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Preparation and characterization of bis-(trimethylsilyl) aminoalanes $[H_2AlN(SiMe_3)_2] \cdot NMe_3$ and $\{HAl[N(SiMe_3)_2]_2\}_n$ Crystal structure determination for tris-(trimethylsilyl) alane trimethylamine adduct $(Me_3Si)_3Al \cdot NMe_3$

Jerzy F. Janik [1], Eileen N. Duesler, Robert T. Paine *

Department of Chemistry, The University of New Mexico, Albuquerque, NM 87131, USA

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Abstract

The adduct $[H_2AlN(SiMe_3)_2] \cdot NMe_3$ (**1**) is obtained in high yield from the reaction between $H_3Al \cdot NMe_3$ and $HN(SiMe_3)_2$. Thermal decomposition of **1** results in disproportionation with formation of hydrogen, free NMe_3, elemental aluminum, and $\{HAl[N(SiMe_3)_2]_2\}_n$ (**2**). Attempted synthesis of a copolymer from the reaction of $[H_2AlN(SiMe_3)_2] \cdot NMe_3$ (**1**) with $[(Me_3Si)_2AlNH_2]_2$ results in the unexpected formation of tris-(trimethylsilyl)alane trimethylamine adduct, $(Me_3Si)_3Al \cdot NMe_3$ (**3**), for which the crystal structure was determined: monoclinic, space group $P2_1/n$, $a = 8.9770(10)$ Å, $b = 15.930(3)$ Å, $c = 15.980(3)$ Å, $V = 2285.1(10)$ Å^3, $Z = 8$, $D = 0.888$ g cm^{-3}, $R = 7.07\%$. © 1997 Elsevier Science S.A.

Keywords: Aluminium; Silicon; Hydrides; Amines

1. Introduction

Amine alane adducts $H_3Al \cdot NR_3$ and (dialkylamido)alanes $H_nAl(NR_2)_{3-n}$ are substituent isomers of organo- and organosilylalanes $R_3Al \cdot NH_3$ and $R_nAl(NH_2)_{3-n}$ ($n = 1,2$, R = alkyl, aryl, $SiMe_3$), and their chemical properties [1,2] suggest that some should be useful solid state materials precursors. Indeed, several amino organoalanes have been evaluated as precursors for aluminum nitride [3,4]. However, the precursors to ceramic conversions are plagued by incomplete alkane removal during pyrolysis. In an effort to circumvent this problem, we have explored elimination chemistry between $(Me_3Si)_3Al \cdot OEt_2$ and ammonia [5–7] which is favored by weak Si–Al bonding in the Lewis acid fragment. New molecular and polymeric precursors are obtained and pyrolyses, depending upon conditions, give AlN–SiC or AlN–Si_3N_4 composites. In contrast, reactions between $(Me_3Si)_3Al \cdot OEt_2$ and hydrazine [8] are more complex and include N–N bond cleavage and trimethylsilyl group transfer chemistry. Combinations of $Al[N(SiMe_3)_2]_3$ and ammonia [9] have also been examined as precursor systems. Samples of AlN or AlN–Si_3N_4 are obtained, but it is difficult to obtain pure AlN due to the presence of strong Si–N–C bonds in the Lewis base fragment.

The simplest AlN precursor results from the idealized system $\{AlH_3\} + NH_3$. This chemistry has been studied [10–12], but even here the ceramic product contains carbon impurities that originate from solvent or the Lewis base used to stabilize $\{AlH_3\}$. On the other hand, pure aluminum nitride is obtained efficiently from reaction of $LiAlH_4$ and NH_4Br in diethyl ether [13]. When organic groups are present on the amine nitrogen atom, other decomposition pathways arise [14]. For example, $H_3Al \cdot NMe_3$ and $H_3Al(NMe_3)_2$ undergo facile decomposition with liberation of amine instead of alkane, and both deposit thin films of elemental aluminum at temperatures as low as 100 °C [15,16]. Finally, thermal decompositions of $[HAl(NMe_2)_2]_2$ and $[Al(NMe_2)_3]_2$ produce aluminum carbonitrides [17].

* Corresponding author.

[1] On leave from the University of Mining and Metallurgy, Krakow, Poland.

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Obviously the thermal chemistry of isometrically related amine alanes and amino organoalanes is complex, and additional studies will be required to understand the similarities and differences in these systems. In this regard, the synthesis of new aminoalanes is receiving much attention [18]. We have briefly described two missing members in the series $\{AlH_3\}$ to $Al[N(SiMe_3)_2]_3$, namely $[H_2AlN(SiMe_3)_2]\cdot NMe_3$ (**1**) and $\{HAl[N(SiMe_3)_2]_2\}_n$ (**2**) [19]. Herein, the preparation and characterization of these compounds are provided in more detail along with the unexpected formation of $(Me_3Si)_3Al\cdot NMe_3$ (**3**) in the reaction of $[H_2AlN(SiMe_3)_2]\cdot NMe_3$ with $[(Me_3Si)_2AlNH_2]_2$.

2. Experimental section

All manipulations were performed under a dry, oxygen-free inert gas atmosphere using standard Schlenk techniques and dry-box equipment. All solvents were rigorously dried over $LiAlH_4$ and distilled from sodium benzophenone ketyl prior to use. The compounds $H_3Al\cdot NMe_3$ [20] and $[(Me_3Si)_2AlNH_2]_2$ [5] were prepared by literature methods. $HN(SiMe_3)_2$ was purchased from Aldrich and used as-received. Elemental analyses were performed at the UNM Microanalytical Laboratory. IR spectra were obtained on a Galaxy 2000 Series FT-IR spectrometer, and mass spectra were recorded from a Finnigan GC/EI-CI mass spectrometer. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a GE-NT360 spectrometer referenced with $(CH_3)_4Si$. Melting point determinations were performed in sealed glass tubes and were uncorrected.

2.1. Synthesis of $[H_2AlN(SiMe_3)_2]\cdot NMe_3$ (1)

A sample of $H_3Al\cdot NMe_3$ (0.36 g, 4.0 mmol) was dissolved in benzene (15 ml) in a Schlenk flask, and $HN(SiMe_3)_2$ (0.65 g, 4.0 mmol) was dissolved in benzene (15 ml) in another Schlenk flask. The two flasks were connected via a stopcock, and the system was thoroughly degassed. The amine solution was slowly added at room temperature to the stirred alane solution, resulting in reaction with gas evolution. The mixture was stirred overnight and the amount of evolved hydrogen (4.0 mmol) was measured using a calibrated manifold and reaction flask. Subsequently, the volatiles were evaporated leaving a viscous oil: 0.97 g, yield 97%. Further, evacuation (1 h) produced a 'wet' crystalline solid (m.p. 35–38 °C). Owing to significant volatility of the product at 23 °C, prolonged evacuation led to noticeable loss of product. ^1H and $^{13}C\{^1H\}$ NMR spectra of the oil and the crystals were recorded, and found to display identical spectroscopic features. Similarly, IR spectra for the oil (neat) and the solid (KBr pellet) were essentially identical; the spectrum for the solid showed additional splitting of a few bands. Anal. Calc. for $C_9H_{29}AlN_2Si_2$: C, 43.50; H, 11.76; N, 11.27. Found: C, 42.72; H, 12.20; N, 10.79. GC/MS: *m/e* (intensity) (ion): 348 (1) ($HAl[N(SiMe_3)_2]_2$, M*), 333 (2) (M* − CH_3), 275 (5) (M* − $SiMe_3$), 259 (2) (M* − $SiMe_3$ − Me − H), 248 (4) ($[H_2AlN(SiMe_3)_2]\cdot NMe_3$, M), 247 (30) (M − H), 233 (20) (M − Me), 189 (1) (M − NMe_3), 188 (25) (M − NMe_3 − H), 174 (35) (M − NMe_3 − Me), 158 (4) (M − NMe_3 − 2Me − H), 146 (20) ($N(SiMe_3)_2$ − Me + H), 130 (20) ($N(SiMe_3)_2$ − 2Me), 116 (5) (M − NMe_3 − $SiMe_3$), 100 (3) ($N(SiMe_3)_2$ − 4Me), 87 (2) ($NSiMe_3$), 73 (5) ($SiMe_3$), 59 (40) (NMe_3), 58 (100) ($SiMe_3$ − Me). IR (KBr), cm^{-1} (intensity): 3007(w,sh), 2973(m,sh), 2953(s), 2911(m), 2897(m), 2864(w), 2833(w), 2799(w), 1808(s), 1790(s), 1481(s), 1465(m), 1449(m), 1407(w), 1248(s), 1182(w), 1102(w), 1000(s), 938(s), 895(s), 838(s), 801(s), 759(s), 719(s), 672(s), 644(m,sh), 620(w,sh), 534(w), 514(w), 449(w). ^1H NMR (C_6D_6): δ 0.37 (18H, $Si(CH_3)_3$), 1.81 (9H, $N(CH_3)_3$). No resonance was detected for the AlH_2 protons. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.0 ($Si(CH_3)_3$), 47.7 ($N(CH_3)_3$).

2.2. Synthesis of $\{HAl[N(SiMe_3)_2]_2\}_n$ (2)

A sample of **1** (0.50 g, 2.0 mmol) was dissolved in toluene (10 ml) and refluxed for 14 h under nitrogen. After 3 to 4 h the solution became milky, and after 14 h a dark gray, metallic precipitate formed. The slurry was filtered and the filtrate evacuated, affording a colorless crystalline solid. The solid was redissolved in a few milliliters of hexane, stored in the refrigerator, and small, thin needles appeared. The crystals were filtered cold and dried: yield 0.25 g, 70% based on the stoichiometric disproportionation reaction (m.p. 95–98 °C). Anal. Calc. for $C_{12}H_{37}AlN_2Si_4$: C, 41.33; H, 10.69; N, 8.03. Found: C, 38.28; H, 10.89; N, 7.39. IR (KBr), cm^{-1} (intensity): 2956(s), 2904(m), 1790(w,br), 1400(w,br), 1259(s), 1185(w), 1034(w,sh), 1000(w,sh), 925(s), 911(s), 876(s), 838(s), 758(m), 674(m), 618(w), 590(w,sh). ^1H NMR (C_6D_6): δ 0.34 (36H, $Si(CH_3)_3$), 4.4 (^1H, AlH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 5.7 ($Si(CH_3)_3$).

2.3. Reaction between $[H_2AlN(SiMe_3)_2]\cdot NMe_3$ (1) and $[(Me_3Si)_2AlNH_2]_2$. Isolation of $(Me_3Si)_3Al\cdot NMe_3$ (3)

A sample of **1** (0.48 g, 1.9 mmol) was dissolved in Et_2O (10 ml) in a 100 ml Schlenk flask, and $[(Me_3Si)_2AlNH_2]_2$ (0.36 g, 0.95 mmol) was dissolved in Et_2O (10 ml) in a second flask. Both flasks were connected through a stopcock,

Table 1
Summary of X-ray diffraction data for $(Me_3Si)_3Al \cdot NMe_3$ (**3**)

Formula	$C_{12}H_{36}AlNSi_3$
Crystal dimensions (mm^3)	$0.207 \times 0.440 \times 0.460$
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	8.9770(10)
b (Å)	15.930(3)
c (Å)	15.980(3)
β (deg)	90.150(10)
V (Å^3)	2285.1(10)
Z	8
Formula weight	152.8
D(calc.) ($g\,cm^{-1}$)	0.888
Absorption coefficient (mm^{-1})	0.229
F(000)	680
Temperature (K)	293
Radiation	Mo Kα (0.71073 Å)
2Θ limit (deg)	45
No. of collected reflections	6484
No. of independent reflections	3008 ($R_{int.} = 3.12\%$)
No. of observed reflections	1629
R (%)	7.07
R_w (%)	6.02
s	1.59

forming a closed system which was thoroughly degassed. The solution containing **1** was cooled to −78 °C, stirred, and slowly combined with the second solution. After warming to 23 °C the mixture became milky, and after 24 h the non-condensible gas (H_2) was measured in a calibrated manifold (0.8 mmol). The condensable volatiles were analyzed by IR spectroscopy and found to contain mostly Et_2O and small quantities of NMe_3, $HSiMe_3$ and $HN(SiMe_3)_2$. The ^1H and $^{13}C\{^1H\}$ NMR spectra for the products in C_6D_6 showed several resonances in the $SiMe_3$, NMe_3 and AlH regions. This mixture continued to slowly evolve H_2 and $HSiMe_3$, and it was redissolved in hexane (20 ml) and refluxed for 20 h under nitrogen during which time a gray, metallic solid, presumably elemental aluminum, formed. Following filtration, the solution was evacuated affording an oil and a crystalline solid. ^1H NMR analysis for this mixture showed one major species and several minor by-products. The crude product was redissolved in hexane (5 ml), and after several hours in the refrigerator large crystals of **3** formed. Melting behavior: 140–160 °C, partial melting with decomposition; 180 °C, completion of melting with color change and bubbling. IR (KBr), cm^{-1} (intensity): 3007(w), 2984(m), 2947(s), 2911(m), 2886(s), 2816(w,sh), 2799(w), 2451(w), 1476(s), 1462(s), 1449(m), 1431(m), 1408(m), 1387(m), 1343(w), 1287(m), 1250(s), 1238(s), 1099(m), 1050(m,sh), 991(s), 932(m), 835(s), 754(m), 731(m), 671(s), 615(m), 583(m,sh), 511(m), 469(w), 428(m), 407(m). ^1H NMR (C_6D_6): δ 0.32 (27H, $Si(CH_3)_3$), 1.85 (9H,$N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.2 ($Si(CH_3)_3$), 50.5 ($N(CH_3)_3$).

2.4. Structure determination of 3

A suitable crystal of **3** was obtained from hexane at −20 °C and was sealed in a glass capillary under dry nitrogen. The crystal was centered on a Siemens R3m/V diffractometer at 293 K and determinations of the crystal class, orientation matrix, and accurate unit cell parameters were performed. Details of the data collection are summarized in Table 1. A total of 6484 reflections were collected by using graphite-monochromated Mo Kα radiation, a scintillation counter, and pulse height analyzer. A total of 1629 reflections were observed ($F > 3.0\sigma(F)$) and used in the final refinement. All calculations were performed on a SHELXTL structure determination system. [2] Neutral atom scattering factors and anomalous dispersion factors were used for all non-hydrogen atoms during refinement. Full-matrix least squares methods were utilized and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ which converged to $R = 7.07\%$ with the goodness of fit of 1.59. Table 2 lists the non-hydrogen atomic coordinates, and Table 3 contains selected bond

[2] The SHELXTL package of programs for calculations and plots is described in Ref. [21]. SHELXTL uses scattering factors and anomalous dispersion terms taken from Ref. [22].

Table 2
Non-hydrogen atom coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} ($Å^2 \times 10^3$) for $(Me_3Si)_3Al \cdot NMe_3$ (3)

	x	y	z	U_{eq} [a]
Al	1255(2)	2827(1)	1748(1)	56(1)
N(1)	2802(6)	2569(3)	2650(3)	71(2)
C(1)	2066(9)	2198(5)	3395(4)	121(4)
C(2)	3566(7)	3347(5)	2911(4)	106(4)
C(3)	3907(8)	1974(5)	2334(5)	126(4)
Si(1)	246(3)	1477(1)	1228(1)	90(1)
C(4)	−1488(9)	1662(5)	623(5)	163(5)
C(5)	−213(11)	661(5)	2006(6)	200(6)
C(6)	1548(11)	935(5)	462(7)	194(6)
Si(2)	2498(2)	3610(1)	612(1)	74(1)
C(7)	1220(8)	3590(5)	−316(4)	114(4)
C(8)	4323(7)	3172(6)	235(5)	130(4)
C(9)	2846(9)	4753(4)	839(4)	130(4)
Si(3)	−708(2)	3701(1)	2390(1)	89(1)
C(10)	−2022(9)	3124(7)	3067(6)	190(6)
C(11)	−1914(9)	4119(6)	1532(5)	172(5)
C(12)	−89(10)	4602(7)	3022(8)	274(9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg) for $(Me_3Si)_3Al \cdot NMe_3$ (3)

Bond lengths			
AlN(1)	2.040(6)	Si(1)C(5)	1.846(9)
AlSi(1)	2.477(3)	Si(1)C(6)	1.903(10)
AlSi(2)	2.471(3)	Si(2)C(7)	1.874(7)
AlSi(3)	2.471(3)	Si(2)C(8)	1.881(7)
N(1)C(1)	1.486(9)	Si(2)C(9)	1.882(7)
N(1)C(2)	1.475(9)	Si(3)C(10)	1.848(9)
N(1)C(3)	1.464(9)	Si(3)C(11)	1.868(9)
Si(1)C(4)	1.854(8)	Si(3)C(12)	1.840(12)
Bond angles			
Si(1)–Al–Si(2)	110.9(1)	Al–Si(1)–C(4)	110.1(3)
Si(1)–Al–Si(3)	111.6(1)	Al–Si(1)–C(5)	117.9(3)
Si(2)–Al–Si(3)	110.2(1)	Al–Si(1)–C(6)	112.6(3)
N(1)–Al–Si(1)	108.1(2)	Al–Si(2)–C(7)	107.2(2)
N(1)–Al–Si(2)	108.2(2)	Al–Si(2)–C(8)	116.3(3)
N(1)–Al–Si(3)	107.8(2)	Al–Si(2)–C(9)	115.0(2)
Al–N(1)–C(1)	110.0(4)	Al–Si(3)–C(10)	114.8(3)
Al–N(1)–C(2)	110.2(4)	Al–Si(3)–C(11)	108.0(3)
Al–N(1)–C(3)	110.3(4)	Al–Si(3)–C(12)	116.9(3)

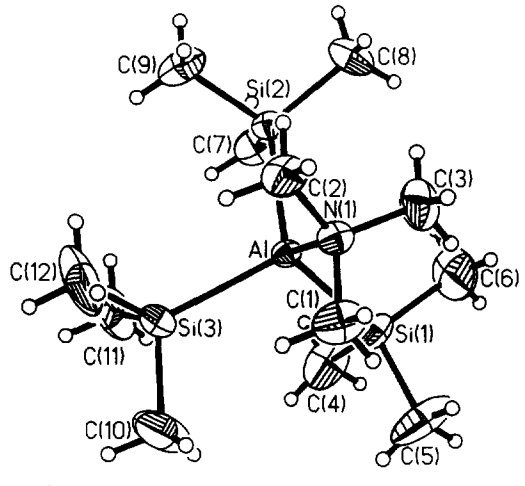

Fig. 1. ORTEP diagram (50% probability) of the molecular structure of $(Me_3Si)_3Al \cdot NMe_3$ (3).

distances and angles. A view of the molecule is shown in Fig. 1. Further details of the refinement, as well as full listings of bond distances and angles, are available in supplementary material.

3. Results and discussion

The [bis-(trimethylsilyl)amino]alane trimethylamine adduct **1** is obtained in high yield from the combination of $H_3Al \cdot NMe_3$ and $HN(SiMe_3)_2$:

$$H_3Al \cdot NMe_3 + HN(SiMe_3)_2 \xrightarrow[\text{benzene}]{\text{r.t.}} \underset{\mathbf{1}}{[H_2AlN(SiMe_3)_2]} \cdot NMe_3 + H_2 \quad (1)$$

The compound is obtained as an oil that slowly forms low melting (m.p. 35–38 °C), slightly volatile crystals. Elemental analyses for **1** are a little low in carbon and nitrogen due to incomplete combustion. This effect has been noted before for related aminoalane compounds [5,6]. The spectroscopic data and the amount of hydrogen gas evolved are consistent with the proposed formulation of **1**. For example, the ^1H NMR spectrum displays peaks at δ 0.37 and 1.81 in a 2:1 ratio assigned to the $Si(CH_3)_3$ and $N(CH_3)_3$ protons respectively. No resonance is unequivocally assigned to AlH_2 protons. The $^{13}C\{^1H\}$ NMR spectrum shows resonances at δ 6.0 and 47.7 ascribed to the $Si(CH_3)_3$ and $N(CH_3)_3$ carbons respectively. An IR spectrum of **1** shows two strong bands at 1808 cm^{-1} and 1790 cm^{-1} typical of AlH_2 vibrations [23]. A mass spectrum shows a low intensity ion at *m/e* 248 that is assigned to the parent ion (M), and logical fragment ions are also detected. Interestingly, the mass spectrum shows an ion at *m/e* 348 corresponding to $\{HAl[N(SiMe_3)_2]_2^+\}$ (M*), which may originate from thermal decomposition of **1** giving **2** (vide infra).

It is important to place this chemistry in the context of related molecules. The substituent isomer of **1**, $\{(Me_3Si)_2AlNH_2\}$, was obtained previously as a base-free dimer, $[(Me_3Si)_2AlNH_2]_2$ [5]. It strongly absorbs NEt_3, but the amine can be completely removed by prolonged evacuation at room temperature [24]. The related unit, $\{H_2AlNMe_2\}$, apparently does not complex with NMe_3, but it forms a trimer, $[H_2AlNMe_2]_3$, both in benzene solution [23] and in the solid state [25]. Larger alkyl groups on the nitrogen atom result in dimeric species in benzene solution [23]. The driving force for Me_3N adduct formation in **1** as opposed to self-condensation may derive from the steric bulk of the $N(SiMe_3)_2$ group or the reduced base strength of the silyl amine nitrogen atom. A steric argument has been employed to justify the formation of the monomeric, base-stabilized molecule $\{H_2Al(tmp)\} \cdot NMe_3$ (tmp = 2,2,6,6-tetramethylpiperidino) from $H_3Al \cdot NMe_3$ and tmpH [26]. In this case, in the absence of trimethylamine, a stable 'pre-elimination' adduct, $H_3Al \cdot (tmpH)$, is also formed. Another modification utilizing $LiAlH_4$ and tmpH · HCl afforded a trimeric H-bridged compound, $(H_2Altmp)_3$ [27].

Under ambient conditions, compound **1** does not display further hydrogen elimination in the presence of excess $HN(SiMe_3)_2$. If more than 1 equiv. of $HN(SiMe_3)_2$ is added to $H_3Al \cdot NMe_3$, the excess $HN(SiMe_3)_2$ can be removed by vacuum evaporation. This contrasts with the behavior of $H_3Al \cdot NMe_3$ toward secondary organoamines $HNMe_2$ and $HNEt_2$, which readily react in a 1:2 ratio to yield the dimeric bis-(dialkylamino)alanes $[HAl(NMe_2)_2]_2$ and $[HAl(NEt_2)_2]_2$ respectively [20,28]. However, reaction of **1** with NH_3, which might be expected to produce transamination of the $AlN(SiMe_3)_2$ site and/or ammonolysis of the AlH_2 group, gives a benzene-soluble polymer [29]. This polymer has been used to form coatings on alumina that are converted at high temperature under ammonia to dense and transparent aluminum nitride coatings.

The reaction of the two substituent isomers, $[H_2AlN(SiMe_3)_2] \cdot NMe_3$ (**1**) and $[(Me_3Si)_2AlNH_2]_2$, was examined in refluxing hexane. It was expected that either transamination or hydrogen elimination would occur with formation of an extended Al–N polymer network. The reaction produced H_2, NMe_3, and $HN(SiMe_3)_2$ in the off-gases, as well as $HSiMe_3$. The last compound was unexpected since the starting materials and the volatile by-products separately do not form $HSiMe_3$ under the conditions employed. Some polymeric material was evident in the raw reaction mixture based on ^1H NMR spectra, and metallic aluminum also precipitated. Unexpectedly, a significant quantity of the adduct $(Me_3Si)_3Al \cdot NMe_3$ (**3**) formed as well. The mechanism of this complicated reaction is currently unknown. The formation of **3** was confirmed by spectroscopic measurements and by a crystal structure determination. The ^1H NMR spectrum shows singlets at δ 0.32 ($Si(CH_3)_3$) and 1.85 ($N(CH_3)_3$) with an integration ratio of 3:1, and the $^{13}C\{^1H\}$ NMR spectrum displays two peaks at δ 3.2 ($Si(CH_3)_3$) and 50.5 ($N(CH_3)_3$). Notably, the IR spectrum of **3** does not display bands in the N–H or Al–H regions. The crystal structure determination shows that the molecule contains pyramidal Al and N atoms with Si–Al–Si bond angles greater than the N–Al–Si bond angles. This is likely due to the greater size of the $SiMe_3$ groups. The steric interactions between the trimethylsilyl and methyl groups are minimized by the staggered conformation (Fig. 1). The average Al–Si distance is 2.473 Å which is comparable with Al–Si

distances in several other molecules, including: $[(Me_3Si)_3Al]_2$TMEDA, 2.472 Å [30]; $(Me_3Si)_3Al \cdot OEt_2$, 2.47 Å [31]; $[(Me_3Si)_2AlNH_2]_2$, 2.473 Å [5]; $[(Me_3Si)_2AlN(H)SiMe_3]_2$, 2.490 Å [8]; $[(Me_3Si)_2AlP(C_6H_5)_2]_2$, 2.478 Å; $[(Me_3Si)_2AlP(C_6H_5)(SiMe_3]_2$, 2.467 Å; $[(Me_3Si)_2AlP(H)(c\text{-}C_6H_{11})]_3$, 2.475 Å [32]. In all cases, these distances are slightly greater than the sum of the covalent radii of Al and Si, 2.43 Å [30]. The most interesting structural feature in **3** is the Al–N bond length, 2.040(6) Å. This distance is shorter than the Al–N distance in the related adduct, $[(Me_3Si)_3Al]_2$TMEDA, 2.069(5) Å [30]. It is also shorter than the Al–N distances in gaseous, monomeric $H_3Al \cdot NMe_3$, 2.063(8) Å [33], and in gaseous, monomeric $Me_3Al \cdot NMe_3$, 2.099(10) Å [34]. The short Al–N distance in **3** is consistent with a greater effective Lewis acidity for $(Me_3Si)_3Al$ compared to the less sterically hindered AlH_3 and trimethylaluminum. This observation, coupled with the relatively weak Al–Si bond, would further suggest a higher kinetic reactivity of **3** towards trimethylsilane elimination compared with alkane elimination. In fact, the combination of $(Me_3Si)_3Al \cdot OEt_2$ and NH_3 does not result in an adduct, $(Me_3Si)_3Al \cdot NH_3$, at room temperature, but instead gives trimethylsilane elimination below 0 °C [5]. This contrasts with the formation of the stable adduct $Me_3Al \cdot NH_3$ under similar conditions, which undergoes methane elimination only at higher temperatures [3].

Compound **1** was conveniently stored without decomposition for several weeks in frozen benzene solutions at 0 °C, but ^{1}H NMR spectroscopy of a sample held at 23 °C for 4 weeks revealed slight decomposition with formation of free NMe_3 and $HN(SiMe_3)_2$. A fresh sample of **1** survived 24 h reflux in hexane without decomposition, and after additional reflux for 24 h in benzene showed traces of decomposition, but the majority of **1** remained unchanged. However, several hours of reflux in toluene promoted an efficient disproportionation reaction as shown in Eq. (2). This reaction is accompanied by the precipitation of a gray, metallic material which, after isolation, showed no IR features and was assumed to be elemental aluminum. If the disproportionation reaction initially produced $H_3Al \cdot NMe_3$, it should, at toluene reflux temperature, decompose to elemental aluminum [15].

$$\underset{\mathbf{1}}{2[H_2AlN(SiMe_3)_2] \cdot NMe_3} \xrightarrow[\text{toluene}]{\text{reflux}} H_3Al \cdot NMe_3 + \underset{\mathbf{2}}{1/n\{HAl[N(SiMe_3)_2]_2\}_n} \quad (2)$$

$$\downarrow$$

$$Al + \tfrac{3}{2}H_2 + NMe_3$$

The primary product, $\{HAl[N(SiMe_3)_2]_2\}_n$ (**2**), is much less soluble than **1**, and it is isolated in 70% yield after recrystallization from cold hexane. Unfortunately, X-ray quality crystals are not obtained. However, the nature of the compound is deduced from its spectroscopic data. The ^{1}H NMR spectrum shows one strong signal at δ 0.34 ($Si(CH_3)_3$ protons) and a very broad resonance at δ 4.4 (Al–H protons) with the integration ratio 36:1. Similarly, the $^{13}C\{^1H\}$ NMR spectrum shows only one signal at δ 5.7 ($Si(CH_3)_3$). The IR spectrum shows a weak and broad absorption at 1790 cm^{-1} that is assigned to an Al–H vibration [18,23]. Similar to **1**, the elemental analysis of **2** is low in carbon and nitrogen, which is consistent with incomplete combustion [5,9,35]. The degree of oligomerization of **2** unfortunately remains unresolved. As mentioned above, the mass spectrum of **1** shows an ion at $m/e = 348(M*)$ which corresponds to a parent ion for the monomeric unit of **2**. Higher mass ions that might result from a dimer or trimer of **2** are not seen. Given that **2** forms as shown in Eq. (2), it is likely that the $M*^+$ species of **2** forms from thermal decomposition of **1** in the heated MS sample cup or in the hot ion source region of the spectrometer. The reduced basicity of the N–$SiMe_3$ nitrogen sites coupled with the significant steric bulk of the $N(SiMe_3)_2$ group seem to mediate against a structure involving N-bridged oligomers. A monomeric structure is possible, although related monomers have only been detected for R_2AlH with extremely bulky R groups [18]. A symmetrical structure involving Al–H–Al bridges is also feasible. The IR spectrum of **2** supports the bridge bonding mode. For example, the weak and broad band at 1790 cm^{-1} compares with a strong and broad band at 1780 cm^{-1} for diethylalane $\{HAlEt_2\}$ in the absence of donor solvents [1]. This molecule has Al–H–Al bridge bonds. In contrast, $[HAl(NEt_2)_2]_2$, with Al–N–Al bridge bonds, displays an Al–H band at 1822 cm^{-1} [28]. In dimeric $[HAl[N\{(CMe_2CH_2)_2CH_2\}]_2]_2$, which contains Al–H–Al bridge bonds, a broad band is found at 1770 cm^{-1}, while the monomeric species with terminal Al–H bonds shows a band at 1858 cm^{-1} [27].

Soon after submitting our manuscript, a paper by Raston and coworkers [36] appeared describing the synthesis of **1** and $H(Cl)Al[N(SiMe_3)_2] \cdot NMe_3$. The properties reported for **1** are nearly identical in all respects to the properties we observe with the exception that they resolve a ^{1}H NMR resonance, δ 3.59, for the H–Al proton, which we did not detect. The reaction chemistry and thermal chemistry for **1** described by us provides important additional information on this novel compound. Unfortunately, our inability to obtain suitable single crystals did not allow us to determine if **1** has a monomeric structure similar to $H(Cl)Al[N(SiMe_3)_2] \cdot NMe_3$ [36].

In conclusion, the formation and reactivity of **1** described here provide additional information on the properties of closely related amino alane species. The data suggest that the two bis-(trimethylsilyl)aminoalanes, **1** and **2**, may be potentially useful precursors for elemental aluminum deposition and AlN and/or $AlN\text{–}Si_3N_4$ ceramic film prepara-

tion. In this regard the high volatility of **1** may be useful in vapor deposition schemes. Also, our preliminary data indicate that a polymeric, benzene-soluble precursor from **1** can be used for aluminum nitride film formation on oxide substrates.

Additional material is available from the Cambridge Crystallographic Data Centre, including H-atom coordinates, anisotropic thermal parameters, a complete listing of bond distances and angles, and a full summary of the data collection material.

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