Synthesis and Characterization of Organoaluminum Silylamido Complexes

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*Summary: The reaction between [Me_2AlCl] and 1 equiv of $HN(SiMe_2H)_2$ in CH_2Cl_2 afforded colorless crystals of [$Cl(Me)Al\{$-$NH(SiMe_2H)\}]_2$ (**1**). The structure of compound **1** has been determined and shows that the bridging $NH(SiMe_2H)$ groups adopt a mutually trans arrangement. The related reaction between [Me_2AlCl] and 1 equiv of $HN(SiMe_2Ph)_2$ in CH_2Cl_2 solution resulted in the isolation of colorless crystals. An X-ray crystallographic study showed that the crystals consist of a mixture of [$Cl(Me)_2Al\{NH(SiMe_2Ph)_2\}$] (**2**) and [$Cl_2(Me)Al\{NH(SiMe_2Ph)_2\}$] (**3**) in a 1:4 ratio. The formation of compound **3** involves the exchange of one of the methyl groups attached to the aluminum atom with a chlorine atom.*

Introduction

Alkylaluminum amides, of the type [$R_2Al\{NR'(R'')\}$], have received considerable attention in recent years because of the application of some of these compounds as precursors to aluminum nitride (AlN).[1−3] In turn, AlN is of interest because it is a hard and refractory material with potential applications as passive barrier layers and protective coatings for high-temperature materials.[4] A number of reviews on the synthesis and structures of aluminum amido complexes are available in the literature.[1−3,5−8] A range of aminoalanes with unusual structures and coordination numbers have been prepared via the reaction of trialkylaluminum complexes, [R_3Al], with sterically demanding amines.[9−14] Orthometalated aminoalanes have been isolated from the thermolysis of mixtures of [R_3Al] with secondary amines containing an aromatic group.[15−18] Recently, the synthesis and characterization of a range of aminoalanes prepared from the reaction of [R_3Al] with dibenzylamine were reported.[19,20]

In the particular case of organoaluminum silylamido complexes, the reaction between [R_3Al] and R'_3SiNH_2 in refluxing hexane was reported to yield the dimeric compounds [$R_2Al\{NH(SiR'_3)\}]_2$ (where R = Me, R'_3 = Ph_3, Et_3; R = ^{i}Bu, R'_3 = Ph_3, $^tBu_2H$).[21] The structures of two of the compounds were reported, namely [$Me_2Al\{\mu$-$NH(SiEt_3)\}]_2$ and [$Me_2Al\{\mu$-$NH(SiPh_3)\}]_2$, which showed that the Al_2N_2 frameworks are planar with the silyl groups orientated *trans* about this ring.[21] The reaction of [Me_3Al] with $HN(SiMe_2H)_2$ was reported to yield [$Me_2Al\{\mu$-$N(SiMe_2H)_2\}]_2$, which was structurally characterized.[22] This compound has also been isolated from the reaction of [$Y\{N(SiMe_2H)_2\}_3(thf)_2$] with varying amounts of [Me_3Al] with the concomitant formation of [$Y\{(\mu$-$Me)_2AlMe_2\}_3$] and [$Me_3Al(thf)$].[23] The aluminum silylamido complexes [$Me_2Al\{\mu$-$NH(SiMe_3)\}]_2$ and [$Me(Cl)Al\{\mu$-$NH(SiMe_3)\}]_2$ have been prepared from the reaction of [Me_2AlCl] or [$MeAlCl_2$], respectively, and $HN(SiMe_3)_2$.[24] The compound [$Me_2Al\{NH(SiMe_3)\}]_2$ has also been prepared from the reaction of [$Cl_2Al\{NH(SiMe_3)\}]_2$ and dimethylmagnesium.[21] Reaction of the dilithium hydrazide $Li_2N_2(SiMe_3)_2$ with 2 equiv of [$(Me_3SiCH_2)_2AlCl$] resulted in the formation of [$(Me_3SiCH_2)_2Al\{\mu$-$NH(SiMe_3)\}]_2$ in low yield along with other products.[25]

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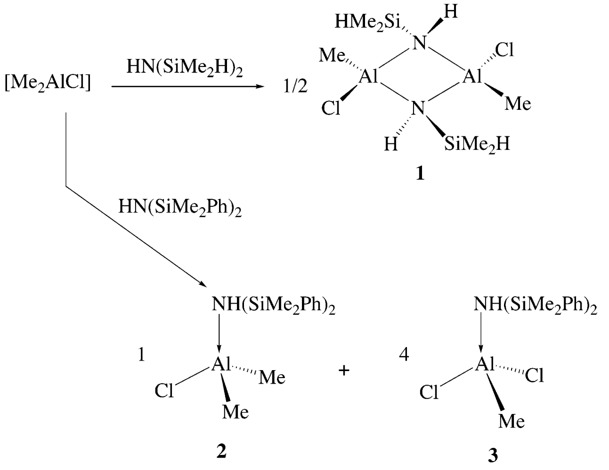
Table 1. Selected Comparative Bond Lengths (Å) and Angles (deg) for 1

	molecule A	molecule B		molecule A	molecule B
Al−N′	1.920(3)	1.923(3)	Al−N	1.924(3)	1.922(3)
Al−C(1)	1.971(3)	1.932(5)	Al−Cl	2.1357(14)	2.151(2)
Al−Al′	2.737(2)	2.737(2)			
N′−Al−N	89.22(13)	89.24(13)	N′−Al−C(1)	113.6(2)	115.9(2)
N−Al−C(1)	115.48(14)	117.6(2)	N′−Al−Cl	110.70(10)	108.16(11)
N−Al−Cl	107.35(11)	106.32(11)	C(1)−Al−Cl	117.08(12)	116.2(2)
Al−N−Al′	90.78(13)	90.76(13)			

Scheme 1



We were interested in exploring the reactivity of organoaluminum(III) complexes with silylamines in more detail. In related reactions of gallium(III) chloride with silylamines complexes such as $[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ were isolated due to the transfer of an aryl ligand from the silyl group of the amine to the Ga center.[26] In this paper, we describe the reactivity of $[Me_2AlCl]$ with the silylamines $HN(SiMe_2Ph)_2$ and $HN(SiMe_2H)_2$. These amines were of interest due to the possibility of transfer of a phenyl or hydride ligand from the silyl group to the Al center. The crystal structure of $[Cl(Me)Al\{\mu\text{-}NH(SiMe_2H)\}]_2$ (**1**) is described. The structures of $[Cl(Me)_2Al\{NH(SiMe_2Ph)_2\}]$ (**2**) and $[Cl_2(Me)Al\{NH(SiMe_2Ph)_2\}]$ (**3**), which co-crystallized, are also reported. The formation of compound **3** involves the exchange of one of the methyl groups attached to the aluminum atom with a chlorine atom.

Results and Discussion

The reaction between $[Me_2AlCl]$ and 1 equiv of $HN(SiMe_2H)_2$ in CH_2Cl_2 at room temperature resulted, after workup, in a 50% yield of colorless crystalline **1** (Scheme 1).

Analytical and spectroscopic data for **1** were consistent with the formulation $[Cl(Me)Al\{NH(SiMe_2H)\}]_2$. The dimeric nature of **1** was confirmed by an X-ray crystallographic study, which shows the crystals to contain two independent C_i-symmetric molecules, both of which have *anti* geometries for their pairs of equivalent substituents (Figure 1). The planar four-membered Al_2N_2 ring has an essentially square geometry with identical Al−N bond lengths (Table 1) and interbond angles within 1° of 90°. Both the conformation and pattern of bonding do not differ appreciably from those observed for the closely related $SiMe_3$ analogue.[24] The only anomalies in the present structure are in the Al−Me and Al−Cl bond lengths, which differ significantly between the two independent molecules; the reasons for these differences are not immediately apparent, as there is no evidence for *syn*/*anti* disorder. Pairs of dimers are, for both independent molecules, loosely linked by weak N−H···Cl hydrogen bonds: [N···Cl], [H···Cl] (Å), [N−H···Cl] (deg), 3.60, 2.75, 158 and 3.50, 2.65, 159 for the two molecules, respectively. There are no other packing interactions of note.

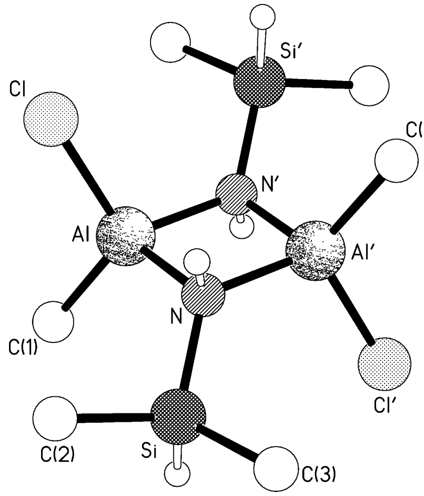


Figure 1. One of the pair of crystallographically independent C_i-symmetric dimers in the structure of **1**.

The formation of compound **1** from the reaction of $[Me_2AlCl]$ and $HN(SiMe_2H)_2$ is surprising. The related reaction between $[Me_2AlCl]$ and $HN(SiMe_3)_2$ was reported to yield the dimeric complex $[Me_2Al\{\mu\text{-}NH(SiMe_3)\}]_2$, which was structurally characterized, via elimination of Me_3SiCl.[24] Therefore, we expected to form $[Me_2Al\{\mu\text{-}NH(SiMe_2H)\}]_2$ by elimination of $Me_2Si(H)Cl$, rather than compound **1**. The isolation of **1** is either the result of direct elimination of Me_3SiH (rather than $Me_2Si(H)Cl$) or via some other rearrangement. If $Me_2Si(H)Cl$ was formed during the reaction (resulting in the formation of $[Me_2Al\{\mu\text{-}NH(SiMe_2H)\}]_2$), reaction of $Me_2Si(H)Cl$ with any unreacted $[Me_2AlCl]$ could lead to the formation of $[MeAlCl_2]$ and Me_3SiH. Reaction of $[MeAlCl_2]$ with $HN(SiMe_2H)_2$ would therefore produce compound **1**. This type of mechanism has been proposed previously for the formation of $[Cl_2Al(SR)]$ and Me_4Si from the reaction of $[MeAlCl_2]$ and Me_3SiSR.[27] Attempts to monitor the reaction between $[Me_2AlCl]$ and $HN(SiMe_2H)_2$ by ^1H NMR were complicated by the formation of geometric isomers (as described below), and a

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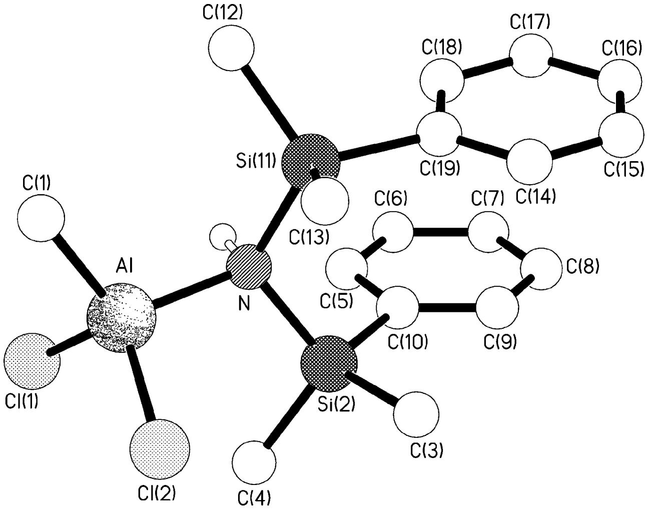

Figure 2. One of the conformers of **3** present in the mixed crystals of **2** and **3**; Al−Cl(1) 2.171(2) Å, Al−N 2.001(2) Å.

number of peaks were observed for each proton environment (Me−Al, Me−Si, H−Si, and N−H).

The mutually *trans* arrangement of the bridging NH-(SiMe$_2$H) groups we observe in **1** is also seen in the solid state structures of all other known dimeric aluminum amido complexes.[1−3,5−8,19,21−25] Five geometrical isomers are possible, namely, the *trans*−*trans* isomer in which the Me−Al groups are *trans* to each other and the Me$_2$-SiH groups are *trans* to each other, the *cis*−*trans*, *trans*−*cis*, *cis*−*cis*, and the all-*cis* isomer (the Al−Me and Me$_2$SiH groups are on the same side of the Al$_2$N$_2$ ring). The NMR data for compound **1** indicated that in solution mixtures of the *trans*−*trans* and *cis*−*cis* isomers were present (∼2:1 ratio). However, the ^{1}H NMR of **1** also contained several weak signals, which are probably due to the presence of a different geometrical isomer. A similar *trans*−*cis* isomerization was reported for the dimeric silylamidoalanes described previously.[21,24]

Treatment of [Me$_2$AlCl] with 1 equiv of HN(SiMe$_2$-Ph)$_2$ in CH$_2$Cl$_2$ at room temperature resulted in the isolation of colorless crystals. A single-crystal structure determination showed that these crystals consist of a 1:4 mixture of [Cl(Me)$_2$Al{NH(SiMe$_2$Ph)$_2$}] (**2**) and [Cl$_2$(Me)Al{NH(SiMe$_2$Ph)$_2$}] (**3**). These two compounds are randomly distributed throughout the crystal and in addition display C(1)/Cl(2) positional disorder. Figure 2 depicts one of the conformers of **3** present in the crystals. The conformation of the NH(SiMe$_2$Ph)$_2$ portion of the structure is stabilized by a π-stacking interaction between the two phenyl rings, which are inclined by only ca. 7° and have centroid···centroid and mean interplanar separations of 3.80 and 3.32 Å, respectively; the C(Ph)-Si···Si−C(Ph) molecular torsion angle is ca. 33°. As was observed for **1**, centrosymmetrically related pairs of molecules are linked by weak N−H···Cl hydrogen bonds [to the ordered chlorine Cl(1)] with [N···Cl], [H···Cl] and [N−H···Cl] of 3.58 Å, 2.69 Å, and 171°, respectively. There are no other notable intermolecular interactions.

The ^{1}H and ^{13}C NMR of the colorless crystals (**2**/**3**) supports the formation of two complexes and shows two different environments for the Al−Me protons. However, three different environments are observed for the Si−Me protons, suggesting that another species is present or a fluxional process is taking place in solution. Compound **2** consists of a simple 1:1 adduct of [Me$_2$-AlCl] with HN(SiMe$_2$Ph)$_2$. However, the formation of compound **3** is complicated and involves the exchange of one of the methyl groups attached to the aluminum atom with a chlorine atom. It is possible that the formation of **3** is the result of a mechanism similar to that described above for **1**, where [Me$_2$AlCl] reacts with Me$_2$Si(Ph)Cl to form [MeAlCl$_2$] and Me$_3$SiPh. Methylaluminum chloride could then react with HN(SiMe$_2$Ph)$_2$ to produce compound **3**. However, we and others have observed the transfer of a methyl or phenyl group from a silylamine to a metal center.[26,28−30] A previous report describing the reaction between [Me$_2$AlCl] and excess HN(SiMe$_3$)$_2$ showed that initially the 1:1 adduct [Cl-(Me)$_2$Al{NH(SiMe$_3$)$_2$}] was formed.[24] After heating this adduct to 50 °C, the amido complex [Me$_2$Al{NH(SiMe$_3$)}] was isolated.[24] The presence of **3** in the crystal structure explains the low yield of the colorless crystals obtained from the reaction of [Me$_2$AlCl] with HN(SiMe$_2$Ph)$_2$. The solid has a broad melting point range, which is consistent with the presence of more than one compound.

In summary, the aluminum silylamido complexes [Cl-(Me)Al{μ-NH(SiMe$_2$H)}]$_2$ (**1**), [Cl(Me)$_2$Al{NH(SiMe$_2$-Ph)$_2$}] (**2**), and [Cl$_2$(Me)Al{NH(SiMe$_2$Ph)$_2$}] (**3**) have been synthesized and structurally characterized. The formation of **1** and **3** shows that the behavior of [Me$_2$-AlCl] and silylamines is interesting and unexpected products can be obtained. Furthermore, it is likely that these reactions are dependent on the reaction procedure (e.g., solvent, temperature), and further studies are currently in progress and will be appear in a future publication.

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-ether and hexanes; CaH$_2$ for CH$_2$Cl$_2$). 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 Brüker AMX400 spectrometer at UCL, referenced to CD$_2$-Cl$_2$, which was dried and degassed over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to SiMe$_4$ (δ 0.00). FT-IR spectra were taken on a Shimadzu FTIR-8200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

Synthesis of 1. A solution of HN(SiMe$_2$H)$_2$ (1.77 mL, 10 mmol) in CH$_2$Cl$_2$ (10 mL) was added slowly to a stirred solution of [Me$_2$AlCl] (10 mL, 1.0 M solution in hexanes) in CH$_2$Cl$_2$ (15 mL) at −78 °C. The reaction mixture was stirred and allowed to warm slowly to room temperature. The resulting colorless solution was reduced in vacuo to give a colorless oil. After standing at room temperature over several weeks colorless crystals of **1** were obtained (0.76 g, 50% yield). Mp: 104−106 °C. Anal. Calcd for C$_3$H$_{11}$NClSiAl: C, 23.76; H, 7.31; N, 9.24. Found: C, 23.19; H, 6.78; N, 9.09. ^{1}H NMR (CD$_2$Cl$_2$): *trans*/*trans* isomer, δ −0.47 (s, 6H, AlC*H*$_3$), 0.44 (s, 12H, SiC*H*$_3$),

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1.01 (s, br, 2H, N*H*), 4.52 (s, 2H, Si*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 1.44 (s, Si*C*H_3), −9.5 (s, br, Al*C*H_3), −0.2 (s, s, Si*H*). ^1H NMR (CD_2Cl_2): *cis/cis* isomer, −0.51 (s, AlC*H*$_3$), 0.31 (s, SiC*H*$_3$), 1.23 (s, br, N*H*), 4.33 (s, Si*H*), 4.64 (s, Si*H*).

Synthesis of 2/3. $HN(SiMe_2Ph)_2$ (1.5 mL, 5 mmol) was added slowly to a stirred solution of [Me_2AlCl] (5 mL, 1.0 M solution in hexane) in CH_2Cl_2 (15 mL) at −78 °C. A white precipitate formed immediately, and the reaction mixture was allowed to warm slowly to room temperature. The resulting colorless solution was reduced in vacuo to a volume of approximately 5 mL. Cooling of this solution to −20 °C afforded colorless crystals after a few days. These crystals were redissolved in diethyl ether (5 mL) and cooled to −20 °C. X-ray quality crystals of **2/3** were obtained after a few weeks at this temperature (15% yield). Mp: 114−122 °C. Anal. Calcd for $C_{17}H_{26}NCl_2Si_2Al$: C, 51.24; H, 6.58; N, 3.52. Found: C, 48.41; H, 6.41; N, 4.79. ^1H NMR (CD_2Cl_2): δ −0.46 (s, AlC*H*$_3$), −0.39 (s, AlC*H*$_3$), 0.30 (s, SiC*H*$_3$), 0.68 (s, SiC*H*$_3$), 0.77 (s, SiC*H*$_3$), 2.21 (s, br, N*H*), 7.26−7.67 (m, SiC$_6$*H*$_5$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −0.12 (s, Al*C*H_3), 0.0 (s, Al*C*H_3), 1.6 (s, Si*C*H_3), 2.2 (s, Si*C*H_3), 3.0 (s, Si*C*H_3), 128.1, 128.5, 128.7 (s, *m*-Si*C*$_6$H$_5$), 129.4, 130.9 (s, *p*-Si*C*$_6$H$_5$), 133.7, 133.9 (s, *o*-Si*C*$_6$H$_5$), 135.7 (s, *ipso*-Si*C*$_6$H$_5$).

X-ray Crystallography. Crystal data for **1**: $C_6H_{22}N_2Si_2Cl_2Al_2$, $M = 303.3$, triclinic, $P\bar{1}$ (no. 2), $a = 6.131(1)$ Å, $b = 9.054(2)$ Å, $c = 16.073(2)$ Å, $\alpha = 91.84(1)°$, $\beta = 98.60(1)°$, $\gamma = 99.14(1)°$, $V = 869.5(2)$ Å^3, $Z = 2$ (there are two crystallographically independent C_i-symmetric molecules in the asymmetric unit), $D_c = 1.158$ g cm^{-3}, μ(Cu Kα) = 5.47 mm^{-1}, $T = 183$ K, colorless blocks; 2578 independent measured reflections, F^2 refinement, $R_1 = 0.047$, $wR_2 = 0.118$, 2216 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 144 parameters. CCDC xxxxxx.

Crystal data for **2/3**: $C_{17.2}H_{26.6}NSi_2Cl_{1.8}Al$, $M = 394.4$, monoclinic, $P2_1/n$ (no. 14), $a = 11.371(2)$ Å, $b = 15.023(3)$ Å, $c = 13.275(2)$ Å, $\beta = 108.93(1)°$, $V = 2145.0(6)$ Å^3, $Z = 4$, $D_c = 1.221$ g cm^{-3}, μ(Cu Kα) = 3.94 mm^{-1}, $T = 183$ K, colorless blocks; 3177 independent measured reflections, F^2 refinement, $R_1 = 0.040$, $wR_2 = 0.102$, 2749 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 202 parameters. The crystals are comprised of a ca. 20:80 mixture of $C_{18}H_{29}NSi_2ClAl$ and $C_{17}H_{26}NSi_2Cl_2Al$, respectively, randomly distributed throughout the crystal. CCDC xxxxxx.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure of compounds **1** and **2/3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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