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Organoaluminum Silylamido Complexes

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The reaction between [Et_2AlCl] and 1 equiv of $HN(SiMe_3)_2$ in CH_2Cl_2 afforded colorless crystals of [$Et_2AlCl\{NH(SiMe_3)_2\}$] (**1**). In contrast, reaction of [Et_2AlCl] with 1 equiv of $HN(SiMe_2H)_2$ or $HN^tBu(SiMe_3)$ resulted in the isolation of dimers, of the type [$EtAlCl\{NH(R')\}$]$_2$ (**2**, R′ = $SiMe_2H$; **3**, R′ = ^tBu). Reaction of [Et_3Al] with 1 equiv of $HN(SiMe_2H)_2$ or $HN(SiMe_3)_2$ yielded the expected dimeric complexes, [$Et_2Al\{N(SiMe_2H)_2\}$]$_2$ (**4**) and [$Et_2Al\{N(SiMe_3)_2\}$]$_2$ (**5**), via ethane elimination. The related reaction between [$MeAlCl_2$] and $HN^tBu(SiMe_3)$ in CH_2Cl_2 solution resulted in the formation of the 1:1 adduct [$MeAlCl_2\{NH_2(^tBu)\}$] (**6**). The structures of compounds **1** and **6** have been determined by X-ray crystallography. In addition, the decomposition of **1** and **6** has been studied by thermal gravimetric analysis.

Introduction

The chemistry of alkylaluminum amido complexes, of the type [$R_2Al\{N(R')R''\}$]$_n$, has received significant attention in recent years due to the potential of these complexes to act as precursors to aluminum nitride (AlN).[1−3] AlN is a hard refractory material and may be used as protective coatings for high-temperature materials and as passive barrier layers.[4] The synthesis and structures of aluminum amido complexes have been highlighted in a number of reviews.[1,2,5−8]

Aluminum silylamido complexes are of interest as precursors for the synthesis of imidometal silicates.[9] These nitrogen analogues of oxidic metallosilicates are prepared via ammonolytic sol−gel chemistry, and from them metal nitridosilicates[10,11] can be formed. A range of organoaluminum silylamido complexes have been reported in the literature.[12−16] Complexes of the type [$R_2Al\{NH(SiR'_3)\}$]$_2$ (R = Me, R'_3 = Ph_3, Et_3; R = ^tBu, R'_3 = Ph_3, $^tBu_2H$) and [$Me_2Al\{N(SiR'_3)_2\}$]$_2$ (R'_3 = Me_2H, Me_3) have been prepared via the elimination of alkane from the reaction of primary or secondary silylamines with organoaluminum compounds.[12−14] Alternatively, metathesis routes have been employed; for example, reaction of [$Cl_2Al\{NH(SiMe_3)\}$]$_2$ with Me_2Mg resulted in the formation of [$Me_2Al\{NH(SiMe_3)\}$]$_2$.[12] The structures of some of the complexes have been reported, such as [$Me_2Al\{\mu\text{-}NH(SiEt_3)\}$]$_2$, [$Me_2Al\{\mu\text{-}NH(SiPh_3)\}$]$_2$, and [$MeAlCl\{\mu\text{-}NH(SiMe_3)\}$]$_2$, which showed that the Al_2N_2 frameworks are planar with the silyl groups oriented trans about this ring.[12,14]

Recently, we reported the synthesis and structural characterization of the aluminum silylamido complexes [$MeAlCl\{\mu\text{-}NH(SiMe_2H)\}$]$_2$, [$Me_2AlCl\{NH(SiMe_2Ph)_2\}$], and [$MeAlCl_2\{NH(SiMe_2Ph)_2\}$].[17] The formation of [$MeAlCl_2\{NH(SiMe_2Ph)_2\}$] from [$Me_2AlCl$] and $NH(SiMe_2Ph)_2$ involved the exchange of one of the methyl groups attached to the aluminum atom with a chlorine atom. These results, along with those obtained by us on some related gallium silylamido complexes,[18,19] indicated that the behavior of silylamines with group 13 species is interesting and can lead to unexpected products. We were interested in developing this chemistry further, and in this paper we describe the reactivity of silylamines with a range of organoaluminum complexes. Furthermore, dehalosilylation reactions (i.e. the elimination of Me_3SiX) have been employed in the synthesis of relatively pure samples of group 13 pnictides, such as GaAs and InAs at low temperatures.[20] Recently, this method was extended to dehydrosilylation reactions (involving the elimination of Me_3SiH) for the

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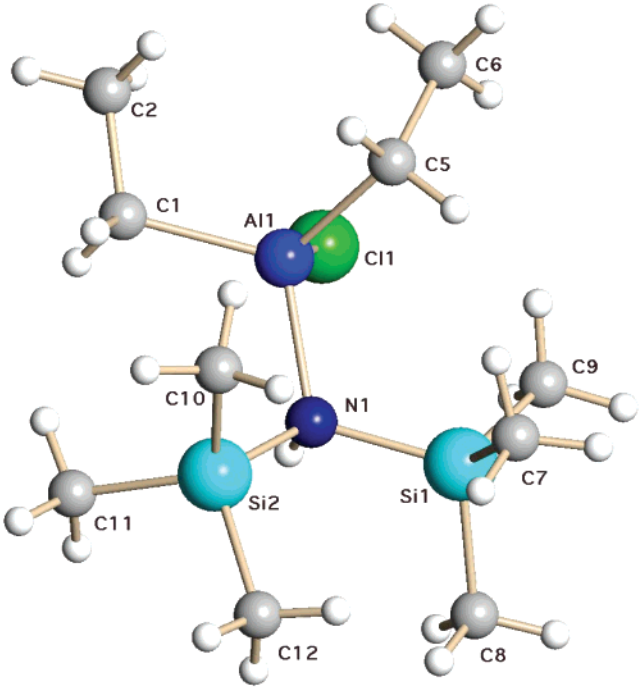
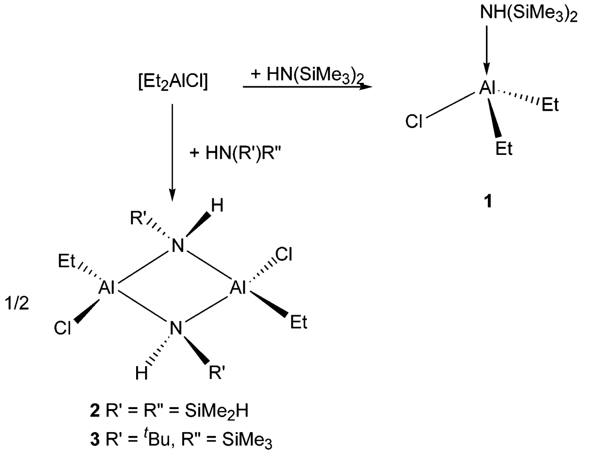


Figure 1. Molecular structure of **1**.

Scheme 1



preparation of GaP, GaAs, AlP, and AlAs nanoparticles.[21] Thus, we have also studied the decomposition of some of the complexes using thermogravimetric analysis (TGA).

Results and Discussion

Treatment of [Et$_2$AlCl] with 1 equiv of HN(SiMe$_3$)$_2$ in toluene at −78 °C, followed by refluxing for 2 h, resulted in the isolation of colorless crystalline **1** (Scheme 1). A single-crystal structure determination showed that these crystals consist of the 1:1 adduct [Et$_2$AlCl{NH(SiMe$_3$)$_2$}] (Figure 1). The central aluminum atom in **1** is bonded to two ethyl groups, one NH(SiMe$_3$)$_2$ ligand, and a chlorine atom (Al(1)−C(1) = 1.970(2) Å, Al(1)−C(5) = 1.993(2) Å, Al(1)−N(1) = 2.0144(18) Å, and Al(1)−Cl(1) = 2.2056(9) Å). The molecule contains a distorted-tetrahedral AlC$_2$NCl core with the angles subtended at the central Al varying from 102.80(6) to 115.49(10)° (Table 1). The geometry of the AlC$_2$NCl core of **1** reflects the larger steric bulk of the NH(SiMe$_3$)$_2$ and ethyl groups in comparison to Cl. The bond lengths and angles observed in **1** do not differ appreciably from those observed in related complexes, such as [Me$_2$AlCl{NH(SiMe$_2$Ph)$_2$}].[17] There are no notable intermolecular interactions.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Al(1)-C(1)	1.970(2)	Al(1)−C(5)	1.993(2)
Al(1)−N(1)	2.0144(18)	Al(1)−Cl(1)	2.2056(9)
C(1)−Al(1)−C(5)	115.49(10)	C(1)−Al(1)−N(1)	112.54(9)
C(5)−Al(1)−N(1)	110.75(8)	C(1)−Al(1)−Cl(1)	104.37(8)
C(5)−Al(1)−Cl(1)	109.89(7)	N(1)−Al(1)−Cl(1)	102.80(6)
Si(1)−N(1)−Al(1)	115.20(9)	Si(2)−N(1)−Al(1)	111.81(9)
Si(2)−N(1)−Si(1)	118.08(9)		

Analytical and spectroscopic data for **1** support the formation of the 1:1 adduct [Et$_2$AlCl{NH(SiMe$_3$)$_2$}]. Interestingly, a previous report describing the reaction between [Me$_2$AlCl] and excess HN(SiMe$_3$)$_2$ showed that initially the 1:1 adduct [Me$_2$AlCl{NH(SiMe$_3$)$_2$}] was formed.[14] After this adduct was heated to 50 °C, the amido complex [Me$_2$Al{NH(SiMe$_3$)}]$_2$ was isolated.[14] In contrast, compound **1** was formed by refluxing a mixture of [Et$_2$AlCl] and HN(SiMe$_3$)$_2$ in toluene (110 °C), suggesting that the adduct with [Et$_2$AlCl] is more stable. It is worth noting that the reaction of [Et$_2$AlCl] and HN(SiMe$_3$)$_2$ at room temperature (in CH$_2$Cl$_2$) resulted in the formation of a mixture of products (including **1** and [EtAlCl$_2${NH(SiMe$_3$)$_2$}]), which explains the low yield of **1** obtained in the reactions.

The reaction between [Et$_2$AlCl] and 1 equiv of HN(SiMe$_2$H)$_2$ or HN^{t}Bu(SiMe$_3$) in CH$_2$Cl$_2$ resulted, after workup, in the formation of colorless crystalline **2** and **3**, respectively (Scheme 1). Analytical and spectroscopic data for **2** and **3** were consistent with the formulation [EtAlCl{NH(R′)}]$_2$ (**2**, R′ = SiMe$_2$H; **3**, R′ = ^{t}Bu). Unfortunately, X-ray-quality crystals of **2** and **3** could not be obtained. However, the dimeric nature of **2** was confirmed by mass spectroscopy (see Experimental Section). It is assumed that both **2** and **3** would adopt dimeric structures similar to those of related complexes, such as the compound [MeAlCl{μ-NH(SiMe$_2$H)}]$_2$ that we previously reported.[17] The formation of **2**, **3**, and [MeAlCl{μ-NH(SiMe$_2$H)}]$_2$ from the reaction of [R$_2$AlCl] with silylamines was surprising, on the basis of previous reports.[14] Thus, treatment of [Me$_2$AlCl] with HN(SiMe$_3$)$_2$ was reported to yield [Me$_2$Al{μ-NH(SiMe$_3$)}]$_2$, via elimination of Me$_3$SiCl.[14] Therefore, we expected to form [R$_2$Al{NH(R′)}]$_2$ by elimination of R′$_3$SiCl, rather than [RAlCl{NH(R′)}]$_2$.[17] Attempts to monitor the reaction between [Et$_2$AlCl] and HN(SiMe$_2$H)$_2$ by ^{1}H NMR were complicated by the formation of geometric isomers, and a number of peaks were observed for each proton environment (Et−Al, Me−Si, H−Si, and N−H). However, mass spectroscopy indicated that these reactions proceed via the elimination of EtSiR′$_3$ to yield **2** and **3**. The NMR data for compound **2** indicated that in solution the trans,trans isomer is the major product with minor peaks present due to the cis,cis isomer. A similar trans−cis isomerization was reported for the dimeric silylamidoallanes described previously.[12,14]

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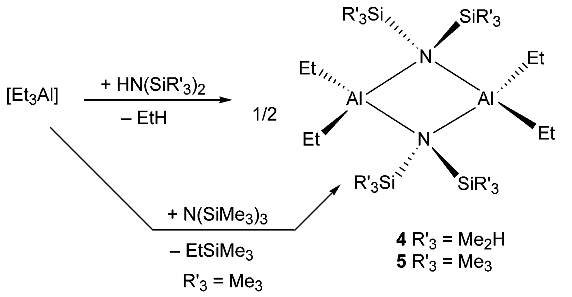
Scheme 2



Diethylaluminum silylamido complexes were isolated from the reactions of triethylaluminum with silylamines (Scheme 2). Thus, the 1:1 reaction of $[Et_3Al]$ with $HN(SiMe_2H)_2$ or $HN(SiMe_3)_2$ resulted in the formation of colorless crystals and an oil, respectively. Analytical and spectroscopic data were consistent with the formulation $[Et_2Al\{N(SiMe_2H)_2\}]_2$ (**4**).

The related reaction between $[Me_3Al]$ and $HN(SiMe_2H)_2$ has been previously shown to yield the dimeric species $[Me_2Al\{\mu\text{-}N(SiMe_2H)_2\}]_2$.[13] Unfortunately, we were unable to obtain an elemental analysis of the oil produced from the reaction between $[Et_3Al]$ and $HN(SiMe_3)_2$, due to decomposition. However, spectroscopic data indicated that $[Et_2Al\{N(SiMe_3)_2\}]_2$ (**5**) had formed rather than $[Et_2Al\{NH(SiMe_3)\}]_2$ (no NH peak was detected in the ^1H NMR or N–H stretch observed in the FT-IR of **5**). Furthermore, the reaction between $[Et_3Al]$ and $N(SiMe_3)_3$ in CH_2Cl_2 was also investigated, and a colorless oil was isolated. From this reaction only compound **5** was expected, the formation of which was confirmed by the $^1H/^{13}C$ NMR data obtained, which was very similar to that obtained from the product of the reaction between $[Et_3Al]$ and $HN(SiMe_3)_2$. Mass spectroscopy confirmed that the complexes were dimeric, as expected; however, it was not possible to isolate X-ray-quality crystals. It is also worth noting that peaks due to the 1:1 adduct $[Et_3Al\{NH(SiR_3)_2\}]$ were also present in the mass spectrum of **4** and **5**, suggesting that minor impurities are present.

The reaction of $[MeAlCl_2]$ and 1 equiv of $HN^tBu(SiMe_2)$ in toluene resulted, after workup, in the formation of colorless crystalline **6**. Analytical and spectroscopic data for **6** were consistent with the formulation $[MeAlCl_2\{NH_2(^tBu)\}]$. The monomeric nature of the adduct **6** was confirmed by an X-ray crystallographic study (Figure 2). Selected bond lengths and angles are given in Table 2.

The structure of **6** shows that the aluminum atom adopts a distorted-tetrahedral geometry. The Al–N bond distance of 1.9641(15) Å is shorter than the corresponding bond distance in **1** but longer than in the related complex $[AlCl_3\{NH_2(^tBu)\}]$ (Al–N = 1.939(2) Å).[22,23] There are no other packing interactions of note. The formation of compound **6** was surprising, as the expected product was either the 1:1 adduct $[MeAlCl_2\{NH(^tBu)(SiMe_3)\}]$ or the dimeric complex $[MeAlCl\{NH(^tBu)\}]_2$.[19] Interestingly, the related complex $[AlCl_3\{NH_2(^tBu)\}]$ was initially isolated from the hydrolysis of the silicenium ylide adduct $[AlCl_3\{N(^tBu)Si(^tBu)_2\}]$.[23] Thus, it is possible that **6** resulted from the hydrolysis of $[MeAlCl_2\{NH(^tBu)(SiMe_3)\}]$ with concomitant formation of $O(SiMe_3)_2$ (eq 1). However, compound **6** was the

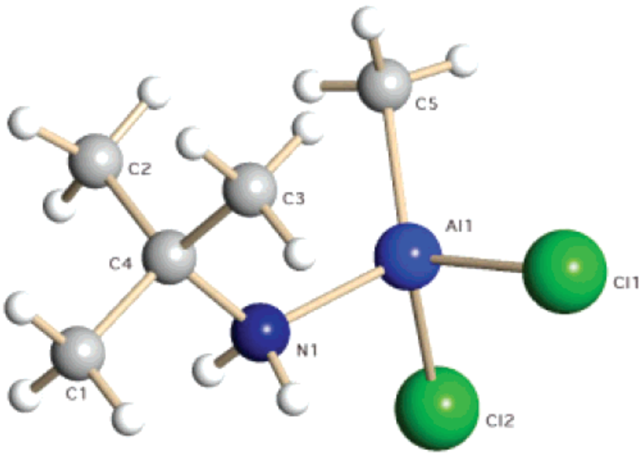


Figure 2. Molecular structure of **6**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

Al(1)–Cl(1)	2.1508(7)	Al(1)–C(5)	1.9408(19)
Al(1)–N(1)	1.9641(15)	Al(1)–Cl(2)	2.1650(7)
C(5)–Al(1)–N(1)	117.29(8)	C(5)–Al(1)–Cl(1)	114.59(7)
N(1)–Al(1)–Cl(1)	103.71(5)	C(5)–Al(1)–Cl(2)	114.44(7)
N(1)–Al(1)–Cl(2)	98.52(5)	Cl(1)–Al(1)–Cl(2)	106.44(3)
C(4)–N(1)–Al(1)	124.49(11)		

$$2[MeAlCl_2\{NH(^tBu)(SiMe_3)\}] + H_2O \rightarrow 2[MeAlCl_2\{NH_2{}^tBu\}] + O(SiMe_3)_2 \quad (1)$$

only product isolated from the reaction of $[MeAlCl_2]$ with 1 equiv of $HN^tBu(SiMe_3)$ on each occasion (reaction repeated three times, including using a new sample of $HN^tBu(SiMe_3)$ and thoroughly dried solvents). Therefore, it is possible that some other rearrangement is taking place, as observed in related reactions of organoaluminum complexes with silylamines.[17,23] Compound **6** can also be prepared via the direct reaction of $[MeAlCl_2]$ with H_2N^tBu.

Recently the 1:1 adduct $[AlCl_3\{NH_2(^tBu)\}]$ was successfully used as a precursor to AlN thin films, with little carbon contamination incorporated.[22] Therefore, to study the decomposition pathways of some of the complexes described herein, thermal gravimetric analyses (TGA) were carried out. TGA of **1** and **6** were studied at 10 °C/min from 20 to 500 °C, under N_2. The decomposition of **1** has an onset temperature of 45 °C and is completed at 460 °C. The TGA of **1** shows a total weight loss of 83%, in good agreement with the calculated value of 85% for the formation of AlN. Three distinct weight losses were observed at 45–170 °C (9%), 172–260 °C (39%), and 270–460 °C (35%). These weight losses correspond to the loss of ethane (calcd 10%), Me_3SiCl (calcd 38%) and $EtSiMe_3$ (37%), respectively, from $[Et_2AlCl\{NH(SiMe_3)_2\}]$ (**1**) to yield AlN. The TGA of **6** is clean and shows a weight loss of 85% with an onset temperature of 110 °C and completion at 260 °C. The calculated total weight loss to form AlN from **6** is 78%, which indicates that some of the weight loss is most likely due to sublimation rather than decomposition.

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Indeed, the related adduct $[\mathrm{AlCl_3\{NH_2(}{}^t\mathrm{Bu)\}}]$[22] was reported to have a high vapor pressure of ∼2.5 Torr at 65 °C, and therefore, **6** is expected to be volatile.

In summary, the aluminum silylamido complexes $[\mathrm{Et_2AlCl\{NH(SiMe_3)_2\}}]$ (**1**), $[\mathrm{EtAlCl\{NH(R)\}}]_2$ (**2**, R = $\mathrm{SiMe_2H}$; **3**, R = ^{t}Bu), $[\mathrm{Et_2Al\{N(SiMe_2H)_2\}}]_2$ (**4**), and $[\mathrm{Et_2Al\{N(SiMe_3)_2\}}]_2$ (**5**) have been synthesized and characterized. The 1:1 adduct $[\mathrm{MeAlCl_2\{NH_2(}{}^t\mathrm{Bu)\}}]$ (**6**) has been isolated from the reaction of $[\mathrm{MeAlCl_2}]$ with $\mathrm{HN}{}^t\mathrm{Bu(SiMe_3)}$. The structures of compounds **1** and **6** have been determined by X-ray crystallography. The formation of **6** shows that the behavior of $[\mathrm{MeAlCl_2}]$ and silylamines is interesting and unexpected products can be obtained. Furthermore, it is likely that these reactions are dependent on the reaction conditions (e.g. solvent and temperature) and a mixture of products are formed initially. The TGA obtained for **1** and **6** suggest that these complexes would be ideal precursors to AlN, and the deposition of films using **1** and **6** is currently being studied.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glovebox. All solvents were distilled from appropriate drying agents prior to use (sodium for toluene; $\mathrm{CaH_2}$ for $\mathrm{CH_2Cl_2}$). All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

Physical Measurements. NMR spectra were recorded on a Bruker AMX400 spectrometer at UCL, referenced to $\mathrm{CDCl_3}$ and $\mathrm{CD_2Cl_2}$, which were dried and degassed over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $\mathrm{SiMe_4}$ (δ 0.00). FT-IR spectra were obtained on a Shimadzu FTIR-8200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

Synthesis of 1. $\mathrm{HN(SiMe_3)_2}$ (1.70 mL, 7.97 mmol) was added dropwise to a solution of $[\mathrm{Et_2AlCl}]$ (1 mL, 7.97 mmol) in toluene (15 mL) at −78 °C. The reaction mixture was stirred and warmed slowly to room temperature and refluxed for 2 h. The resulting colorless solution was cooled to room temperature and reduced in vacuo to give a white crystalline solid. The solid was redissolved in $\mathrm{CH_2Cl_2}$ (3 mL) and cooled to −20 °C. X-ray-quality crystals of **1** were obtained after a few weeks at this temperature (0.30 g, 15% yield). Mp: 148−150 °C. Anal. Calcd for $\mathrm{C_{10}H_{29}NAlClSi_2}$: C, 42.60; H, 10.37; N, 4.97. Found: C, 42.69; H, 10.18; N, 4.38. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 0.05 (m, $\mathrm{AlC}H_2\mathrm{CH_3}$, $\mathrm{Si(C}H_3\mathrm{)_3}$), 1.02 (t, $\mathrm{AlCH_2C}H_3$), 2.70 (br, NH). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 1.1 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 2.5 ($\mathrm{Al}C\mathrm{H_2CH_3}$), 3.24 ($\mathrm{AlCH_2}C\mathrm{H_3}$). IR (KBr disk, cm^{-1}): 2908 s, 2869 vs, 1564 m, 1396 m, 1369 s, 1259 s, 1168 w, 1041 s, 982 m, 941 m, 794 m, 655 m. MS (CI): m/z 56 (EtAl), 73 ($\mathrm{SiMe_3}$), 173 ($\mathrm{Et_2AlNH(SiMe_3)}$), 180 ($\mathrm{Et(Cl)AlNH(SiMe_3)}$), 281 ($\mathrm{Et_2(Cl)AlNH(SiMe_3)_2}$).

Synthesis of 2. $\mathrm{HN(SiMe_2H)_2}$ (0.70 mL, 3.98 mmol) was added dropwise to a solution of $[\mathrm{Et_2AlCl}]$ (0.5 mL, 3.98 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL) at −78 °C. The reaction mixture was stirred and warmed slowly to room temperature. The resulting colorless solution was reduced in vacuo to give a colorless oil. The oil was cooled to −20 °C, resulting in the formation of colorless crystals after a few days (0.2 g, 15% yield). Mp: 125−128 °C. Anal. Calcd for $\mathrm{C_4H_{13}AlClNSi(CH_2Cl_2)_{0.5}}$: C, 25.97; H, 6.78; N, 6.73. Found: C, 25.0; H, 6.82; N, 7.21. ^{1}H NMR (δ/ppm; $\mathrm{CD_2Cl_2}$): δ 0.04 ($\mathrm{AlC}H_2\mathrm{CH_3}$), 1.02−1.18 (m, $\mathrm{AlCH_2C}H_3$), $\mathrm{Si}Me_2\mathrm{H}$), 3.93−4.20 (N$H$, $\mathrm{SiMe_2}H$). IR (KBr disk, cm^{-1}): 3311 s, 1564 s, 1261 s, 981 m, 792 m, 578 s. MS (CI): m/z 60 ($\mathrm{SiMe_2H}$), 74 ($\mathrm{HNSiMe_2H}$), 91 (EtAlCl), 120 ($\mathrm{Et_2AlCl}$), 223 ($\mathrm{Et(Cl)AlN(SiMe_2H)_2}$), 332 ($\mathrm{Et(Cl)AlNH(SiMe_2H))_2}$.

Synthesis of 3. $\mathrm{HN}{}^t\mathrm{Bu(SiMe_3)}$ (1.50 mL, 7.97 mmol) was added dropwise to a solution of $[\mathrm{Et_2AlCl}]$ (1 mL, 7.97 mmol) in toluene (15 mL) at −78 °C with stirring. The reaction mixture was stirred and warmed slowly to room temperature. The resulting colorless solution was reduced in vacuo to give a pale yellow oil. Cooling of this oil to −20 °C afforded colorless crystals after a few days (0.56 g, 44% yield). Anal. Calcd for $\mathrm{C_6H_{15}AlClN}$: C, 44.04; H, 9.24; N, 8.56. Found: C, 44.19; H, 9.89; N, 8.62. ^{1}H NMR ($\mathrm{CDCl_3}$): δ −0.07 (q, J = 8 Hz, 2H, $\mathrm{CH_3C}H_2\mathrm{Al}$), 1.04 (t, J = 5 Hz, 3H, $\mathrm{C}H_3\mathrm{CH_2Al}$), 1.37 (s, 9H, $\mathrm{NC(C}H_3\mathrm{)_3}$), 3.02 (br, 1H, N$H$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 2.6 ($\mathrm{AlC}H_2\mathrm{CH_3}$), 10.3 ($\mathrm{AlCH_2C}H_3$), 32.1 ($\mathrm{NC(}C\mathrm{H_3)_3}$), 69.6 ($\mathrm{N}C\mathrm{(CH_3)_3}$). MS (CI): m/z 58 (^{t}Bu), 74 ($\mathrm{H_2N}{}^t\mathrm{Bu}$), 86 ($\mathrm{AlEt_2}$), 91 (EtAlCl), 100 ($\mathrm{Et_2AlN}$), 130 ($\mathrm{Et(Cl)AlNC(CH_3)}$), 147 ($\mathrm{Et(Cl)AlNC(CH_3)_2}$), 157 ($\mathrm{Et_2AlNH}{}^t\mathrm{Bu}$), 327 ($\mathrm{Et(Cl)AlNH}{}^t\mathrm{Bu)_2}$. IR (KBr disk, cm^{-1}): 2942 vs, 2902 vs, 2942 vs, 2791 w, 2729 w, 1570 m, 1465 m, 1456 m, 1407 m, 1377 s, 1351 w, 1291 w, 1260 m, 1232 w, 1200 s, 1176 w, 1023 w, 990 s, 953 w, 928 w, 896 m, 848 s, 801 s, 764 w, 668 s, 629 s, 533 w, 455 w.

Synthesis of 4. A solution of $\mathrm{HN(SiMe_2H)_2}$ (3.1 mL, 17.5 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise to a solution of $[\mathrm{Et_3Al}]$ (2.4 mL, 17.5 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) at −78 °C with stirring. The evolution of a colorless gas was observed on addition of the amine. The mixture was stirred and warmed to room temperature. The solvent was removed in vacuo, resulting in a white crystalline solid. This solid was dissolved in a minimum amount of $\mathrm{CH_2Cl_2}$ (∼5 mL) and cooled to −20 °C, affording colorless plates (3.24 g, 85%). Mp: 106−107 °C. Anal. Calcd for $\mathrm{C_8H_{24}NSi_2Al}$: C, 44.19; H, 11.13; N, 6.44. Found: C, 45.17; H, 11.81; N, 6.09. ^{1}H NMR (δ/ppm; $\mathrm{CDCl_3}$): δ 0.25 (q, J = 24 Hz, 4H, $\mathrm{AlC}H_2\mathrm{CH_3}$), 0.38 (s, 12H, $\mathrm{Si(C}H_3\mathrm{)_2H}$), 1.08 (t, J = 17 Hz, 6H, $\mathrm{AlCH_2C}H_3$), 4.68 (s, 2H, $\mathrm{Si(CH_3)_2}H$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 3.8 ($\mathrm{Si(}C\mathrm{H_3)_2H}$, $\mathrm{Al}C\mathrm{H_2CH_3}$), 10.0 ($\mathrm{AlCH_2}C\mathrm{H_3}$). IR (KBr, cm^{-1}): 2750 w, 2180 vs, 1411 m, 1258 vs, 1235 w, 1197 m, 1100 w, 913 s br, 847 s br, 785 m, 682 m, 629 s, 552 s, 500 w, 415 m. MS (CI): m/z 74 ($\mathrm{HNSiMe_2H}$), 133 $\mathrm{HN(SiMe_2H)_2}$, 188 ($\mathrm{EtAlNSiMe_2H}$), 217 ($\mathrm{Et_2AlN(SiMe_2H)_2}$), 247 ($\mathrm{Et_3Al{\cdot}NH(SiMe_2H)_2}$), 346 ($\mathrm{Et_2AlN(SiMe_2H)_2)_2} - \mathrm{Me_2SiH}$.

Synthesis of 5. (a) $\mathrm{HN(SiMe_3)_2}$ (3.69 mL, 17.5 mmol) was added to a solution of $[\mathrm{Et_3Al}]$ (2.4 mL, 17.5 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) in a dropwise manner at room temperature. The mixture was stirred for 2 h, during which time a slight warming and the formation of a white vapor were observed. The solvent was removed under vacuum to give a colorless liquid (4.17 g). ^{1}H NMR δ/ppm ($\mathrm{CDCl_3}$): δ 0.13 (s, 18H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 0.31−0.34 (m, 4H $\mathrm{AlC}H_2\mathrm{CH_3}$), 1.07 (t, J = 17 Hz, 6H, $\mathrm{AlCH_2C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 0.3 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 5.0 (s, $\mathrm{Al}C\mathrm{H_2CH_3}$), 8.3 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$). IR (KBr, cm^{-1}): 2949 s, 2902 s, 2867 s, 1464 w, 1404 w, 1260 s, 1250 ws, 989 s, 893 s, 835 s, 755 w, 675 m, 645 m, 621 m, 552 m, 475 w. MS (CI): m/z 56 (EtAl), 73 ($\mathrm{SiMe_3}$), 143 ($\mathrm{EtAlNSiMe_3}$), 216 ($\mathrm{EtAlN(SiMe_3)_2}$), 245 ($\mathrm{Et_2AlN(SiMe_3)_2}$), 275 ($\mathrm{Et_3Al{\cdot}NH(SiMe_3)_2}$), 388 ($\mathrm{Et_2AlN(SiMe_3)_2)_2} - \mathrm{Me_3SiEt}$), 490 ($\mathrm{Et_2AlN(SiMe_3)_2)_2}$.

(b) A solution of $\mathrm{N(SiMe_3)_3}$ (2.04 g, 8.75 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added to a solution of $[\mathrm{Et_3Al}]$ (1.2 mL, 8.75 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL) in a dropwise manner. The mixture was stirred for 30 min at room temperature. The mixture was warmed slightly, and a white vapor was observed. The solvent was removed under vacuum, yielding a colorless liquid. ^{1}H NMR (δ/ppm; $\mathrm{CDCl_3}$): δ 0.20 (s, 18H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 0.33 (q, J = 23 Hz, 4H, $\mathrm{AlC}H_2\mathrm{CH_3}$), 1.10 (t, J = 14 Hz, 6H, $\mathrm{AlCH_2C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 0.3 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 5.5 (s, $\mathrm{Al}C\mathrm{H_2CH_3}$), 8.6 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$). IR (Nujol, cm^{-1}): 2944 s, 2902 s, 2865 s, 1460 w, 1409 w, 1253 s, 1261 s, 983 w, 918 vs, 846 s, 822 m, 765 m, 668 m, 620 m, 545 w, 473 w, 401 m.

Synthesis of 6. $\mathrm{HN}{}^t\mathrm{Bu(SiMe_3)}$ (1.20 mL, 6.46 mmol) was added dropwise to a solution of $[\mathrm{MeAlCl_2}]$ (1 mL, 6.46 mmol) in toluene (15 mL) at −78 °C with stirring. The reaction mixture was stirred and warmed slowly to room temperature.

The resulting pale yellow solution was reduced in vacuo to give a colorless crystalline solid. The solid was redissolved in toluene (5 mL) and cooled to −20 °C. X-ray-quality crystals of **6** were obtained after a few days at this temperature (0.522 g, 44% yield). Mp: 57−58 °C. Anal. Calcd for $C_5H_{14}AlCl_2N$: C, 32.28; H, 7.58; N, 7.53. Found: C, 30.53; H, 7.11; N, 7.41. Repeat: C, 32.23; H, 7.27; N, 7.44. ^{1}H NMR (δ/ppm; CD_2Cl_2): δ −0.45 (s, 3H, AlCH_3), 1.44 (s, 9H, NC(CH_3)$_3$), 3.47 (br, s, 2H, NH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 1.10 ($AlCH_3$), 30.4 (NC(CH$_3$)$_3$), 55.4 (NC(CH$_3$)$_3$). IR (KBr disk, cm^{-1}): 3300 s, 3205 s, 2941 s, 1564 m, 1475 s, 1407 s, 1379 m, 792 m, 574 s. MS (CI): *m*/*z* 57 (^{t}Bu), 74 (H_2N^tBu), 99 ($AlNH^tBu$), 150 (Me(Cl)$AlNH^tBu$), 187 ($MeAlCl_2 \cdot NH_2{}^tBu$), 447 (Me(Cl)$AlNH^tBu)_3$.

X-ray Crystallography. Crystal data for **1**: $C_{10}H_{29}AlClNSi_2$, $M_r = 281.95$, monoclinic, $P2_1/n$, $a = 8.852(2)$ Å, $b = 13.087(3)$ Å, $c = 14.642(4)$ Å, $\beta = 93.782(4)°$, $V = 1692.6(7)$ Å^3, $Z = 4$, $D_c = 1.106$ g cm^{-3}, μ(Mo Kα) = 0.397 mm^{-1}, $T = 150(2)$ K, colorless blocks; 4018 independent reflections (3409 with $|F_o| > 4\sigma(|F_o|)$), F^2 refinement, R1 = 0.0462, wR2 = 0.1086, 148 parameters. CCDC 238298.

Crystal data for **6**: $C_5H_{14}AlCl_2N$, $M_r = 186.05$, orthorhombic, $P2_12_12_1$, $a = 6.2541(5)$ Å, $b = 10.3327(6)$ Å, $c = 15.1307(9)$ Å, $V = 977.77(11)$ Å^3, $Z = 4$, $D_c = 1.264$ g cm^{-3}, μ(Mo Kα) = 0.684 mm^{-1}, $T = 150(2)$ K, colorless blocks; 2312 independent reflections (2210 with $|F_o| > 4\sigma(|F_o|)$), F^2 refinement, R1 = 0.0306, wR2 = 0.0737, 86 parameters. CCDC 238299.

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Supporting Information Available: Tables giving X-ray crystallographic data and additional figures for the structures of compounds **1** and **6**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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