16 ppm), and ¹³C NMR spectra were referenced to the solvent signal (δ = 128.39 ppm). ²⁹Si NMR spectra were referenced to external Me₄Si in C₆D₆. FTIR spectra were recorded using a Nicolet Magna 550 FTIR spectrometer equipped with ATR in the range of 4000–530 cm^{–1}. Melting points were determined in Pyrex capillary tubes sealed under nitrogen with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Columbia Analytical Services in Tucson, AZ. DippN(H)SiMe₃,^[21] MesN(H)SiMe₃,^[22] and Ph₂Si{N(H)Mes}₂,^[23] were prepared using modified literature procedures. The new aluminum amides **1–4** were synthesized according to a general method.^[8]

Melting Point Depression Experiment: 0.17 g of **1** was dissolved in benzene (5.0 g). The freezing point of the mixture was measured by slowly cooling the mixture, and the temperature was recorded once every 15 s. This procedure was repeated three times. Calculated molality 0.102 mol/Kg (molecular weight 333.57 g/mol); experimental molality 0.103 mol/Kg (molecular weight 330 g/mol).

Et₂AlN(Dipp)SiMe₃ (1): The synthesis of compounds **1–4** is illustrated by the procedure for **1**, which is described here. A solution of DippN(H)SiMe₃ (2.0 g, 8.0 mmol) in hexanes (50 mL) was treated with Et₃Al (0.98 g, 8.6 mmol) in hexanes (20 mL) at 0 °C under nitrogen. The reaction mixture was stirred for 1 h at room temperature and refluxed for an hour to ensure the completion of the reaction. The solvent and volatile side products were removed under reduced pressure to afford a light yellow oil; yield 2.6 g, 97%. ¹H NMR (C₆D₆, 400.13 MHz): δ = 0.15 (q, 4 H, *J* = 8.2 Hz, AlCH₂), 0.17 (s, 9 H, SiMe₃), 1.03 (t, 6 H, *J* = 8.2 Hz, AlCH₂CH₃), 1.14 [d, 6 H, *J* = 6.9 Hz, CH(CH₃)₂], 1.23 [d, 6 H, *J* = 6.9 Hz,

CH(CH₃)₂], 3.51 [sept, 2 H, CH(CH₃)₂], 7.05 (s, 3 H, aromatic). ¹³C{¹H} NMR (C₆D₆, 100.62 MHz): δ = 1.9 (s, broad, AlCH₂), 3.1 (SiMe₃), 8.7 (AlCH₂CH₃), 24.5 [CH(CH₃)₂], 24.9 [CH(CH₃)₂], 28.8 [CH(CH₃)₂], 123.9 (*m*-C), 124.3 (*p*-C), 144.6 (*i*-C), 145.1 (*o*-C). ²⁹Si NMR (C₆D₆, 79.49 MHz): δ = 3.88 ppm. C₁₉H₃₆AlNSi (333.56): calcd. C 68.41, H 10.88; found C 67.41, H 10.65.

***i*Bu₂AlN(Dipp)SiMe₃ (2):** A solution of DippN(H)SiMe₃ (2.7 g, 10.8 mmol) in hexanes (50 mL) was treated with 6.8 g of 25%/wt hexanes solution of diisobutylaluminum hydride (DIBAL) (12 mmol, 1.7 g) to afford a colorless viscous oil; yield 4 g, 95% based on DippN(H)SiMe₃. ¹H NMR (C₆D₆, 400.13 MHz): δ = 0.22 (s, 9 H, SiMe₃), 0.34 [d, *J* = 7.6 Hz, 4 H, CH₂CH(CH₃)₂], 1.00 [d, 12 H, *J* = 6.6 Hz, CH₂CH(CH₃)₂], 1.22 [d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂], 1.24 [d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂], 1.97 [sept, 2 H, *J* = 6.7 Hz, CH₂CH(CH₃)₂], 3.55 [sept, 2 H, *J* = 6.9 Hz, CH(CH₃)₂], 7.05 (m, 3 H, aromatic). ¹³C{¹H} NMR (C₆D₆): δ = 3.5 (SiMe₃), 23.9 [CH₂CH(CH₃)₂], 24.9 [CH(CH₃)₂], 25.1 [CH(CH₃)₂], 26.3 [CH₂CH(CH₃)₂], 28.7 [CH(CH₃)₂], 28.8 [CH₂CH(CH₃)₂], 124.0 (*m*-C), 124.4 (*p*-C), 144.8 (*i*-C), 145.1 (*o*-C). ²⁹Si NMR (C₆D₆, 79.49 MHz): δ = 3.91 ppm.

Et₂AlN(Mes)SiMe₃ (3): A solution of MesN(H)SiMe₃ (10 mmol, 2.07 g) in hexanes (50 mL) was treated with AlEt₃ (10 mmol, 1.14 g) to obtain **3** as a light yellow oil; yield 2.5 g, 86%. ¹H NMR (C₆D₆, 400.13 MHz): δ = 0.09 (q, *J* = 8.2 Hz, 4 H, Al-CH₂CH₃), 0.13 (s, 9 H, SiMe₃), 0.98 (t, *J* = 8.2 Hz, 6 H, Al-CH₂CH₃), 2.15 [s, 6 H, *o*-Me(Mes)], 2.16 [s, 3 H, *p*-Me(Mes)], 6.83 [s, 2 H, *m*-H(Mes)], ¹³C{¹H} NMR (C₆D₆, 100.62 MHz): δ = 1.81 (Al-CH₂CH₃), 3.18 (SiMe₃), 8.72 (Al-CH₂CH₃), 21.21 [*o*-Me(Mes)], 21.19 [*p*-Me(Mes)], 129.65 (*m*-C), 131.9 (*p*-C), 134.5 (*o*-C), 145.3 (*i*-C). ²⁹Si NMR (C₆D₆, 79.49 MHz): δ = 3.72 ppm. C₁₆H₃₀AlNSi (291.48): calcd. C 65.93, H 10.37; found C 64.37, H 10.05.

***i*Bu₂AlN(Mes)SiMe₃ (4):** A solution of MesN(H)SiMe₃ (10.0 mmol, 2.07 g) in hexanes (50 mL) was treated with 5.92 g of 25%/wt hexanes solution of DIBAL (10.4 mmol, 1.48 g) to obtain **4** as colorless viscous oil of ca. 90% purity; yield 2.6 g, 75% based on amine. ¹H NMR (C₆D₆, 400.13 MHz): δ = 0.18 (s, 9 H, SiMe₃), 0.29 [d, *J* = 7.4 Hz, 4 H, CH₂CH(CH₃)₂], 0.96 [d, 12 H, *J* = 6.5 Hz, CH₂CH(CH₃)₂], 1.85 [m, 2 H, CH₂CH(CH₃)₂], 2.15 [s, 3 H, *p*-Me(Mes)], 2.21 [s, 6 H, *o*-Me(Mes)], 6.85 [s, 2 H, *m*-H(Mes)]. ¹³C{¹H} NMR (C₆D₆, 100.62 MHz): δ = 3.5 (SiMe₃), 21.2 [*p*-Me(Mes)], 21.3 [*o*-Me(Mes)], 23.8 [CH₂CH(CH₃)₂], 26.3 [CH₂CH(CH₃)₂], 28.9 [CH₂CH(CH₃)₂], 129.7 (*m*-C), 132.0 (*p*-C), 134.5 (*o*-C), 145.6 (*i*-C). ²⁹Si NMR (C₆D₆, 79.49 MHz): δ = 3.87 ppm.

MesN(H)SiPh₃: A solution of MesNH₂ (20 mmol, 2.7 g) in benzene (50 mL) was treated with a 1.6 M solution of *n*BuLi in hexanes (22 mmol, 13.75 mL, 10% excess) at 0 °C. The resulting slurry was stirred for 30 min at room temperature followed by addition of triphenylsilyl chloride (20 mmol, 5.89 g) to the reaction mixture. The resulting mixture was heated at 80 °C for 15 h and then cooled to room temperature and filtered through a celite bed to remove the LiCl salt. The solvent was removed under reduced pressure to afford 7.63 g (97% crude yield) of a pale white solid and used as such without further purification. ¹H NMR (C₆D₆, 400.13 MHz): δ = 2.09 [s, 6 H, *o*-Me(Mes)], 2.15 [s, 3 H, *p*-Me(Mes)], 3.05 (br. s, w_{1/2} = 6 Hz, 1 H, NH), 6.72 [s, 2 H, *m*-H(Mes)], 7.18 (m, 9 H, Ph), 7.71 (m, 6 H, Ph). ¹³C{¹H} NMR (C₆D₆, 100.62 MHz): δ = 20.6 [*o*-Me(Mes)], 20.7 [*p*-Me(Mes)], 128.1 [*p*-C(Ph)], 129.7 [*m*-C(Mes)], 129.9 [*m*-C(Ph)], 131.3 [*p*-C(Mes)], 132.0 [*o*-C(Mes)], 135.9 [*o*-C(Ph)], 136.5 [*i*-C(Ph)], 140.1 [*i*-C(Mes)].

Et₂AlN(Mes)SiPh₃ (5): A 1.6 M solution of *n*-butyllithium in hexanes (14 mmol, 8.75 mL) was added dropwise to a slurry of

MesN(H)SiPh₃ (13.7 mmol, 5.39 g) in hexanes (50 mL) at 0 °C. The reaction mixture was stirred for 2 h. The solvent and volatile side products were removed in vacuo. Hexanes (50 mL) was added to the dry solid followed by addition of AlEt₂Cl (13.7 mmol, 1.65 g) at 0 °C. The reaction mixture was stirred overnight at 50 °C. The light yellow clear solution was separated from the LiCl by cannula and concentrated under reduced pressure to obtain a yellow viscous oil. The viscous oil was dissolved in hexanes (ca. 10 mL) and allowed to crystallize at room temperature for two days. Colorless blocks were obtained which were used for X-ray diffraction; yield 1.2 g, 18.3%; m.p. 92–95 °C. ¹H NMR (400.13 MHz, C₆D₆): δ = 0.06 (q, *J* = 8.2 Hz, 4 H, AlCH₂CH₃), 0.96 (t, *J* = 8.2 Hz, 6 H, Al-CH₂CH₃), 2.13 (s, 6 H, *o*-Me), 2.17 (s, 3 H, *p*-Me), 6.75 [s, 2 H, *m*-H(Mes)], 7.17 (m, 9 H, Ph), 7.62 (m, 6 H, Ph). ¹³C{¹H} NMR (100.62 MHz, C₆D₆): δ = 2.73 (AlCH₂CH₃), 8.79 (AlCH₂CH₃), 21.19 (*p*-Me), 21.97 (*o*-Me), 128.60 (*p*-Ph), 130.15 (*m*-Mes), 130.27 (*m*-Ph), 132.78 (*p*-Mes), 135.88 (*o*-Mes), 136.63 (*o*-Ph), 138.19 (*i*-Ph), 143.41 (*i*-Mes). C₃₁H₃₆AlNSi (477.69): calcd. C 77.94, H 7.60; found C 77.7, H 7.0.

Ph₂Si{N(Mes)AlEt₂}₂ (6): A 1.6 M solution of *n*BuLi in hexanes (20.0 mmol, 12.5 mL) was added dropwise to a slurry of Ph₂Si{N(H)Mes}₂ (9.9 mmol, 4.50 g) in hexanes (50 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent and volatile side products were removed in vacuo. Hexanes (50 mL) was added to the dry solid followed by addition of AlEt₂Cl (2.41 g, 20.0 mmol) at 0 °C. The reaction mixture was allowed to stir overnight at room temperature. The product precipitated as a white solid, and at this point all volatile side products were removed, and the remaining dry solid was dissolved in dichloromethane (50 mL). Lithium chloride was filtered off, and the colorless filtrate was concentrated to 20 mL and kept in a

freezer to obtain a light yellow crystalline solid; m.p. 162–164 °C; yield 2.0 g, 32%. ¹H NMR (400.13 MHz, C₆D₆): δ = 0.74 (br. s, *w*_{1/2} = 40 Hz, 4 H, Al-CH₂CH₃), 1.08 (t, *J* = 7.7 Hz, 6 H, Al-CH₂CH₃), 2.08 (s, 12 H, *o*-Me), 2.30 (s, 6 H, *p*-Me), 6.69 [s, 4 H, *m*-H(Mes)]; 6.9–7.02 (m, 6 H, Ph), 7.35 (br. s, 4 H, Ph). ¹³C{¹H} NMR (100.62 MHz, C₆D₆): δ = 5.8 (br., Al-CH₂CH₃), 9.5 (Al-CH₂CH₃), 20.9 [*p*-Me(Mes)], 22.7 [br., *o*-Me(Mes)], 127.7 [*m*-C(Ph)], 130.2 [*p*-C(Ph)], 130.8 [*o*-C(Mes)], 134.3 [*o*-C(Mes)], 136.3 [*o*-C(Mes)], 137.5, 141.9 [*i*-C(Mes)]. ²⁹Si NMR (C₆D₆, 79.49 MHz): δ = –24.4. C₃₈H₅₂Al₂N₂Si (618.88): calcd. C 73.75, H 8.47; found C 73.63, H 8.18.

{MesN(SiMe₃)Al(*i*Bu)(μ-H)}₂(μ-LiH)(μ-*i*BuAlH) (7): A solution of MesN(H)SiMe₃ (prepared from old *n*BuLi) (2.07 g, 10 mmol) in hexanes (30 mL) was treated with 6.5 g of 25 wt.-% hexanes solution of DIBAL (1.62 g, 11.4 mmol) at 0 °C under nitrogen. The reaction mixture was stirred for 1 h at room temperature and refluxed for an hour to ensure the completion of the reaction. The solvent and volatile side products were removed under reduced pressure and the resulting light yellow solution viscous oil was dissolved in a minimum amount of benzene (3–5 mL) for crystallization. A colorless crystalline solid was obtained after 1 d at room temperature; m.p. 254 °C; yield 600 mg, 8% based on amine. ¹H NMR (400.13 MHz, C₆D₆): δ = 0.19 (s, 18 H, SiMe₃), 0.56–0.60 [m, 8 H, CH₂CH(CH₃)₂], 1.23 [d, *J* = 6.5 Hz, 12 H, CH₂CH(CH₃)₂], 1.28 [d, *J* = 6.5 Hz, 12 H, CH₂CH(CH₃)₂], 1.99 [s, 6 H, *p*-Me(Mes)], 2.2 [br., 12 H, *o*-Me(Mes)], 2.1–2.2 (br., 2 H, Al-H or Li-H), 2.1–2.2 [br., 4 H, CH₂CH(CH₃)₂], 2.99–3.6 (br., 2 H, Al-H or Li-H), 6.59 [br., 4 H, *m*-H(Mes)]. ¹³C{¹H} NMR (100.62 MHz, C₆D₆): δ = 3.1 (SiMe₃), 20.9 [*o*-Me(Mes)], 21.0 [*p*-Me(Mes)], 21.8 [CH₂CH(CH₃)₂], 23.3 [CH₂CH(CH₃)₂], 27.0 [CH₂CH(CH₃)₂], 27.4 [CH₂CH(CH₃)₂], 28.6 [CH₂CH(CH₃)₂], 28.7 [CH₂CH(CH₃)₂],

Table 1. Crystal data and refinement details for compounds 5–7.

	5	6	7
Empirical formula	C ₃₁ H ₃₆ AlNSi	C ₃₈ H ₅₂ Al ₂ N ₂ Si	C ₄₀ H ₈₀ Al ₃ LiN ₂ Si ₂
Formula weight	477.68	618.87	733.12
<i>T</i> [K]	100(2)	100(2)	100(2)
Wavelength [Å]	1.54178	1.54178	1.54178
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄	<i>Cc</i>
<i>a</i> [Å]	14.9904(14)	11.190(4)	11.6332(8)
<i>b</i> [Å]	10.1017(10)	12.262(4)	33.555(2)
<i>c</i> [Å]	17.878(2)	15.112(5)	12.8301(12)
<i>α</i> [°]	90	69.298(14)	90
<i>β</i> [°]	95.538(8)	79.722(12)	104.585(9)
<i>γ</i> [°]	90	66.716(10)	90
<i>V</i> [Å ³]	2694.6(5)	1779.9(10)	4846.9(6)
<i>Z</i>	4	2	4
<i>D</i> _{calcd.} [Mg m ^{–3}]	1.177	1.155	1.005
<i>μ</i> (Cu- <i>K</i> _α) [mm ^{–1}]	1.213	1.259	1.370
<i>F</i> (000)	1024	668	1616
Crystal size [mm]	0.25 × 0.22 × 0.15	0.48 × 0.28 × 0.24	0.52 × 0.32 × 0.26
Crystal color and habit	colorless block	yellow block	colorless block
<i>θ</i> [°]	4.97–52.63	4.77–67.12	2.63–69.47
Reflections collected	13572	21264	17623
Independent reflections	3082 [<i>R</i> (int) = 0.0849]	5956 [<i>R</i> (int) = 0.0792]	4511 [<i>R</i> (int) = 0.0480]
Data/restraints/parameters	3082/0/312	5956/3/407	4511/12/406
<i>wR</i> ₂ (<i>F</i> ² all data) ^[a]	0.1310	0.1585	0.2451
<i>R</i> ₁ (<i>F</i> obsd. data) ^[a]	0.0533	0.0541	0.0876
Goodness-of-fit on <i>F</i> ²	1.000	1.003	1.026
Observed data [<i>I</i> > 2σ(<i>I</i>)]	1955	4090	4012
Absolute structure parameter			0.06(7)
Largest diff. peak and hole [e/Å ³]	0.185 and –0.258	0.271 and –0.435	0.972 and –0.711

[a] *wR*₂ = {*S* [*w*(*F*_o² – *F*_c²)/*S* [*w*(*F*_o²)]}^{1/2} *R*₁ = *S*||*F*_o| – |*F*_c||/*S*||*F*_o|.

131.3 (Mes), 149.9 (Mes). IR: $\nu(\text{Al-H})$ 1754 cm^{-1} (br). $\text{C}_{40}\text{H}_{80}\text{Al}_3\text{-LiN}_2\text{Si}_2$ (733.12): calcd. C 65.53, H 11.00; found C 65.13, H 10.70.

X-Ray Crystallography: Intensity data for compounds **5–7** were collected using a diffractometer with a Bruker APEX ccd area detector and graphite-monochromated Cu-K_α radiation ($\lambda = 1.54178 \text{ \AA}$) at 100(2) K. The data were corrected for absorption by the semi-empirical method.^[24] The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 .^[25] Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the displacement parameters of the bonded atoms. Hydrogen atoms bonded to the aluminum centers in **7** were located on a difference map, and their positions were allowed to refine independently. A single isotropic displacement parameter was refined for these hydrogen atoms. Some details of the data collections and refinements are given in Table 1, and selected bond lengths and angles are given in the Figure legends.

CCDC-788550 (for **5**), -788551 (for **6**), and -788552 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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