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Novel Aluminum Hydride Derivatives from the Reaction of $H_3Al{\cdot}NMe_3$ with the Cyclosilazanes $[Me_2SiNH]_3$ and $[Me_2SiNH]_4$

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The amine hydrogen atoms of the cyclic trimeric silazane $[Me_2SiNH]_3$ are readily replaced by the $H_2Al{\cdot}NMe_3$ group in a simple aminolyis reaction of $[Me_2SiNH]_3$ with $H_3Al{\cdot}NMe_3$ to afford the aluminum amides $(Me_2SiNAlH_2{\cdot}NMe_3)_n(Me_2SiNH)_{3-n}$ (**1**, $n = 3$; **2**, $n = 1$; **4**, $n = 2$). The monosubstituted amide **2** could not be isolated, because it undergoes condensation to the tricyclic compound 1,1′,2,2′-$(HAlNMe_3)_2$ $(\overline{\mathrm{NSiMe_2NSiMe_2N(H)Si}}\mathrm{Me_2})_2$ (**3**). Contrary to these results the analogous reactions of the more flexible cyclic tetrameric silazane $[Me_2SiNH]_4$ with $H_3Al{\cdot}NMe_3$ did not give simple aluminum amides, but complicated mixtures were obtained from which the interesting polycyclic species $Al_5C_{22}H_{73}N_{10}Si_8{\cdot}C_6H_6$ (**5**) and $Al_6C_{22}H_{76}N_{10}Si_8{\cdot}1/4\ C_6H_{14}$ (**6**) could be isolated in low yields. A key step in the formation of **5** and **6** is a low-temperature dehydrosilylation reaction which leads to cleavage of the silazane ring. Compounds **1**, **3**, and **4** were characterized spectroscopically (^1H, ^{13}C, ^{27}Al NMR and FTIR) and by single crystal X-ray diffraction, whereas **5** and **6** were characterized by X-ray diffraction only. Thermolysis experiments involving **1** and **3** indicate that the onset of Al−N bond formation via dehydrosilylation is accompanied by loss of trimethylamine and formation of larger aggregates, which are stable to further silane elimination to at least 620 °C.

Introduction

The multitude and complexity of aluminum−nitrogen compounds has fascinated chemists for more than 30 years.[1−3] In addition, recent developments in materials science, which demand easy access to aluminum nitride in a variety of forms such as single crystals, powders of various particle sizes and shapes, or thin films, sparked interest in the synthesis of new organometallic precursors, the most promising of which were believed to be aluminum amides or imides.[4] However, most of the investigated precursor molecules gave AlN which was significantly contaminated with carbon due to incomplete decomposition of the precursor or competing additional decompositon pathways.[5] In the late 1980s Wells pioneered the dehalosilylation reaction (i.e., elimination of Me_3SiX) for the synthesis of the compound semiconductors GaAs and InAs.[6−8] This method was recently extended to include dehydrosilylation reactions (i.e., Me_3SiH elimination) for low-temperature routes to AlP, AlAs, GaP, and GaAs nanoparticles.[9,10] Access to the trimethylamine solvated, toluene soluble inorganic salt $(Me_3NAl)_4S_6$ was obtained via dehydrosilylation of $H_3Al{\cdot}NMe_3$ and $(Me_3Si)_2S$.[11] Attempts to extend this method toward the synthesis of AlN using bistrimethylsilylamide and -amine complexes of aluminum hydride, $(Me_3Si)_2NAlH_2{\cdot}NMe_3$ or $H_3Al{\cdot}N(H)(SiMe_3)_2$, were unsuccessful so far.[12,13] Given that neither $H_3Al{\cdot}NMe_3$ nor $[Mes^*AlH_2]_2$ react with $(Me_3Si)_2O$ even at high temperatures and i-Bu_2AlH only at elevated temperatures (130 °C) in the absence of solvents, but readily with the cyclic siloxanes $[Me_2SiO]_3$ ($n = 3$, 4, 5),[14−16] we were interested to learn if such a difference in reactivity is also observed for the related silazanes. Herein we describe the initial results of our investigations of cyclic silazanes as substrates for the synthesis of novel silyl substituted aluminum hydrides and the thermolysis of two of the products.

Experimental Section

General Procedures. Due to the high oxygen and moisture sensitivity of the aluminum containing compounds discussed here, all reactions were performed in a dry, oxygen-free nitrogen atmosphere

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by using either modified Schlenk techniques or an Innovative Technologies drybox. Solvents were freshly distilled from sodium/potassium alloy. $H_3Al{\cdot}NMe_3$[17] was prepared according to literature procedures. $[Me_2SiNH]_3$ and $[Me_2SiNH]_4$ were purchased from Aldrich and used after vacuum distillation or sublimation. Infrared spectra were recorded in the range 4000−400 cm^{-1} as a Nujol mull between KBr plates using either a Bio-Rad FT-155 or a Nicolet Nexus 470 FTIR spectrometer. Unless otherwise noted NMR spectra were recorded at 20−23 °C on a Varian Unity Plus 400 MHz spectrometer. ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or C_7D_8 as internal reference (δ = 7.15 or 2.09 ppm). ^{13}C NMR spectra were referenced to the solvent signals (δ = 128.0 or 20.4 ppm). ^{27}Al NMR spectra were referenced to an aqueous $Al(NO_3)_3$ solution as external standard (δ = 0 ppm). TGA measurements of the compounds **1** and **3** were carried out with a DuPont Instruments 951 Thermogravimetric analyzer with a heating rate of 5 °C/min. The samples were loaded under N_2 atmosphere, the purge gas was helium. GC/MS data were obtained with a Finnegan GCQ spectrometer. Melting point determinations were performed in sealed glass tubes and are uncorrected.

Synthesis of 1,3,5-$(H_2Al{\cdot}NMe_3)_3(NSiMe_2)_3$ (1). A precooled (−50 °C) solution of $[Me_2SiNH]_3$ (0.82 g, 3.7 mmol) in toluene (30 mL) was added slowly to a solution of $H_3Al{\cdot}NMe_3$ (1.0 g, 11.2 mmol) in toluene (30 mL) at −50 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. After concentrating the solution in vacuo (20 mL), large colorless crystals were grown at −30 °C for one week. Concentration of the mother liquor and subsequent cooling for another week afforded a second batch of crystalline **1**. Yield: 1.27 g (72%). Mp: 148−150 °C (decomp). ^1H NMR (400 MHz, C_6D_6): 0.81 (s, $Si(CH_3)_2$, 18 H), 2.01 (s, $N(CH_3)_3$, 27 H), 4.2 (s, broad, AlH_2, 6 H). $^{13}C\{^1H\}$ NMR (C_6D_6): 9.95 ($Si(CH_3)_2$, 48.26 ($N(CH_3)_3$). $^{27}Al\{^1H\}$ NMR (104.22 MHz, C_6D_6): 140 (s, broad). $w_{1/2} \approx 8340$ Hz. IR (KBr, Nujol): ν_{AlH}= 1810 (m), 1790 (s), 1751 (m) cm^{-1}.

Synthesis of 1,1′,2,2′-$(HAlNMe_3)_2(\overline{NSiMe_2NSiMe_2N(H)SiMe_2})_2$ (3). A precooled (−50 °C) solution of $[Me_2SiNH]_3$ (0.94 g, 4.3 mmol) in toluene (30 mL) was added slowly to a solution of $AlH_3{\cdot}NMe_3$ (0.77 g, 8.6 mmol) in toluene (30 mL) at −50 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. After removal of the volatile materials under reduced pressure, the colorless solid was crystallized from benzene solution (15 mL) at room temperature for one week. Compound **3** was isolated as colorless needles. Yield: 550 mg (21%). Mp: 150 °C (decomp). ^1H NMR (C_7D_8): −0.02 (s, br, 1 H), 0.20 (s, br, 6 H), 0.22 (s, br 6 H), 0.34 (s, br, 6 H), 0.58 (s, br, 6 H), 0.70 (s, br,6 H), 1.05 (s, br, 3 H), 1.30 (s, br, 1 H), 2.03 (s, $N(CH_3)_3$, 18 H), 3.70 (s, br, AlH, 4 H). ^1H NMR (C_7D_8, 70 °C): 0.059 (s, br, NH, 2 H), 0.21 (s, 12 H), 0.47 (s, br, 12 H), 0.68 (s, 6 H), 1.07 (s, br, 6 H), 2.13 (s, $N(CH_3)_3$, 18 H), 3.7 (s, br, AlH, 2 H). $^{13}C\{^1H\}$ NMR (C_7D_8, 70 °C): 7.69 ($Si(CH_3)_3$), 9.73 ($Si(CH_3)_3$), 10.85 ($Si(CH_3)_3$), 11.05 ($Si(CH_3)_3$), 47.74 ($N(CH_3)_3$). $^{27}Al\{^1H\}$ NMR (C_7D_8, 104.22 MHz): 147 (s, broad), $w_{1/2}$ = 7160 Hz. $^{27}Al\{^1H\}$ NMR (C_7D_8, 104.22 MHz, 70 °C): 122 (s, broad), $w_{1/2}$ = 3960 Hz. IR (KBr, Nujol): ν_{NH}= 3368 (w) cm^{-1}, ν_{AlH}= 1798 (m) cm^{-1}.

Synthesis of 1,3-$(H_2Al{\cdot}NMe_3)_2(\overline{NSiMe_2NSiMe_2N(H)SiMe_2})$ (4). A precooled (−50 °C) solution of $[Me_2SiNH]_3$ (0.62 g, 2.8 mmol) in toluene (30 mL) was added slowly to a solution of $H_3Al{\cdot}NMe_3$ (0.5 g, 5.6 mmol) in toluene (30 mL) at −50 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The clear colorless reaction mixture was concentrated to ca. 30 mL and cooled to −28 °C for 2 days to give a small amount of crystals of **3**. Concentration of the mother liquor to ca. 20 mL and subsequent cooling for 3 days afforded small colorless crystals of **4**. Crystals suitable for X-ray diffraction were obtained by recrystallization from toluene at −28 °C. Yield: 250 mg (23%). Mp: 97−110 °C (decomp). ^1H NMR (400 MHz, C_6D_6): 0.56 (s, $Si(CH_3)_2$, 12H), 0.73 (s, $Si(CH_3)_2$, 6H), 1.93 (s, $N(CH_3)_3$, 18H), 4.1 (s, broad, AlH_2, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6): 7.20 ($Si(CH_3)_2$, 8.51 ($Si(CH_3)_2$, 47.72 ($N(CH_3)_3$). $^{27}Al\{^1H\}$ NMR (104.22 MHz, C_6D_6): 134 (s, broad), $w_{1/2} \approx 2330$ Hz. IR (KBr, Nujol): ν_{NH} = 3391(w) cm^{-1}, ν_{AlH} = 1803(m), 1788(m), 1767 (st) cm^{-1}.

Reactions of $H_3Al{\cdot}NMe_3$ with $[Me_2SiNH]_4$. Typically, a precooled (−50 °C) solution of $[Me_2SiNH]_4$ (0.58 g, 2.0 mmol) in hexanes (30 mL) was added slowly to a suspension of $H_3Al{\cdot}NMe_3$ (0.71 g, 8.0 mmol) in hexanes (30 mL) at −50 °C. The reaction mixture was held at −50 °C for 2−3 h, slowly warmed to room temperature, and stirred for an additional 8−10 h to give a clear colorless solution. Concentration under reduced pressure to ca. 30 mL and subsequent cooling to −28 °C afforded small amounts (ca. 100−150 mg) of crystalline solids. ^1H NMR spectra of these solids indicated the presence of several compounds. Crystals of $Al_5C_{22}H_{73}N_{10}Si_8{\cdot}C_6H_6$ (**5**) were obtained from recrystallization of a 20 mg sample of the crystalline first crop from C_6H_6 (2 mL) at room temperature by slow evaporation of the solvent inside the drybox. On one occasion the crystalline first crop contained a few crystals of sufficient quality for X-ray diffraction, one of which was characterized as $Al_6C_{22}H_{76}N_{10}Si_8{\cdot}$ 1/4 C_6H_{14} **(6)**.

Thermolysis Experiments. Schlenk tubes containing ca. 100 mg samples of compounds **1** or **3** were placed in a preheated 100 °C oilbath. The temperature was slowly (ca. 30 min) raised to 180−200 °C. After melting and subsequent gas evolution, the products solidified. Both thermolyzed products were practically insoluble in C_6D_6. An FTIR spectrum of the solid derived from **1** showed medium to strong bands in the Si−H (2127 cm^{-1}) and Al−H (1867 cm^{-1}) region, whereas the solid derived from **3** displayed no absorption in either region but two weak N−H stretches at 3367 and 3406 cm^{-1}. Condensable volatile materials formed during the thermolysis of **3** were trapped in a −78 °C Schlenk flask, dissolved in C_6D_6, and analyzed by ^1H NMR spectroscopy and GC/MS. The ^1H NMR spectrum showed signals due to toluene, Me_3N (2.05 ppm), and an unidentified singlet at 0.42 ppm. The presence of Me_3N was confirmed by GC/MS (m/z = 58.1, 100%, ($Me_2N{=}CH_2^+$)).

For the solution studies, samples of ca. 15 mg of **1** or **3** in 0.5 mL of C_7D_8 in sealed NMR tubes were heated to 110−120 °C for 18 h. Compound **3** remained essentially unchanged, whereas the formation of a gray, spongy precipitate was observed for **1**. An ^1H NMR spectrum of the supernatant clear, colorless solution showed that **1** was mostly consumed and the spectrum displayed a variety of broad signals in the Me−Si region (0.7−0.0 ppm), a broad singlet for Me_3N (2.05 ppm) and broad signals in the Si−H and Al−H region (3.5−5.5 ppm). A small amount of Me_2SiH_2 (−0.01 ppm (t, CH_3), $^3J_{HH}$= 4.1 Hz, 3.90 ppm (sept, SiH))[18,19] was also detected.

X-ray Structure Determinations. Crystals were removed from the Schlenk tube under a stream of N_2 gas and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[20] The data were collected in the range of 158 and 183 K (see Table 1) with a Siemens P4 diffractometer using Mo Kα (λ = 0.71073 Å) radiation. The data were corrected for Lorentz and polarization effects. Absorption corrections were not applied because it was judged to be insignificant. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using all reflections. The crystallographic programs employed were those of the SHELXTL program suite.[21] In the final refinement cycles all the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included in the refinement with idealized parameters except of those bound to aluminum or nitrogen, which were located in the difference map and refined isotropically. Some details of the data collections and refinements are given in Table 1, and selected bond distances and angles are listed in Tables 2 and 3. Further details are given in the Supporting Information.

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Table 1. Crystallographic Data for **1** and **3**−**6**

	1	**3**	**4**	**5**	**6**
formula	$Al_3C_{15}H_{51}N_6Si_3$	$Al_2C_{18}H_{58}N_8Si_6$	$C_{12}H_{41}Al_2N_5Si_3$	$Al_5C_{22}H_{73}N_{10}Si_8 \cdot C_6H_6$	$Al_6C_{22}H_{76}N_{10}Si_8 \cdot 1/4C_6H_{14}$
fw	480.83	609.22	393.73	915.63	889.07
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
temp, K	163(2)	158(2)	173(2)	178(2)	183(2)
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	triclinic
space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*-1	*P*2(1)2(1)2	*P*-1
a, Å	18.229(2)	12.595(2)	8.4452(9)	21.991(2)	13.094 (2)
b, Å	12.341(2)	8.742(2)	12.068(2)	13.937(2)	13.111 (3)
c, Å	13.340(2)	16.023(3)	12.949(2)	17.5586(10)	16.595 (3)
α, deg	90	90	70.669(13)	90	75.199 (14)
β, deg	96.906(7)	96.59(2)	79.541(10)	90	82.330 (130)
γ, deg	90	90	73.873(11)	90	86.94 (2)
V, $Å^3$	2979.4(6)	1752.5(5)	1190.5(3)	5381.7(8)	2729.3 (8)
Z	4	2	2	4	2
$\delta_{calcd.}$, g cm^{-3}	1.072	1.154	1.098	1.130	1.082
μ, mm^{-1}	0.260	0.310	0.277	0.312	0.320
R1[a], %	3.41	4.26	5.13	4.18	6.14
wR2[b], %	8.70	10.42	13.30	9.71	15.81

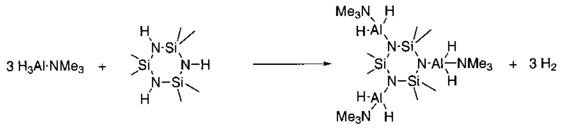
[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) for Compounds **1**, **3**−**6**

1		**3**		**4**		**5**		**6**	
Al(1)−N(1)	1.8221(14)	Al(1)−N(3)	1.846(2)	Al(1)−N(1)	1.824(3)	Al(1)−N(1)	2.004(3)	Al(1)−N(1)	1.841(3)
Al(1)−N(4)	2.035(2)	Al(1)−N(2A)	1.847(2)	Al(1)−N(4)	2.031(3)	Al(1)−N(5)	2.148(3)	Al(1)−N(9)	1.894(3)
Al(1)−H(1)	1.50(2)	Al(1)−N(4)	2.051(3)	Al(1)−H(1)	1.53(4)	Al(1)−H(1)	1.40(4)	Al(1)−H(3)	1.57(4)
Al(1)−H(2)	1.54(2)	Al(1)−H(1)	1.55(3)	Al(1)−H(2)	1.45(4)	Al(2)−N(1)	1.951(3)	Al(1)−N(10)	2.049(3)
Al(2)−N(2)	1.8436(13)			Al(2)−N(2)	1.836(2)	Al(2)−N(2)	1.839(4)	Al(2)−N(2)	1.840(3)
Al(2)−N(5)	2.054(2)			Al(2)−N(5)	2.055(3)	Al(2)−N(5)	1.866(3)	Al(2)−N(9)	1.932(3)
Al(2)−H(3)	1.58(2)			Al(2)−H(3)	1.52(3)	Al(2)−H(2)	1.49(6)	Al(2)−H(4)	1.41(4)
Al(2)−H(4)	1.49(2)			Al(2)−H(4)	1.47(3)	Al(3)−N(3)	1.840(4)	Al(2)−H(5)	1.73(4)
Al(3)−N(3)	1.8238(13)					Al(3)−N(5)	1.893(3)	Al(3)−N(3)	1.936(3)
Al(3)−N(6)	2.026(2)					Al(3)−N(4)	2.014(4)	Al(3)−N(9)	1.908(3)
Al(3)−H(5)	1.51(2)					Al(3)−H(3)	1.53(4)	Al(3)−H(6)	1.49(4)
Al(3)−H(6)	1.54(2)							Al(3)−H(7)	1.58(5)
								Al(4)−N(3)	1.970(3)
								Al(4)−N(4)	2.093(3)
								Al(4)−H(5)	1.78(4)
								Al(4)−H(8)	1.67(4)
								Al(5)−N(7)	1.870(3)
								Al(5)−N(8)	1.994(3)
								Al(5)−H(9)	1.58(4)
								Al(6)−N(6)	1.852(4)
								Al(6)−N(4)	1.888(3)
								Al(6)−N(5)	2.035(3)
								Al(6)−H(10)	1.52(4)

Results and Discussion

Syntheses and Structures. The reaction of $H_3Al \cdot NMe_3$ with hexamethylcyclotrisilazane $[Me_2SiNH]_3$ in a 3:1 molar ratio at low temperature in toluene solution proceeds cleanly and essentially quantitatively to afford the tris-aluminum amide 1,3,5-$(H_2Al \cdot NMe_3)_3(NSiMe_2)_3$ **(1)** via hydrogen elimination (eq 1). Due to its high solubility the isolated crystalline yield is only about 72%.



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(1)

Compound **1** is highly sensitive toward moisture but is stable under oxygen- and moisture-free conditions in the solid state as well as in solution. The structure of **1** (Figure 1) features a six-membered Si_3N_3 ring, in which each nitrogen is bound to a $H_2Al \cdot NMe_3$ group. The ring is puckered and displays a chair conformation similar to that of the parent silazane, $[Me_2SiNH]_3$, in the gas phase.[22] The $H_2Al \cdot NMe_3$ groups are rotated away from each other in such a way that two NMe_3 groups point up and the third one down when viewed with respect to the Si_3 plane. The metric parameters are within the expected ranges for amine stabilized aluminum amides with average Al−N(amide), Al−N(amine), Al−H and Si−N distances of 1.830(10), 2.038(12), 1.53(3), and 1.735(5) Å, respectively.[13,23,24] The amide nitrogen atoms N(1), N(2), and N(3) are basically planar (Σ(Si−N−Si,Al) = 357.6°, 355.4°, and 358.6°) as is typical for a nitrogen atom bound to three electropositive atoms.[25]

Interestingly, attempts to substitute only one or two of the three amine hydrogens of the silazane $[Me_2SiNH]_3$ were less straightforward and afforded clean products only in low to moderate yields. Treatment of $[Me_2SiNH]_3$ with 1 equiv of

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Table 3. Selected Bond Angles (deg) for Compounds **1** and **3**−**6**

1		**3**		**4**		**5**		**6**	
Si(1)−N(1)−Si(2)	114.57(7)	Si(2)−N(1)−Si(1)	133.5(2)	Si(1)−N(1)−Si(2)	115.41(14)	Si(1)−N(1)−Si(2)	126.0(2)	Si(1)−N(1)−Si(2)	120.1(2)
Si(1)−N(1)−Al(1)	124.40(7)	Si(2)−N(1)−H(2)	114(3)	Si(1)−N(1)−Al(1)	118.83(13)	Si(1)−N(1)−Al(2)	135.2(2)	Si(1)−N(1)−Al(1)	111.2(2)
Si(3)−N(2)−Si(2)	117.61(7)	Si(1)−N(1)−H(2)	113(3)	Si(2)−N(1)−Al(1)	125.54(14)	Si(2)−N(2)−Si(3)	150.0(2)	Si(2)−N(1)−Al(1)	128.8(2)
Si(2)−N(2)−Al(2)	120.95(7)	Si(2)−N(2)−Si(3)	111.10(13)	Si(2)−N(2)−Si(3)	114.24(13)	Si(2)−N(2)−Al(2)	92.7(2)	H(4)−Al(2)−H(5)	113(2)
Si(1)−N(3)−Si(3)	114.08(7)	Si(2)−N(2)−Al(1A)	122.72(13)	Si(2)−N(2)−Al(2)	123.76(13)	Si(3)−N(2)−Al(2)	116.8(2)	H(4)−Al(2)−H(5)	113(2)
Si(1)−N(3)−Al(3)	125.14(7)	Si(3)−N(2)−Al(1A)	123.60(13)	Si(3)−N(2)−Al(2)	121.39(14)	Si(4)−N(3)−Si(3)	120.9(2)	H(5)−Al(4)−H(8)	86(2)
H(1)−Al(1)−H(2)	114.9(12)	Si(1)−N(3)−Si(3)	110.76(13)	Si(1)−N(3)−Si(3)	128.8(2)	Si(4)−N(3)−Al(3)	116.1(2)	N(8)−Al(5)−H(9)	131.0(13)
H(3)−Al(2)−H(4)	115.8(11)	Si(1)−N(3)−Al(1)	135.88(14)	H(1)−Al(1)−H(2)	111.6(25)	Si(3)−N(3)−Al(3)	122.5(2)	N(4)−Al(5)−H(9)	123.3(14)
H(5)−Al(3)−H(6)	114.0(12)	Si(3)−N(3)−Al(1)	113.36(12)	H(3)−Al(2)−H(4)	117.3(31)	N(1)−Al(1)−N(1A)	131.0(2)	N(7)−Al(5)−N(8)	83.40(14)
						N(5)−Al(1)−N(5A)	143.0(2)	Si(3)−N(2)−Si(2)	137.4(2)
						N(2)−Al(2)−H(2)	119(2)	Si(3)−N(2)−Al(2)	114.7(2)
						N(5)−Al(2)−H(2)	123(2)	Si(2)−N(2)−Al(2)	107.7(2)
						N(1)−Al(2)−H(2)	118(2)	Si(7)−N(7)−Si(6)	147.9(2)
						N(2)−Al(2)−N(5)	108.3(2)	Si(7)−N(7)−Al(5)	94.4(2)
								Si(6)−N(7)−Al(5)	116.5(2)

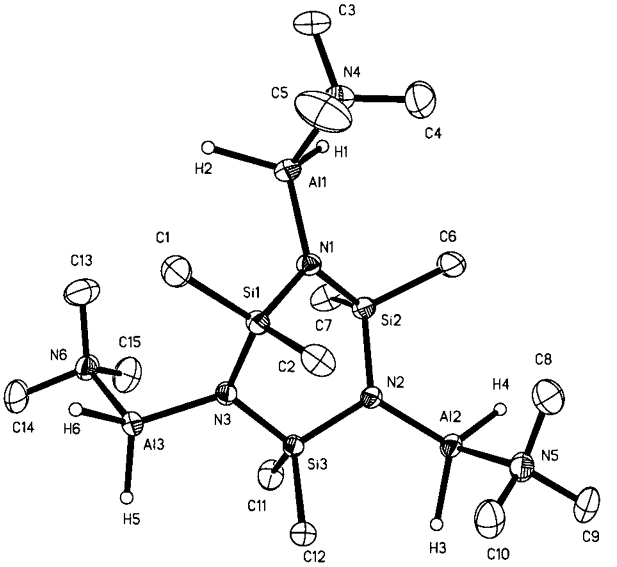
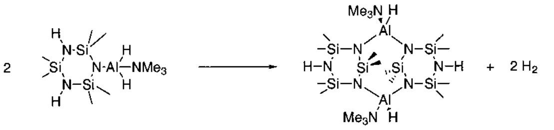


Figure 1. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **1**. Methyl hydrogen atoms are omitted for clarity.

$H_3Al{\cdot}NMe_3$ did not lead to the expected monosubstituted product $[(Me_2SiNH)_2Me_2SiNAlH_2{\cdot}NMe_3]$ (**2**) but to the tricyclic aluminum-bridged compound **3** instead, most likely by condensation of two molecules of **2** (eq 2).



(2)

2 **3**

Large, well-shaped crystals of **3** were obtained by crystallization from benzene solution. Higher yields of **3** can be obtained if the alane/silazane ratio is increased to 3:2. The structure of **3** was determined by X-ray crystallography. Compound **3** crystallizes in the form of centrosymmetric molecules in which two silazane rings are bridged by two μ-$HAl{\cdot}NMe_3$ groups (Figure 2). Contrary to compound **1**, in **3** the silazane rings adopt a boat conformation whereas the central eight-membered $Al_2Si_4N_4$ ring exists in a chairlike conformation with the aluminum bound trimethylamine ligands trans to each other. The Al−N(amide), Al−N(amine), Al−H, and Si−N distances in **3** with average values of 1.846(2), 2.051(3), 1.55(3), and 1.732(10) Å are similar to those observed in **1**. The coordination around the amide nitrogen atoms is distorted trigonal planar (Σ(Si−N−Si,Al,H) = 360.5°, 357.4°, and 360.0°). The widest internal angle Si−N−Si is observed for the hydrogen substituted N(1) with 133.5(2)°. ^1H NMR spectra of C_6D_6 or C_7D_8 solutions of **3** display broad signals for the SiMe protons indicating dynamic behavior. Heating to 70 °C causes some of these peaks to sharpen.

If an alane/silazane ratio of 2:1 is employed for the intended synthesis of the disubstituted silazane $[(Me_2SiNH)(Me_2SiNAlH_2{\cdot}NMe_3)_2]$ **(4)**, a mixture of two as yet unidentified compounds is formed initially. Repeated crystallizations afford small quantities of **3**, and compound **1** can be identified in the mother liquor. On one occasion crystals have been isolated whose spectroscopic data (^1H, $^{13}C\{^1H\}$, ^{27}Al NMR and FTIR) are in agreement with those expected for the disubstituted species **4**. A possible explanation for the observed difficulties in isolating **4** may be found in ligand exchange processes such as eq 3,

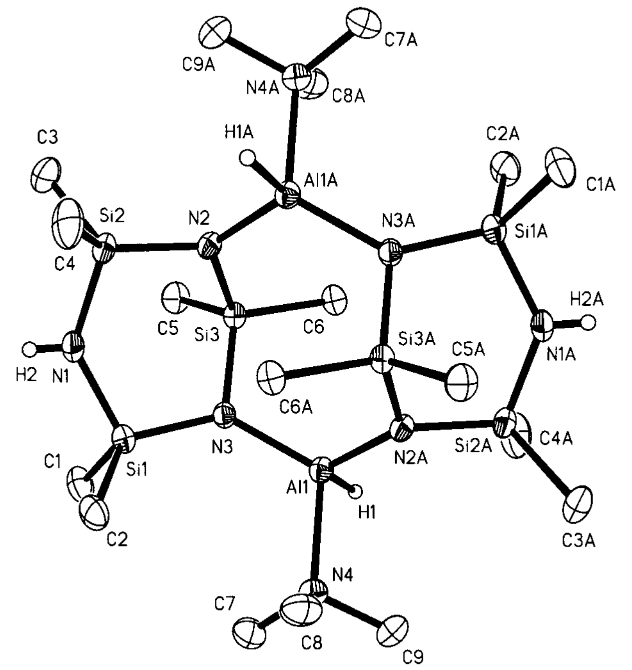
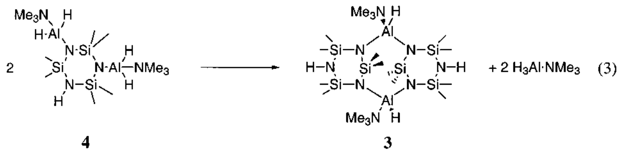


Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **3**. Methyl hydrogen atoms are omitted for clarity.

which are typical for aluminum compounds.[1] The low solubility of **3** in aromatic solvents would then shift the equilibrium toward the formation of **3** and $H_3Al{\cdot}NMe_3$.



(3)

The structure of **4** was confirmed by X-ray crystallography. It is similar to that of **3** without the second silazane ring (Figure 3). The silazane core adopts a twist-boat conformation with the $AlH_2{\cdot}NMe_3$ groups rotated around the Al−N(amide) bond in such a way that the Me_3N groups are oriented in a mutual trans fashion. The geometry around the amide nitrogens is distorted trigonal planar (Σ(Si−N−Si,Al,H) = 359.8°, 359.4°, and 360.0°). The widest internal angle within the silazane ring is found at N(3) with Si(1)−N(3)−Si(3) = 128.8(2)°. Bonding to aluminum decreases the internal ring angles at the amide nitrogens N(1) and N(2) to 115.41(14)° and 114.24(13)° while at the same time widening the external Si−N−Al angles to 118.83(13)−125.54(14)°. The average Al−N(amide), Al−N(amine), and Al−H distances with 1.830(5), 2.043(5), and 1.49(6) Å are within the expected range.

Given our success in forming the new compounds **1**, **3**, and **4** starting from the trimeric silazane $[Me_2SiNH]_3$, we decided to extend this method to include the larger more flexible tetrameric octamethylcyclotetrasilazane $[Me_2SiNH]_4$. Unfortunately, we have not been able to isolate simple aluminum hydride derivatives of this silazane. In addition to the expected formation of Al−N bonds by H_2 elimination, there is also a facile cleavage of Si−N bonds by the Al−H moiety to give Al−N and Si−H bonds at or even below room temperature. The Si−H group can be easily detected in the NMR and IR spectra of the crude products as sharp multiplets in the range of 5.4−4.6 ppm as well as a medium intensity band around 2100 cm^{-1}. This additional pathway of Al−N formation together with the high flexibility of the eight-membered silazane ring and possible exchange processes similar to those in eqs 2 and 3 may account for the observed difficulty in obtaining pure products. Nevertheless, we have been able to isolate small amounts of crystalline material from various fractions of our recrystallization attempts. In general, these crystalline fractions were mixtures of compounds. In a few cases, however, this crystalline material contained single crystals which were characterized as the novel aluminum amide species **5** and **6** by X-ray crystallography. Unfortunately, despite our efforts, we have not been able to isolate either compound in sufficient quantities for analysis other than XRD. However, repeated attempts have shown that it appears to be essential to mix the reagents at low temperature (ca. −50 °C) and maintain this temperature for several hours before warming to room temperature for workup. Variation of the alane/silazane ratio from 4:1 to 2:1 does not seem to significantly affect the outcome. However, it should be pointed out that dehydrosilylation of silylamines with aluminum hydrides is rare at low temperatures[24] and compounds **5** and **6** are only the second and third examples of products obtained by this type of reaction that were characterized by X-ray crystallography.

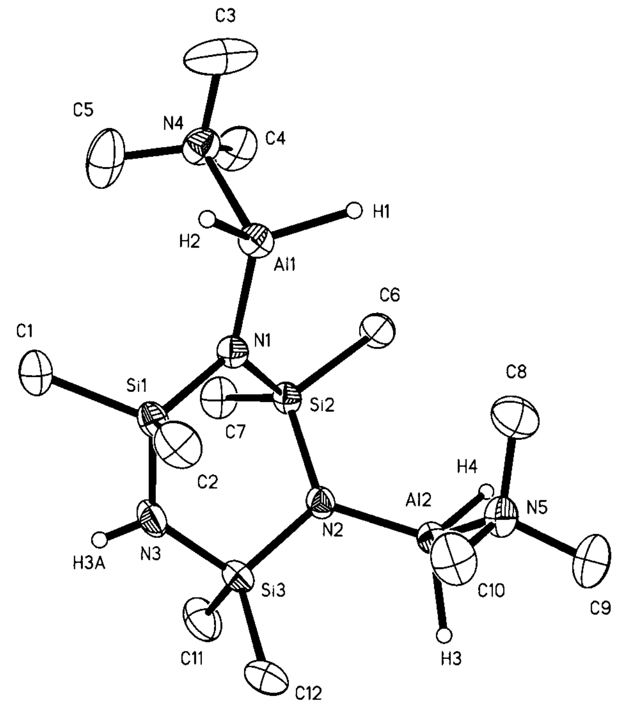


Figure 3. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **4**. Methyl hydrogen atoms are omitted for clarity.

The structures of **5** and **6** (Figures 4 and 5) are closely related to each other. Both compounds are best described as consisting of a unique 16-membered $Al_2Si_6N_8$ macrocyle in which the silazane nitrogen atoms, with the exception of N(3) and N(3a) in **5** and N(1) and N(6) in **6**, are bound to bridging aluminum hydride to generate six four- and six-membered AlSiN rings. The asymmetric unit of a crystal of **5** contains two independent half-molecules of **5** and two independent half-molecules of benzene. The two halves of each molecule of **5** are related by a 2-fold rotational axis through the central Al−H group (Al(1)−H(1), Al(4)−H(4)). Both molecules are essentially identical, and for simplicity the discussion will focus on the molecule containing Al(1). Al(1) is five-coordinate in a slightly distorted square pyramidal fashion to one hydrogen and four amide nitrogen atoms. The Al(1)−H(1) distance (1.40(4)) is

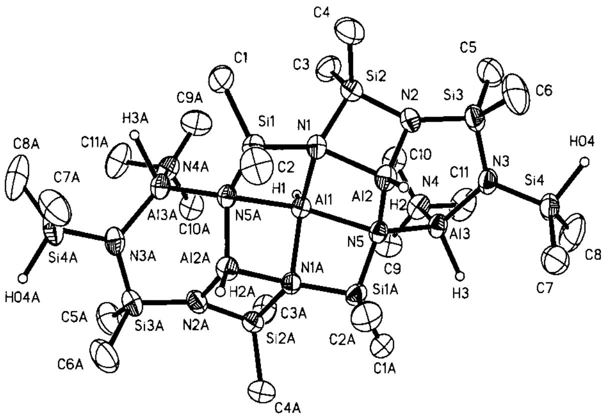


Figure 4. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **5**. Methyl hydrogen atoms are omitted for clarity.

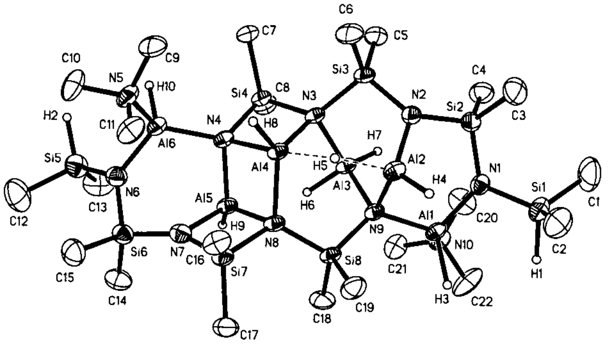


Figure 5. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **6**. Methyl hydrogen atoms are omitted for clarity.

quite short, whereas the Al−N distances appear elongated with 2.004(3) Å (Al(1)−N(1)) and 2.148(3) Å (Al(1)−N(5)). A similar arrangement with, however, less variation of the Al−N distances was reported for the core of HAl[(EtN(CH$_2$)$_2$NEt)-AlH$_2$]$_2$.[26] Al(2) and Al(2a) are four-coordinate in a distorted tetrahedral arrangement. The Al(2)−H(2) distance is 1.49(6) Å and the Al(2)−N distances range from 1.839(4) (N(2)) Å over 1.866(3) (N(5)) Å to 1.951(3) (N(1)) Å. The amide nitrogens N(2), N(2a), N(3), and N(3a) at the periphery of the molecule are three-coordinate with essentially planar geometry (Σ(Al,Si−N−Si,Al) = 359.5° and 359.5°) and feature shorter Al−N distances with Al(3)−N(3) = 1.840(4) Å and Al(2)−N(2) = 1.839(4) Å. Interestingly, the environment at N(2) is quite irregular, almost T-shaped with a significant widening of the Si(2)−N(2)−Si(3) angle to 150.0(2)°, presumably due to the contraints related to the inclusion of N(2) into the four-membered ring formed by N(2), Al(2), N(1), and Si(2).

The structure of **6** can be formally derived from that of **5** by simply adding one molecule of AlH$_3$. The framework of **6** remains essentially the same as in **5** but the μ_3-Al(2)−H(2) unit has been replaced by two μ_2-AlH$_2$ groups (Al(2), Al(3)). A very unusual feature is the location of the hydride H(5) as an almost perfectly symmetrical bridge between the five-coordinate (trigonal bipyramidal) Al(4) and the four-coordinate (tetrahedral) Al(2). The Al−H distances of 1.73(4) Å for Al(2)−H(5) and 1.78(4) Å for Al(4)−H(5), however, are typical for μ_2-bridging aluminum hydrides.[27] The other metrical data are similar to those observed for **5** and some are listed in Tables 2 and 3.

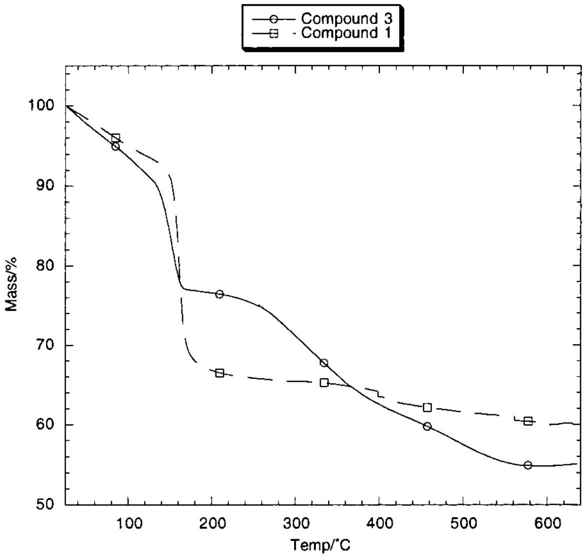
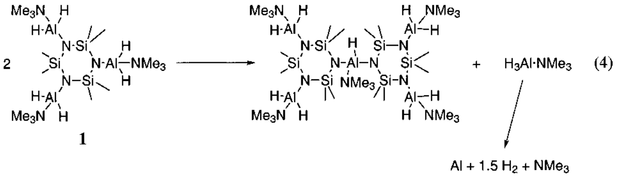


Figure 6. TGA traces of **1** and **3**.

Thermal Stability. The present study of the synthesis of aluminum hydride derivatives of cyclic silazanes was undertaken with the intent to find new low-temperature routes to AlN. Therefore, the thermal stability of compounds **1** and **3**, which can be synthesized in gram quantities, was investigated both in solution and in the solid state. Solutions of compounds **1** and **3** in toluene can be heated to reflux without detectable decomposition. However, prolonged heating (18 h) of a C$_7$D$_8$ solution of **1** in a sealed NMR tube to ca. 120 °C leads to the formation of a gray, spongy precipitate, which we assume is aluminum metal in analogy to the results obtained by Paine and co-workers.[12] NMR spectra of the supernatant liquid display, besides the signals of **1**, broadened signals in the SiMe region indicating formation of larger aggregates. A possible explanation may be ligand exchange processes with concomitant formation of H$_3$Al·NMe$_3$ which decomposes at temperatures in excess of 100 °C[28] (eq 4). A similar process was suggested for the thermal decomposition of the related (Me$_3$Si)$_2$NAlH$_2$·NMe$_3$.[12]



In addition, a small amount of Me$_2$SiH$_2$ is formed. In the solid state, both **1** and **3** are stable until their melting points of 148 and 150 °C, at which both decompose with gas evolution. However, no aluminum metal formation is observed. TGA experiments in the range of 23−620 °C show the loss of NMe$_3$ at about 150 °C for both compounds (Figure 6). Thereafter, **1** remains virtually unchanged until 620 °C, whereas for **3**, additional mass loss of ca. 24% is recorded.

Bulk thermolysis of ca. 100 mg samples of **1** and **3** at 180−200 °C afforded colorless solids. Trimethylamine, traces of toluene, and an as yet unidentified species were detected in the trapped (−78 °C) volatile fraction of the thermolysis of **3** using ^{1}H NMR spectroscopy and GC/MS. IR-spectra of the remaining solids show intense Si−H and Al−H (2127 and 1867 cm^{-1}) bands for the thermolysis product of **1** and no Al−H(term.) band

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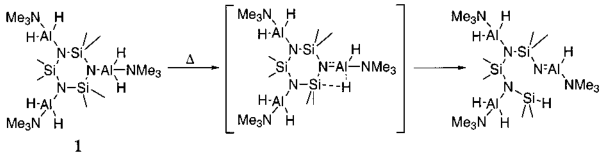
for the thermolysis product of **3**. Both solids are only sparingly soluble in C_6D_6 and display broad signals in the SiMe region.

The crystal structure of **1** indicates that Me_2SiH elimination should be facile, given the relative closeness of Me_2Si and Al−H (e.g., H(3)···Si(3) = 3.08 Å) and the possibility that the putative intermediate should be stabilized sufficiently by the Me_3N donor (eq 5).



(5)

1

Nevertheless, the temperatures required are still in excess of 150 °C and elimination of the remaining Me_2Si groups does not take place below 620 °C (see Figure 6). A similar high temperature requirement was noted for Mes*Al(H)N$(SiMe_3)_2$,[29] which also featured a geometry conducive to facile Me_3SiH elimination. On the other hand, the Si−H formation even below room temperature in the $H_3Al·NMe_3/[Me_2SiNH]_4$ system shows that there are accessible low energy pathways for this reaction. Extensive studies by Interrante and Sauls et al. have found that amines catalyze the thermolytic decomposition of aluminum amides $[R_2AlNH_2]_n$ to imides $[RAlNH]_n$ and finally AlN.[5,30,31] A similar process may be at work in the $H_3Al·NMe_3/[Me_2SiNH]_4$ system with the possible exception that the catalyzing amine is of intermolecular origin. The only other well documented Me_3SiH elimination at low temperature also involves a flexible bidentate ligand.[24]

Conclusion

Reaction of $H_3Al·NMe_3$ with $[Me_2SiNH]_3$ afforded new aminolysis products **1**, **3**, and **4** in good to moderate yields. Employment of the larger and more flexible cyclosilazane $[Me_2SiNH]_4$ led to complex mixtures from which the crystalline ring cleavage compounds **5** and **6** could be isolated. While thermolysis studies of **1** and **3** indicate onset of dehydrosilylation at moderately high temperatures of 150 °C, this is accompanied by loss of trimethylamine and formation of larger aggregates. Further significant mass loss was not observed for **1** below 620 °C, and some loss is observed for **3**. Dehydrosilylation already at or below room temperature is observed for the $[Me_2SiNH]_4/H_3Al·NMe_3$ system suggesting alternative low-energy pathways. We are currently investigating this system in more detail and plan to include additional silazanes such as $[Me(H)SiNH]_4$[32] or $(MeSi)_6(NH)_9$[33] into our studies.

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Supporting Information Available: Five X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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