A Synthetic and Theoretical Study of the Aggregation of Amidoaluminium Hydrides: Solid-State Structure of the Trimethylamine Adduct $[(Me_3Si)_2NAl(Cl)(H) \cdot NMe_3]$

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The amidoaluminium hydride complexes $[(Me_3Si)_2NAl(X)(H) \cdot NMe_3]$, X = H (**1**), Cl (**2**), were prepared by the metallation of bis(trimethylsilyl)amine by $Al(X)(H)_2 \cdot NMe_3$ (X = H and Cl). The molecular structure of **2** as a monomeric Lewis base adduct with four-coordinate aluminium centres and terminal amido groups was confirmed by X-ray crystal structure determination. We also find that bis(trimethylsilyl)amine forms a thermally stable adduct of alane, $(Me_3Si)_2N(H) \cdot AlH_3$ (**3**). Ab initio molecular orbital calculations on the possible products arising from these reactions yielding **1** and **2** revealed that the amido-bridged species, $\{(\mu\text{-}H_2N)Al(X)H\}_2$ (X = H and Cl), are favoured over nitrogen donor Lewis base adduct formation, $H_2NAl(X)(H) \cdot NH_3$ (X = H and Cl), and then chloro-bridged, $\{H_2NAl(\mu\text{-}X)(H)\}_2$, (X = Cl only), and hydrido-bridged species, $\{H_2NAl(X)(\mu\text{-}H)\}_2$ (X = H and Cl).

The structural types established for aluminium hydride complexes has escalated in recent years[1]. This is a result of a resurgence in interest of the chemistry of these compounds for use in the deposition of aluminium-containing films for microelectronic application[2] and as reagents in organic synthesis[3]. Aluminium hydride complexes with covalent aluminium-heteroatom bonds have been targeted as potential single-source precursors for the deposition of binary compounds of these elements[4], e.g. gallium arsinide. Early studies of amidoaluminium hydride complexes focused on small amido groups existing as oligomeric species bridged through the amido nitrogen atoms; larger substituents on the nitrogen atoms resulted in dimers rather than trimers, e.g. $[\{H_2Al(\mu\text{-}N\mathit{i}Pr_2)\}_2]$[5] and $[\{H_2Al(\mu\text{-}NMe_2)\}_3]$[6]. More recent accounts involving the bulky amido ligands $-N\{C(Me)_2CH_2\}_2CH_2$ and $-N\{C(Me)(H)CH_2\}_2CH_2$ have given rise to different structural types including hydride-bridged oligomers[7] and monomeric Lewis base adducts[8]. These findings have been rationalised as being in consequence of the steric hindrance of the amido groups blocking amido nitrogen bridging. Herein we have quantified the relative energetics of the bonding possibilities which amidoaluminium hydride species, H_2NAlH_2, can adopt by an ab initio molecular orbital study; this has been extended to include the chloro-substituted species $H_2NAl(Cl)H$. Included are the syntheses of two amidoaluminium hydride complexes of relevance to these calculations featuring the ubiquitous amido ligand $-N(SiMe_3)_2$ and the thermal stable secondary amine adduct of alane with the protonated amine.

Results and Discussion

The aluminium hydride derivatives prepared in this study are shown in the reaction scheme. The trimethylamine–aluminium hydride adducts $Al(X)(H)_2 \cdot NMe_3$ (X = H and Cl) react with bis(trimethylsilyl)amine in diethyl ether at 0 °C to afford the products $[(Me_3Si)_2NAl(X)(H) \cdot NMe_3]$, X = H (**1**), Cl (**2**) upon warming to room temperature. In contrast to this, bis(trimethylsilyl)amine is not metallated under similar conditions using AlH_3 (prepared in situ by the reaction of $Li[AlH_4]$ with HCl in diethyl ether). The analogous reactions to those presented in the reaction scheme involving 2,2,6,6-tetramethylpiperidine yield similar complexes to the present study, viz. $[CH_2\{CH_2C(Me)_2\}_2NAl(H)_2 \cdot NMe_3]$ and $[CH_2\{CH_2C(Me)_2\}_2N(H) \cdot AlH_3]$[8]. Compounds **1**–**3** are low-melting point solids for which crystals of single crystal X-ray diffraction quality could only be obtained for the chloro derivative **2**. Compounds **1** and **3** proved too air-sensitive for reliable, accurate microanalysis. Nevertheless, the chemical integrity of the compounds is established by spectroscopic data and given further credence by the structurally authenticated compounds **2**, $[CH_2\{CH_2C(Me)_2\}_2NAl(H)_2 \cdot NMe_3]$ and $[CH_2\{CH_2C(Me)_2\}_2N(H) \cdot AlH_3]$[8]. Compound **3** is exceptionally stable with respect to elimination of hydrogen to form an amido species, decomposing only above 100 °C to yield the secondary amine

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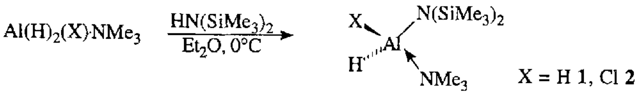
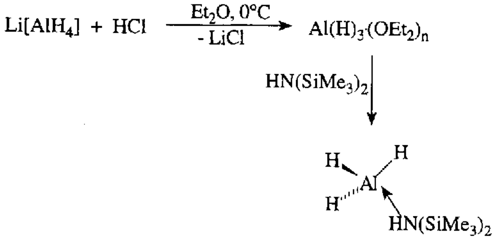
and aluminium metal, c.f., $[CH_2\{CH_2C(Me)_2\}_2N(H) \cdot AlH_3]$[8] and $[Me_2N(H) \cdot AlH_3]$[9] which decompose above 165 and −20 °C to yield aluminium metal and the aluminium amide species, respectively, as products. Clearly the steric hindrance around the amine in the cases of **3** and $[CH_2\{CH_2C(Me)_2\}_2N(H) \cdot AlH_3]$ stabilises the adduct with respect to hydrogen elimination and amide formation; the pathway for thermal decomposition instead being loss of the secondary amine followed by decomposition of AlH_3 at elevated temperatures to give aluminium metal. Compound **1** decomposes above 110 °C to yield aluminium metal without aluminium nitride formation. This decomposition pathway for **1** is in contrast to the use of arsinogallanes[4], for example, which contain direct group 13-group 15 covalent bonds as precursors for the preparation of group 13/15 compounds, but similar decomposition pathways have been noted for the related bulky phosphino-alane $[(2,4,6\text{-}C_6H_2)_2PAl(H)_2 \cdot NMe_3]$ which decomposes to aluminium metal hydrogen, and $(2,4,6\text{-}Me_3C_6H_2)_2PH$ above 125 °C[10].



X = H **1**, Cl **2**



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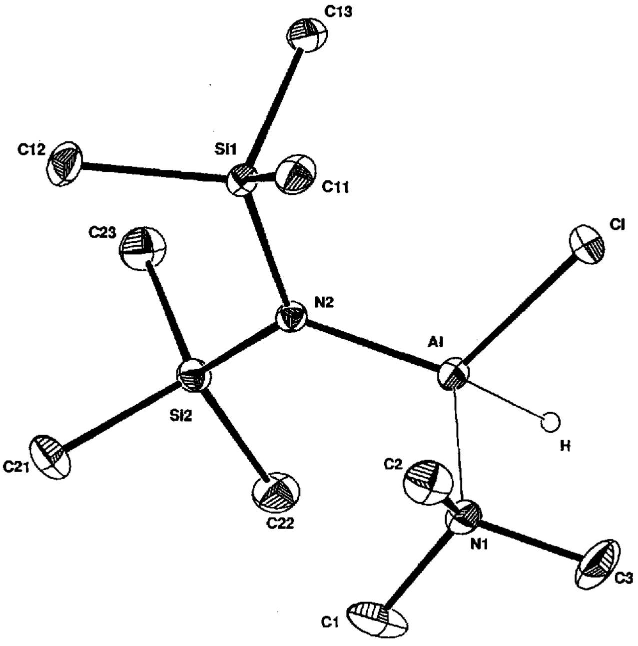
Compounds **1**−**3** were characterised by ^1H-, ^{13}C-NMR and IR spectroscopy, and for **1** and **3**, ^{27}Al NMR and solution molecular mass determinations. The compounds have characteristically strong, broad Al−H stretching frequencies of 1790, 1865, and 1800 cm^{-1}, for **1**−**3**, respectively. The Al−H stretching frequencies of **1** and **2** reflect the effect of the chloro substituent on the electronic saturation of the aluminium centre altering the force constant of the Al−H bond. Moreover, a comparison of the Al−H band for **1** and **3** with $Al(H)_3 \cdot NMe_3$ reflects the mutual influences of the usual shift to higher frequency caused by replacement of a hydrido substituent by an amido group and the replacement of trimethylamine by the weak Lewis base donor bis(trimethylsilyl)amine[11]. The ^1H- and ^{13}C-NMR data for **1**−**3** are largely unexceptional, the typical upfield shift is noted for the hydride resonance of the aminoalane **1**, $\delta = 3.59$, relative to the Lewis base adduct of the trihydride species **3**, $\delta = 4.30$. The resonance for the hydride atom of **2** could not be located owing to the broad nature of the aluminium hydride resonance, making the signal indistinguishable from the base line in this case. Solution molecular mass determinations for **1** and **3** yielded levels of association of 0.91 ± 0.07 and 1.84 ± 0.06, respectively, being diagnostic of the presence of monomeric and dimeric species present in solution. The presence of a dimer in solution for **3** is consistent with findings for 1:1 Lewis base adducts of AlH_3 with ethers[12] and our findings for tertiary amines of weak donor strength which are dimeric in the solid state[13]. In those examples the association was by way of hydride bridging and the concomitant formation of five-coordinate aluminium centres. The ^{27}Al-NMR spectra of **1** and **3** do not reflect any anticipated difference in the coordination number of the aluminium centres, both complexes have broad featureless resonances typical of aluminium nuclei in asymmetric four-coordinate environments[14], $\delta = 138$ ($w_{1/2} = 2700$ Hz) and 129 ($w_{1/2} = 2600$ Hz), respectively.

The molecular structure of **2** is shown in Figure 1. The complex crystallises in the acentric space group $P2_12_12_1$ (no. 19) with four chiral molecules in the unit cell, the asymmetric unit containing one molecule of **2**. An occupancy disorder was apparent which indicated a partial population of **2** and **1**. Refinement of the population parameter for the chlorine atom gave a population of 0.816(5); this model was confirmed by ^1H- and ^{13}C-NMR spectroscopy of crystalline samples of **2** which show the presence of **2** and **1** in a ca. 4:1 ratio.

Figure 1. Molecular structure of $[(Me_3Si)_2NAl(Cl)(H) \cdot NMe_3]$ **2** (thermal ellipsoids at 20% probability). Selected interatomic distances [Å] and angles [°]: Al−Cl 2.119(2), Al−N1 2.016(5), Al−N2 1.823(4), Al−H 1.62(5), N2−Si1 1.748(4), N2−Si2 1.731(4); Cl−Al−N1 101.0(2), Cl−Al−N2 115.8(1), Cl−Al−H 95(2), N1−Al−N2 111.1(2), N1−Al−H 102(2), N2−Al−H 128(2), Al−N2−Si1 120.4(2), Al−N2−Si2 119.7(2), Si1−N2−Si2 118.4(2)



The structure determination shows **2** to be monomeric in the solid state, the four-coordinate aluminium atom being in a distorted tetrahedral environment having a (amido)(Cl)(H)(amine) coordination environment which has also been authenticated in the intramolecularly coordinated aluminium amide complex $[\{HN(tBu)CH_2CH_2NtBu\}\text{-}Al(Cl)H]$[15]. The amido ligand is terminal, the electronic requirements of the aluminium centre being alternatively satisfied by coordination of a molecule of trimethylamine.

As such, the three-coordinate amido nitrogen atom is planar [Σ(Si−N−Al,Si) = 358.5°] and the Al−N distance, 1.823(4) Å, is in the lower range established for amidoaluminium complexes[16]. The Al−N(amine) distance, 2.016(5) Å, is typical, as is the Al−Cl distance of 2.119(2) Å for a terminally bound chlorine atom.

Table 1. Non-hydrogen and refined hydrogen atom coordinates and isotropic thermal parameters for **2**

Atom	x/a	y/b	z/c	U, Å^2	Population
Al	0.5365(2)	0.56461(9)	0.5372(1)	0.0311(4)[a]	
Cl	0.6417(2)	0.5444(1)	0.6966(1)	0.0443(6)[a]	0.816(5)
Si1	0.5865(2)	0.37654(8)	0.4859(1)	0.0288(4)[a]	
Si2	0.3519(2)	0.46930(9)	0.3599(1)	0.0311(4)[a]	
N1	0.6830(5)	0.6397(3)	0.4586(4)	0.037(1)[a]	
N2	0.5002(4)	0.4711(2)	0.4524(3)	0.026(1)[a]	
C1	0.6262(8)	0.6625(5)	0.3439(6)	0.070(3)[a]	
C2	0.8268(7)	0.6024(4)	0.4435(6)	0.054(2)[a]	
C3	0.6988(8)	0.7171(4)	0.5280(7)	0.069(3)[a]	
C11	0.7873(6)	0.3875(3)	0.5153(5)	0.044(2)[a]	
C12	0.5793(7)	0.2988(3)	0.3663(5)	0.045(2)[a]	
C13	0.4987(7)	0.3290(3)	0.6148(5)	0.045(2)[a]	
C21	0.4110(7)	0.4542(4)	0.2084(5)	0.053(2)[a]	
C22	0.2430(7)	0.5677(4)	0.3615(6)	0.052(2)[a]	
C23	0.2169(7)	0.3865(4)	0.3987(6)	0.052(2)[a]	
H	0.420(6)	0.632(3)	0.588(4)	0.04(2)	

[a] Isotropic equivalent thermal parameters.

Ab initio molecular orbital calculations were undertaken on model systems in order to establish the energetically favourable products from the 1:1 stoichiometric metallation of secondary amines by $Al(X)(H)_2 \cdot NMe_3$ (X = H and Cl). Computational requirements necessitated replacement of trimethylamine by ammonia and bis(trimethylsilyl)amine by NH_2. Unsolvated monomeric species and ammonia-solvated monomers were investigated as were various unsolvated dimeric aggregates of the species. The minima located for the $H_2NAl(Cl)H$ system are shown in Figure 2. The optimised structures for the H_2NAlH_2 system were analogous (with the obvious exclusion of the chloro-bridged species). Again, computational restrictions did not permit oligomers of higher order than dimers to be studied, but we note the experimental observation of such species in related systems[7,17,18]. All the structures were fully optimized within the indicated point group and were found to be true minima by frequency analysis. The dimeric species investigated were restricted to the centro-symmetric (*trans*) isomers; the analogous dimers of C_2 symmetry were not investigated, but should be of comparable energy. The total energies (RHF/D95*//RHF/D95*) and point group symmetries of the various computed structures are shown in Table 2. The association energies of the solvated and aggregated species (at the same level of theory) are also shown in Table 2 and include zero point energy corrections[19].

The calculations show that amido-bridged dimers are the energetically favourable products for the amidoaluminium species investigated to gain coordination saturation for the aluminium atoms. Some 5−8 kcal/mol higher in energy are the amine-solvated monomers[13,20]. Well above these structures chloro- and hydrido-bridged structures of comparable stability exist and are the least favourable species identified in this study. The neglect of trimeric species from these calculations will not affect the sign of the relative stabilities of the amido-bridged and Lewis base-solvated species, indeed

Figure 2. Computed geometries (HF/D95*) for, (**A**) $H_2NAl(Cl)H$, (**B**) $\{(\mu\text{-}H_2N)Al(Cl)H\}_2$, (**C**) $H_2NAl(Cl)(H) \cdot NH_3$, (**D**) $\{H_2NAl(Cl)(\mu\text{-}H)\}_2$, and (**E**) $\{H_2NAl(\mu\text{-}Cl)(H)\}_2$

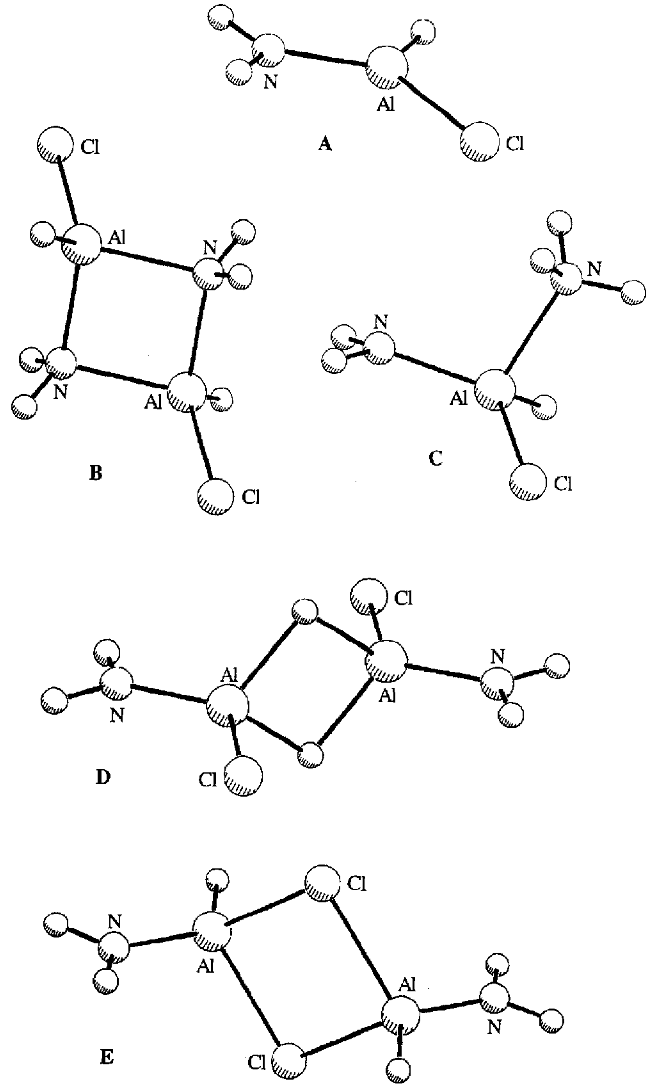


Table 2. Computed total energies (RHF/D95*//RHF/D95*), association energies of the solvates/dimers (per monomeric unit) and point group symmetries of the aluminium amide species. Total energy for NH_3 (C_{3v} symmetry) −56.199089 au, ZPE = 0.037080 au

Molecule	Point group	Total energy (au)	Zero point energy (au)	Association energy (kcal/mol)
H_2NAlH_2	C_{2v}	-298.711281	0.041326	-
$\{(\mu\text{-}H_2N)AlH_2\}_2$	D_{2h}	-597.512516	0.089436	-26.09
$H_2NAl(H)_2 \cdot NH_3$	C_s	-354.944655	0.083214	-18.50
$\{H_2NAl(\mu\text{-}H)(H)\}_2$	C_{2h}	-597.442547	0.086002	-5.22
$H_2NAl(Cl)H$	C_s	-757.693710	0.036451	-
$\{(\mu\text{-}H_2N)Al(Cl)H\}_2$	C_2	-1515.483658	0.078946	-28.30
$H_2NAl(Cl)(H) \cdot NH_3$	C_1	-813.934208	0.078234	-23.03
$\{H_2NAl(Cl)(\mu\text{-}H)\}_2$	C_{2h}	-1515.402239	0.075777	-3.75
$\{H_2NAl(\mu\text{-}Cl)(H)\}_2$	C_{2h}	-1515.408030	0.073207	-6.37

the effect can only be to increase the energetic separation of these two structural motifs if the amido-bridged trimers are more stable than dimers for the reasons of reduced steric strain (or other reasons). Consideration of higher oligomers for the chloro- and hydrido-bridged species may alter the relative energies of these two bridging modes, but it is unlikely that higher oligomers would be of comparable energy to amido-bridged or Lewis base-solvated species which in energy lie well below these bonding alternatives in this study.

In the context of experimentally observed findings in this paper and elsewhere these calculations are in complete agreement. In cases where the amido ligand is not very bulky amido-bridged oligomeric complexes have been isolated (e.g., $[\{H_2Al(\mu\text{-}NiPr_2)\}_2]$[5] $[\{H_2Al(\mu\text{-}NMe_2)\}_3]$[6], $[\{H_2Al[\mu\text{-}N\{C(Me)(H)CH_2\}_2CH_2]\}_2]$[7], and $[\{H_2Al[\mu\text{-}N(CH_2CH_2)_2S]\}_2]$[21]) even in the presence of tertiary amines as potential Lewis base donors. However, when the amido ligand is bulky and a tertiary amine has been present (from $Al(H)_3 \cdot NMe_3$ for example) the Lewis base-solvated monomer has been observed (e.g., $[CH_2\{CH_2C(Me)_2\}_2NAl(H)_2 \cdot NMe_3]$[8], **1** and **2**). Presumably the steric bulk of the amido substituents prevents it from acting as a bridging ligand in these cases (which is well noted for metal amide chemistry[22]) making Lewis base solvation the best alternative. Bulky amido substituents in the absence of potential Lewis bases have yielded hydride-bridged oligomers (e.g., $[\{CH_2\{CH_2C(Me)_2\}_2NAl(\mu\text{-}H)(H)\}_3]$). Unsolvated $H_2NAl(Cl)H$ analogues have not been reported but this study shows that either chloro- or hydrido-bridged oligomers are feasible if the amido ligand is large. The association energies of the chloro- and hydrido-bridged dimers in this study are small and comparable to crystal packing forces[23]. With certain suitably bulky amido ligands, unsolvated monomeric analogues of the species H_2NAlH_2 and $H_2NAl(Cl)H$ could be accessible.

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Experimental

NMR: Varian Gemini 200 at 200, 50.3, and 52.1 MHz (^1H, ^{13}C, and ^{27}Al, respectively, with TMS, TMS and 0.8 M $[Al(H_2O)_6]^{3+}$ as the standards). – X-ray structure analyses: Enraf-Nonius CAD4, Mo-K_α radiation, graphite monochromator, crystal dimensions 0.1 × 0.1 × 0.1 mm, 297 K, $2\Theta/\omega$ mode, $4 < 2\Theta < 50°$ $(+h, +k, +l)$, 3306 measured reflexions, 2663 independent reflexions, $I > 2.5\sigma(I)$, 2321 observed independent reflexions, $\mu = 5.55$ cm^{-1} (no absorption correction), structure solution by direct methods, full-matrix refinement, solution and refinement with XTAL 3.0[24], number of refined parameters 139, $R = 0.063$, $R_w = 0.079$. All non-hydrogen atoms were refined anisotropically. A population disorder was apparent in the refinement concerning partial hydride occupancy of the chloride position. This disorder was modelled by refining the population of the chlorine atom [0.816(5)], but no population was given to the hydride atom. The other hydride atom was located and refined in x, y, z and U_{iso}, all other hydrogen atoms were calculated and constrained at estimated positions (C–H = 1.0 Å) with temperature factors fixed at $1.5 \cdot U_{ii}$ (attached carbon atom). a = 9.114(2), b = 15.983(2), c = 11.685(3) Å, V = 1700.7(5) Å^3, orthorhombic, $P2_12_12_1$ (no. 19), Z = 4, $\rho_{calcd.}$ = 1.22 gcm^{-3}. Further details of the crystal structure refinement are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404958. – Molecular Orbital calculations: Gaussian 92/DFT Revision G.4[25] (D95* basis set). – CHClN analyses: Chemical and MicroAnalytical Services Pty. Ltd. – Molecular mass determinations: Signer Method[26]. – $Al(H)_3 \cdot NMe_3$[9] and AlH_3[27] were prepared by adapted literature procedures, $Al(Cl)(H)_2 \cdot NMe_3$ was prepared by the addition of $HgCl_2$ to $Al(H)_3 \cdot NMe_3$, all other reagents were purchased from Aldrich and used without purification. – All synthetic procedures were conducted under dry argon by using standard Schlenk and glove box techniques. Anhydrous solvents were used.

Trimethylamine–[Bis(trimethylsilyl)amino]alane (**1**): Neat bis(trimethylsilyl)amine (1.00 ml, 0.77 g, 4.74 mmol) was added to an ethereal solution of $[Al(H)_3 \cdot NMe_3]$ (0.42 g, 4.74 mmol) at 0 °C. There was a slow gas evolution as the reaction mixture was brought to room temp. and stirred for a further 3 h, after which time the solvent was removed in vacuo to afford a clear liquid of the title compound which was distilled in vacuo and slowly solidified, yield 0.68 g (58%), b.p. 100–102 °C/3 Torr. – ^1H NMR ([D$_6$]benzene): δ = 0.40 (s, 18H, SiCH$_3$), 1.83 (s, 9H, NCH$_3$), 3.59 (br., 2H, AlH). – ^{13}C NMR ([D$_6$]benzene): δ = 6.1 (s, SiCH$_3$), 47.8 (s, NCH$_3$). – ^{27}Al NMR (THF): δ = 138 ($w_{1/2}$ = 2700 Hz). – IR (nujol): $\tilde{\nu}$ = 1790 (br., AlH). – Mol. mass (THF): 226 ± 18, assoc. 0.91 ± 0.07.

Trimethylamine–[Bis(trimethylsilyl)amino]chloroalane (**2**): To a solution of $Al(Cl)(H)_2 \cdot NMe_3$ (0.33 g, 2.68 mmol) in diethyl ether (30 ml) was added bis(trimethylsilyl)amine (0.43 g, 2.66 mmol) at −80 °C. On warming to room temp. gas evolved, and the reaction mixture was stirred overnight. The solution was filtered, and volatile compounds were removed in vacuo. The title compound was recrystallised from hexane (15 ml) on slow cooling to −30 °C, yield 0.45 g (60%), m.p. 53–54 °C, 155 °C (gas evolution), 205 °C (dec.). – ^1H NMR ([D$_6$]benzene): δ = 0.39, 0.41 (4:1, s, 18H, SiCH$_3$), 1.84 (s, 9H, NMe$_3$). – ^{13}C NMR ([D$_6$]benzene): δ = 6.1, 6.4 (1:4, s, SiCH$_3$), 47.5 (s, NMe$_3$). – IR (nujol): $\tilde{\nu}$ = 1865 (br., AlH). – $C_9H_{28}AlClN_2Si_2$ (282.9): calcd. C 38.21, H 9.97, Cl 12.53, N 9.90; found C 38.41, H 10.56, Cl 12.39, N 10.22.

Bis(trimethylsilyl)amine–Alane (**3**): Neat bis(trimethylsilyl)amine (2.00 ml, 1.53 g, 9.48 mmol) was added to an ethereal solution of alane (0.284 g, 9.48 mmol) at 0 °C. After stirring for 2 h at room temp. the solvent was removed in vacuo to afford a colourless oil of the title compound which was distilled in vacuo and slowly solidified, yield 0.96 g (53%), b.p. 90 °C/3 Torr. – ^1H NMR ([D$_6$]benzene): δ = 0.36 (s, 18H, SiCH$_3$), 0.52 (br., 1H, NH), 4.30 (br., 3H, AlH). – ^{13}C NMR [(D$_6$]benzene): δ = 5.5 (s, SiCH$_3$). – ^{27}Al NMR (THF): δ = 129 ($w_{1/2}$ = 2600 Hz). – IR (nujol): $\tilde{\nu}$ = 3380 (NH), 1800 (br., AlH). – Mol. mass (benzene): 352 ± 10, assoc. 1.84 ± 0.06.

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