

Reactions of Tris[bis(trimethylsilyl)amino]aluminum with Ammonia and Pyrolysis Studies

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[[$(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$]₂ (1) and [[$(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2$]₃Al (2) were prepared from reaction of ammonia with $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ in 1:1 and 1:2 mole ratios, respectively. The structures were established by molecular weight, NMR and infrared spectroscopy, and single-crystal X-ray diffraction analysis. [[$(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$]₂: monoclinic, $P2_1/c$, $Z = 4$, $a = 9.162$ (2) Å, $b = 14.580$ (3) Å, $c = 34.444$ (5) Å, $\beta = 94.94$ (1)°, $V = 4584$ (2) Å³. The structure shows the presence of a central, planar, approximately square, four-membered ring. Al(1)-N(1)-Al(2)-N(2) with Al(1)-N(1) = 1.944 (5) Å, Al(1)-N(2) = 1.926 (5) Å, Al(1)-N(1)-Al(2) = 95.3 (2)°, N(1)-Al(1)-N(2) = 84.2 (2)°. [[$(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2$]₃Al: monoclinic $C2/c$, $Z = 8$, $a = 25.993$ (3) Å, $b = 15.092$ (2) Å, $c = 41.084$ (5) Å, $\beta = 107.49$ (1)°, $V = 15373$ (4) Å³. The structure features a central hexacoordinate Al atom joined to three tetracoordinate Al atoms by NH_2 bridges. Thermolysis of 1 at 225 °C gave pentane-soluble $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$ characterized by mass balance data, molecular weight, and NMR and infrared spectroscopy. Pyrolysis of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$ both in vacuo and under ammonia failed to give pure AlN; silicon and carbon were retained. Thermolysis of 2 at 200 °C resulted in a loss of $5\text{HN}(\text{SiMe}_3)_2$; this process was unaffected by the presence of ammonia. Further pyrolysis in an inert atmosphere gave $6\text{AlN}\cdot\text{Si}_3\text{N}_4$; AlN was formed in ammonia.

Introduction

Aluminum nitride, in view of its high thermal conductivity, among other desirable properties, is of interest in electronic applications, in particular in packaging of electronic microcircuits.¹ Having a processable ceramic precursor to a degree determines stoichiometry and simplifies greatly the manufacturing process. The general benefits of preceramic precursors have been discussed.^{2,3} For nitride ceramics, such as aluminum nitride and boron nitride, it is of importance to have nitrogen incorporated in the preceramic material and to have substituents that provide for readily formed volatile leaving groups. In aluminum nitride, these aspects have been addressed⁴⁻⁷ by ammonolysis of soluble aluminum compounds or by introducing additional nitrogen sources into the molecule, as exemplified by the dialkylaluminum azide system.⁸

Carbon retention is one of the persistent problems in the transformation of organometallics into carbon-free ceramics.^{3,9} Absence of metal-carbon bonds minimizes this problem, as was shown by the utilization of (tri-

methylsilyl)amino substituents in the boron nitride synthesis.^{10,11} It is well established that reactions of trialkylalanes with ammonia lead to adducts and amino- and imino-substituted alanes.^{12,13} Whether the amino compounds are formed via the adducts¹³ or by a competing process is arguable.¹⁴ We report here the study of reactions of ammonia with $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$, the objective of which was to produce ceramic precursors.

Experimental Section

General Procedures. Operations were carried out in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo. Infrared spectra were recorded on a Perkin-Elmer Model 1330 infrared spectrophotometer; solids as double mulls (Kel-F oil No. 10 and Nujol); liquids as capillary films; gases in 10-cm cells. Molecular weights were determined in benzene by using a Mechrolab Model 302 vapor pressure osmometer. The mass spectra (EI) were obtained from a Du Pont Model 21-491B spectrometer using a heated solids probe. The spectrometer was attached to a Varian Aerograph Model 2700 gas chromatograph equipped with a flame-ionization detector and a Du Pont 21-094 data acquisition and processing system. Gas chromatography was performed by employing a 10 ft \times 1/8 in. stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G and using a programming rate of 8 °C/min from 50 to 300 °C. NMR spectra were recorded on a Varian VXR-200 superconducting spectrometer using C_6D_6 as solvent and TMS

(1) Baker, R. T.; Bolt, J. D.; Reddy, G. S.; Roe, D. C.; Staley, R. H.; Tebbe, F. N.; Vega, A. J. In *Mater. Res. Soc. Symp. Proc.*; Brinker, C. J.; Clark, D. E.; Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, 1988; Vol. 121, p 471.

(2) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* 1984, 14, 297.

(3) Seyferth, D.; Wiseman, G. H.; Schwark, J. M.; Yu, Y. F.; Poutasse, C. A. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 143-155.

(4) Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W.; Garbaskas, M.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* 1986, 73, 359.

(5) Interrante, L. V.; Sigel, G. A.; Garbaskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* 1989, 28, 252.

(6) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* 1987, 26, 4341.

(7) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* 1988, 27, 4335.

(8) Boyd, D. C.; Haasch, R. T.; Mantell, D. R.; Schultze, R. K.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* 1989, 1, 119.

(9) Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci.* 1986, 24, 173.

(10) Paciorek, K. J. L.; Harris, D. H.; Krone-Schmidt, W.; Kratzer, R. H. In *Ultrastructure Processing of Advanced Ceramics*; MacKenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988, p 89.

(11) Paciorek, K. J. L.; Krone-Schmidt, W.; Harris, D. H.; Kratzer, R. H.; Wynne, K. J. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; p 372.

(12) Bahr, G. (Work by Wiberg, E.) In *Inorganic Chemistry, Part 2*; FIAT Review of WWII German Science; Klemm, W., Ed.; Dieterich'sche Verlagsbuchhandlung, Wiesbaden, FGR, 1948; Vol. 24.

(13) Mole, T.; Jeffrey, E. A. *Organoaluminum Chemistry*; Elsevier: New York, 1972.

(14) Beachley, O. T.; Tessier-Youngs, C. *Inorg. Chem.* 1979, 18, 3188.

as an external standard. Thermal gravimetric analyses were carried out in nitrogen from room temperature to 1000 °C at 10 °C/min with a Du Pont 990/951 system. X-ray diffraction patterns were obtained with a Philips PW 1710 automated powder diffractometer, using Cu K α radiation. Energy-dispersive X-ray analyses were obtained on a JEOL JSM 840-II scanning electron microscope at 20 keV. Vacuum-line techniques were utilized where applicable; volatile products were separated by fractional condensations and quantified and identified by a combination of volume measurement, quantitative infrared spectral analysis, and GC/MS. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Results of these analyses are generally poor but are nevertheless given here to show how poor they can be and to save other investigators in this ceramic precursor area the frustration of not being able to obtain acceptable data on otherwise unambiguously characterized materials such as compounds 1 and 2. Resistance to combustion is one characteristic of ceramics, and this seems to also apply to their precursors where during combustion the possibility of formation of a ceramic, especially a carbide, exists.

Materials. Ammonia (Matheson Gas Products) was purified by trap-to-trap distillation and dried over potassium. Al[N(SiMe₃)₂]₃ was prepared as described in the literature.¹⁵ All the solvents were rigorously dried with appropriate drying agents and degassed.

Reaction of Al[N(SiMe₃)₂]₃ and NH₃ in a 1:1 Ratio. With use of a vacuum line, a stirred, degassed solution of Al[N(SiMe₃)₂]₃ (2.08 g, 4.09 mmol) in heptane (18.33 g) was exposed at room temperature to ammonia (4.46 mmol) over 21 h. Specifically, the premeasured quantity of ammonia, in an ampule, was allowed to warm slowly from -196 °C to room temperature, and as the ammonia was volatilized, it was absorbed by the reaction mixture. Thus, the pressure in the system never reached 1 atm. After the 21 h of exposure, the volatiles, collected by evaporation in vacuo, consisted of heptane, hexamethyldisilazane (0.42 g, 2.60 mmol), and ammonia (<0.11 mmol). From the involatile solid residue, the starting material was removed by sublimation in vacuo at 110 °C. The sublimation residue (0.65 g, 43.6% yield, based on Al[N(SiMe₃)₂]₃ originally employed) was crystallized from hexanes, producing fine, colorless needles of [(Me₃Si)₂N]₂Al(NH₂)₂, mp 219–221 °C (dec). The material was stable in air. Anal. Calcd for C₂₄H₇₆Al₂N₆Si₈: C, 39.62; H, 10.53; Al, 7.42; N, 11.55; MW, 727.56. Found: C, 32.22; H, 9.61; Al, 7.08; N, 10.24; MW, 740 (by osmometry in benzene). IR (cm⁻¹, Kel-F/Nujol mull) 3415 (m, sh), 3396 (m, sh), 3357 (w), 3335 (w), 2948 (m), 2899 (w), 1263 (s), 1246 (s), 920 (s, br), 873 (s, br), 852 (s, br), 835 (s, br), 757 (m), 671 (s), 619 (m); MS (70 eV) *m/e* (rel intensity, ion) 726 (9%, M), 711 (28%, M - Me), 550 (100%, M - Me - (Me₃Si)₂NH), 348 (53%, (Me₂Si)Me₃SiNAlN(SiMe₃)₂NH₂), 275 (51%, (Me₃Si)₂NAl(NH₂)NSiMe₃), 203 (30%, (Me₃Si)₂NAl(NH₂), 146 (67%, (Me₂Si)Me₃SiNH), 130 (44%, (MeSi)Me₃SiN), 73 (53%, Me₃Si); ¹H NMR (C₆D₆) δ 0.47 (Me₃Si, 36 H), 1.75 (NH, 2 H).

Reaction of Al[N(SiMe₃)₂]₃ and NH₃ in a 1:2 Ratio. A stirred, degassed solution of Al[N(SiMe₃)₂]₃ (9.73 g, 19.1 mmol) in heptane (76.77 g) was exposed at room temperature to ammonia (38.5 mmol) over a period of 18 h. The volatiles collected by evaporation in vacuo consisted of heptane, hexamethyldisilazane (4.30 g, 27.2 mmol), and ammonia (0.93 mmol). The residue was recrystallized from benzene, resulting in the isolation of 3.31 g (59.3% yield) of colorless prisms of [(Me₃Si)₂N]₂Al(NH₂)₂Al, mp 191 °C (dec). Anal. Calcd for C₃₆H₁₂₀Al₄N₁₂Si₁₂: C, 37.07; H, 10.37; Al, 9.25; N, 14.41; MW, 1166.40. Found: C, 39.01; H, 10.55; Al, 9.69; N, 14.50; MW 1150 (by osmometry in benzene). IR (cm⁻¹, Kel-F/Nujol mull) 3410 (s), 3330 (m), 2943 (s), 2895 (m), 1477 (m), 1436 (m), 1400 (m), 1262 (s), 1247 (s), 920 (s, br), 872 (s, br), 822 (s, br), 760 (s), 720 (m), 672 (s), 637 (s), 603 (m); ¹H NMR (C₆D₆) δ 1.50, 1.44 (NH, 6 H), 0.82, 0.76 (NH, 6 H), 0.45, 0.37 (Me₃Si, 108 H). The TGA (to 1000 °C at 10 °C/min in nitrogen atmosphere) showed a ceramic yield of 24.1%, which is higher than 14.1% calculated for pure AlN.

Low-Temperature Pyrolysis of [(Me₃Si)₂N]₂Al(NH₂)₂. Preparation of [(Me₃Si)₂NAlNH]₄. A 366.7-mg (0.504 mmol) sample was heated in an evacuated ampule at 225 °C for 16 h.

After this cooled to room temperature, the volatiles were collected and quantified: (Me₃Si)₂NH, 1.10 mmol. The white solid (189 mg) remaining in the tube was found to be soluble in hexane, benzene, and Et₂O. Anal. Calcd for C₂₄H₇₆Al₄N₈Si₈: C, 35.61; H, 9.46; Al, 13.33; N, 13.84; MW, 809.51. Found: C, 30.54; H, 8.35; Al, 14.69; N, 11.62; MW, 790 (by vapor pressure depression in pentane). IR (cm⁻¹, Kel-F/Nujol mull) 3376 (w), 2947 (m), 2892 (w), 1257 (s), 1063 (w, br), 937 (s, br), 892 (s), 841 (s), 760 (m), 730 (m), 677 (m), 618 (w); ¹H NMR δ 0.35 (Me₃Si, 72 H), 0.09 (NH, 4 H). Attempts at crystallization were unsuccessful. The TGA (to 1000 °C at 10 °C/min in a nitrogen atmosphere) showed a ceramic yield of 53.8%, which is higher than 20.23% calculated for pure AlN.

Pyrolysis of [(Me₃Si)₂NAlNH]₄. In vacuo an 80-mg (0.099 mmol) sample was gradually heated from room temperature to 900 °C over 4 h; a black residue remained, showing carbon retention. The volatiles were collected and quantified: CH₄, 0.67 mmol; (Me₃Si)₂NH, 0.05 mmol. A white sublimate, determined by infrared analysis to be [(Me₃Si)₂NAlNH]₄, was deposited on the walls of the quartz tube outside the heated zone.

Pyrolysis of [(Me₃Si)₂NAlNH]₄ in an Ammonia Atmosphere. A 128.2-mg sample was heated in a tube furnace in an ammonia atmosphere (500 mmHg) under the following conditions: 25–310 °C, 5 h; 310 °C, 14.5 h; 310–770 °C 2.5 h; 770–980 °C 1.5 h. A black residue (74.4 mg) was obtained, corresponding to a ceramic yield of 58%, which is higher than 20.23% calculated for pure AlN.

Pyrolysis of [(Me₃Si)₂N]₂Al(NH₂)₂Al. [(Me₃Si)₂N]₂Al(NH₂)₂Al (713.9 mg, 0.612 mmol) was weighed into a 20-mL ampule, which was evacuated, sealed, and placed in an oven at 200 °C for 16 h. After the tube had cooled to room temperature, the volatiles were collected and quantified: (Me₃Si)₂NH, 3.09 mmol. The white solid remaining in the tube was found to be insoluble in hexane, benzene, and Et₂O. Anal. Calcd for C₆H₂₅Al₄N₇Si₂: C, 20.05; H, 7.01; Al, 30.02; N, 27.28. Found: C, 16.85; H, 6.61; Al, 30.32; N, 14.35. IR (cm⁻¹, Kel-F/Nujol mull) 2945 (w), 1245 (m), 905 (s, br), 830 (s, br), 753 (s, br), 673 (s, br). A portion of the solid (173.3 mg) was transferred to a quartz tube, which was evacuated and heated from room temperature to 900 °C over 3 h. A white solid residue remained. The volatiles were collected and quantified: CH₄, 2.24 mmol; NH₃, 0.25 mmol; (Me₃Si)₂NH, 0.03 mmol. A portion of the low-temperature thermolysis product was heated to 1000 °C over 8 h in flowing N₂ (0.2–0.3 standard cubic feet per hour (SCFH)) and held at 1000 °C for 8 h. This was followed by heating to 1600 °C over 4 h and 4 h residence at the temperature.

Another portion of the low-temperature thermolysis product was heated from room temperature to 1000 °C over 8 h, followed by an additional 8 h at 1000 °C in a horizontal quartz furnace tube under ammonia flow (0.2–0.3 SCFH).

X-ray Crystal Structure Determination. X-ray data were collected by using a Nicolet R3m/V diffractometer with Cu K α radiation and a highly oriented graphite crystal monochromator and were corrected for Lorentz and polarization effects. An empirical absorption correction based on the ϕ dependence of 10 reflections with χ ca. 90° was applied. Space group determinations were based on the extinctions present and the *E* value statistics and were confirmed by the structure solutions. Calculations were carried out using SHELXTL.¹⁶ The parameters refined by full-matrix least-squares¹⁷ methods include the atom coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The function minimized during least-squares refinement was $\sum w(F_o - F_c)^2$. Scattering factors and corrections for anomalous dispersion were from ref 17. The methyl hydrogens were treated as rigid groups and allowed to rotate about the Si-C bonds with the coordinate shifts of the carbon atoms applied to the bonded hydrogens; the C-H bond length was fixed at 0.96 Å, and the angle H-C-H at 109.5°. Further details of data collection and refinement are given in Table I. Tables of complete bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates and isotropic displacement coefficients, and observed

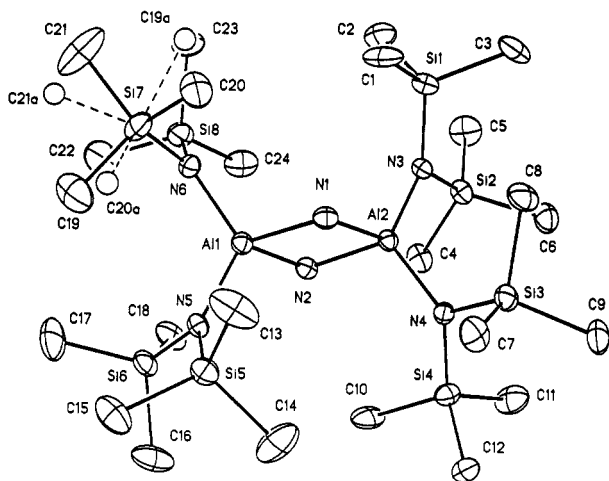
(16) Sheldrick, G. M. SHELXTL(80), minicomputer programs for structure determination, University of Göttingen, 1980.

(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1969.

(15) Paciorek, K. J. L.; Nakahara, J. H.; Masuda, S. R. *Inorg. Chem.*, in press.

Table I. Summary of Crystallographic Data for $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ and $[(\text{Me}_2\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$

chem formula	$\text{C}_{24}\text{H}_{76}\text{N}_6\text{Al}_2\text{Si}_8$	$\text{C}_{36}\text{H}_{120}\text{N}_{12}\text{Al}_4\text{Si}_{12} \cdot 1/2(\text{C}_6\text{H}_{14})$
fw	727.6	1209.5
space group	$P2_1/c$	$C2/c$
temp, K	295	295
γ , Å	1.54178	1.54178
ρ (calcd), g/cm ³	1.054	1.045
μ , cm ⁻¹	27.8	26.5
a , Å	9.162 (2)	25.993 (3)
b , Å	14.580 (3)	15.092 (2)
c , Å	34.444 (5)	41.084 (5)
β , deg	94.94 (1)	107.49 (1)
V , Å ³	4584 (2)	15373 (4)
Z	4	8
$R(F)$	0.0634	0.0774
$R_w(F)$	0.0573	0.0699
transmission coeff	0.49–0.80	0.6813–0.8420

**Figure 1.** Thermal ellipsoid (probability level 20%) plot of **1**; the $(\text{CH}_3)_3$ group at Si(7) is disordered. Dotted bonds and circles represent the lower (45%) of the two occupancies. Hydrogen atoms omitted for clarity.

and calculated structure factors are available in the supplementary material (see the paragraph at the end of the paper).

A single crystal of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$, $0.63 \times 0.31 \times 0.34$ mm, obtained as a colorless needle from a saturated hexane solution and sealed in a thin capillary under helium, was employed. Methyl hydrogen isotropic thermal parameters were restrained to be equal within the compound for all but the Me_3 group on Si(7). These methyl groups were disordered, as indicated in Figure 1, and the hydrogens were fixed at idealized positions with their own set of isotropic thermal parameters. The amino hydrogens were refined isotropically. Atomic coordinates and the equivalent isotropic displacement coefficients are given in Table II, and pertinent bond distances and angles in Table III.

A single crystal of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$, $0.22 \times 0.25 \times 0.37$ mm, obtained as a colorless prism from a saturated hexane solution, cocrystallized with hexane in a 2:1 ratio. Determination was made in air. Methyl hydrogen isotropic thermal parameters were restrained to be equal. The amino hydrogens were fixed at idealized positions with common isotropic thermal parameters. A molecule of hexane, which sits on a center of symmetry, is poorly defined and was refined isotropically. Atomic coordinates and the equivalent isotropic displacement coefficients are given in Table IV, and pertinent bond distances and angles in Table V.

Results and Discussion

Starting Material Synthesis and Characterization.

Reaction of $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ with ammonia in a 1:1 ratio gave the dimer $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ (**1**). The process appears to be essentially analogous to that observed for $\text{Al}(\text{SiMe}_3)_3$. The reaction proceeded only very slowly at 0°C ($\sim 8\%$ of the expected hexamethyldisilazane obtained in 4 h). There were no indications of an initial complex

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$

	x	y	z	$U(\text{eq})^a$
Al(1)	2178 (2)	3460 (1)	1495 (1)	42 (1)
Al(2)	3061 (2)	2038 (1)	993 (1)	39 (1)
Si(1)	4317 (2)	3067 (1)	260 (1)	58 (1)
Si(2)	2136 (2)	1574 (1)	154 (1)	54 (1)
Si(3)	5291 (2)	546 (1)	1218 (1)	53 (1)
Si(4)	2226 (2)	50 (1)	1327 (1)	57 (1)
Si(5)	2912 (2)	2782 (1)	2369 (1)	58 (1)
Si(6)	-99 (2)	3346 (1)	2089 (1)	61 (1)
Si(7)	3192 (2)	5473 (1)	1576 (1)	79 (1)
Si(8)	803 (2)	5101 (1)	958 (1)	70 (1)
N(1)	3994 (5)	2909 (4)	1361 (2)	45 (2)
N(2)	1265 (5)	2559 (3)	1149 (2)	44 (2)
N(3)	3172 (4)	2296 (3)	470 (1)	42 (1)
N(4)	3446 (4)	876 (3)	1181 (1)	41 (1)
N(5)	1719 (4)	3184 (3)	1989 (1)	44 (1)
N(6)	2055 (5)	4669 (3)	1323 (1)	52 (2)
C(1)	5506 (8)	3752 (4)	618 (2)	92 (3)
C(2)	3278 (8)	3967 (4)	-38 (2)	90 (3)
C(3)	5577 (7)	2482 (5)	-68 (2)	91 (3)
C(4)	314 (6)	1323 (4)	344 (2)	72 (2)
C(5)	1662 (8)	2062 (5)	-343 (2)	95 (3)
C(6)	3091 (7)	464 (4)	89 (2)	78 (3)
C(7)	6193 (7)	720 (5)	1723 (2)	75 (3)
C(8)	6366 (6)	1255 (5)	892 (2)	76 (3)
C(9)	5610 (8)	-672 (4)	1066 (2)	83 (3)
C(10)	477 (6)	551 (4)	1483 (2)	82 (3)
C(11)	1680 (9)	-813 (4)	940 (2)	94 (3)
C(12)	2967 (7)	-636 (4)	1762 (2)	74 (3)
C(13)	4870 (7)	3071 (7)	2322 (2)	113 (4)
C(14)	2879 (10)	1521 (4)	2398 (2)	122 (4)
C(15)	2561 (9)	3269 (6)	2853 (2)	103 (3)
C(16)	-782 (8)	2411 (6)	2406 (2)	109 (4)
C(17)	-427 (9)	4474 (5)	2314 (2)	121 (4)
C(18)	-1395 (6)	3307 (5)	1635 (2)	80 (3)
C(22)	-724 (9)	5746 (6)	1165 (2)	122 (4)
C(23)	1672 (9)	5878 (5)	613 (2)	102 (3)
C(24)	-115 (7)	4211 (4)	634 (2)	87 (3)
C(19)	2941 (25)	5454 (18)	2107 (5)	118 (9)
C(20)	5220 (16)	5177 (16)	1563 (8)	97 (8)
C(21)	3126 (38)	6679 (16)	1452 (11)	160 (16)
C(19A)	4785 (29)	5743 (24)	1278 (12)	146 (15)
C(20A)	3736 (58)	5220 (27)	2073 (10)	312 (30)
C(21A)	2171 (38)	6603 (22)	1589 (10)	124 (14)

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

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$

Bond Distances			
Al(1)–N(1)	1.944 (5)	Si(5)–N(5)	1.735 (4)
Al(1)–N(2)	1.926 (5)	Si(6)–N(5)	1.746 (4)
Al(2)–N(1)	1.940 (5)	Si(5)–C(13)	1.864 (7)
Al(2)–N(2)	1.930 (5)	Si(5)–C(14)	1.843 (6)
Al(1)–N(6)	1.846 (4)	Si(5)–C(15)	1.863 (7)
Al(1)–N(5)	1.836 (4)	Al(1)–Al(2)	2.870 (2)
Bond Angles			
Al(1)–N(1)–Al(2)	95.3 (2)	Si(1)–N(3)–Si(2)	116.6 (2)
Al(1)–N(2)–Al(2)	96.2 (2)	Si(5)–N(5)–Si(6)	116.4 (2)
N(1)–Al(1)–N(2)	84.2 (2)	N(6)–Si(7)–C(19)	111.2 (8)
N(1)–Al(2)–N(2)	84.2 (2)	C(20)–Si(7)–C(21)	103.1 (13)
Al(1)–Al(2)–N(1)	42.4 (2)	N(6)–Si(7)–C(19A)	108.7 (11)
N(1)–Al(1)–N(5)	113.1 (2)	C(20A)–Si(7)–C(21A)	104.9 (17)
N(5)–Al(1)–N(6)	120.0 (2)	Si(7)–C(19A)–C(20)	70.4 (18)
Al(1)–N(6)–Si(7)	117.2 (2)	Si(7)–C(20)–C(19A)	69.2 (15)
Al(1)–N(6)–Si(8)	126.2 (2)	Si(7)–C(21A)–C(21)	69.2 (22)

formation nor did $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ form an ether complex such as the one produced by $\text{Al}(\text{SiMe}_3)_3$.¹⁸ Conducting the reaction in ether failed to increase the dimer yield above that obtained in heptane. **1** was found to be in-

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_3\text{Al}$

	x	y	z	$U(\text{eq})^a$
C(1)	-20 (5)	12913 (5)	945 (3)	119 (6)
C(2)	-961 (3)	11653 (8)	742 (2)	107 (5)
C(3)	33 (3)	11250 (6)	566 (2)	79 (4)
C(4)	-950 (3)	10636 (7)	1492 (3)	103 (5)
C(5)	-556 (4)	12519 (6)	1615 (3)	121 (6)
C(6)	55 (3)	11059 (7)	2041 (2)	99 (5)
C(7)	1568 (4)	11261 (8)	2531 (2)	131 (6)
C(8)	2262 (3)	10020 (8)	2259 (3)	111 (5)
C(9)	1254 (4)	9432 (7)	2324 (2)	108 (5)
C(10)	1111 (4)	12779 (6)	1810 (3)	124 (7)
C(11)	1426 (4)	11942 (6)	1235 (2)	89 (5)
C(12)	2217 (4)	12081 (8)	1925 (3)	135 (7)
C(13)	-703 (4)	8476 (7)	2006 (3)	117 (6)
C(14)	-1190 (4)	6653 (7)	1808 (3)	128 (7)
C(15)	-28 (3)	7010 (6)	1937 (2)	88 (5)
C(16)	-1925 (4)	8526 (7)	1362 (3)	124 (7)
C(17)	-1922 (3)	6997 (6)	897 (3)	110 (6)
C(18)	-1611 (3)	8834 (6)	736 (2)	85 (5)
C(19)	-555 (4)	6734 (6)	-84 (2)	92 (5)
C(20)	-1630 (3)	7222 (7)	1 (2)	103 (5)
C(21)	-731 (4)	8535 (5)	117 (2)	83 (4)
C(22)	-1146 (4)	5208 (6)	401 (2)	99 (5)
C(23)	54 (3)	5445 (6)	620 (3)	89 (5)
C(24)	-560 (3)	5564 (5)	1131 (2)	78 (4)
C(25)	2541 (3)	9913 (6)	1406 (2)	88 (5)
C(26)	3167 (3)	8831 (7)	1040 (3)	100 (5)
C(27)	2745 (3)	7976 (6)	1557 (2)	83 (4)
C(28)	2089 (4)	10217 (6)	529 (2)	94 (5)
C(29)	2253 (4)	8432 (7)	242 (3)	107 (6)
C(30)	1151 (3)	9102 (6)	220 (2)	72 (4)
C(31)	1131 (4)	5246 (6)	1467 (3)	110 (6)
C(32)	2347 (4)	5406 (7)	1618 (3)	114 (6)
C(33)	1708 (4)	6686 (6)	1891 (2)	87 (5)
C(34)	1597 (4)	4888 (5)	763 (3)	93 (5)
C(35)	2479 (3)	6213 (7)	801 (3)	97 (5)
C(36)	1336 (3)	6558 (6)	372 (2)	81 (4)
N(1)	797 (2)	9902 (3)	1087 (1)	41 (2)
N(2)	415 (2)	9306 (3)	1574 (1)	49 (3)
N(3)	42 (2)	11171 (4)	1316 (1)	53 (3)
N(4)	1254 (2)	10834 (4)	1789 (1)	54 (3)
N(5)	-215 (2)	8850 (3)	910 (1)	44 (2)
N(6)	288 (2)	7471 (3)	1267 (1)	46 (2)
N(7)	-873 (2)	7774 (4)	1296 (2)	55 (3)
N(8)	-645 (2)	7015 (4)	620 (2)	51 (3)
N(9)	1348 (2)	8409 (3)	1432 (1)	48 (2)
N(10)	766 (2)	8100 (3)	790 (1)	44 (2)
N(11)	1615 (2)	6655 (4)	1119 (1)	52 (3)
N(12)	1968 (2)	8559 (4)	902 (1)	47 (2)
Si(1)	-207 (1)	11713 (2)	924 (1)	70 (1)
Si(2)	-335 (1)	11343 (2)	1597 (1)	74 (1)
Si(3)	1561 (1)	10428 (2)	2196 (1)	79 (1)
Si(4)	1491 (1)	11858 (2)	1698 (1)	81 (1)
Si(5)	-714 (1)	7498 (2)	1728 (1)	81 (1)
Si(6)	-1545 (1)	8007 (2)	1087 (1)	78 (1)
Si(7)	-882 (1)	7349 (2)	195 (1)	71 (1)
Si(8)	-582 (1)	5872 (2)	685 (1)	66 (1)
Si(9)	2572 (1)	8808 (2)	1212 (1)	66 (1)
Si(10)	1874 (1)	9031 (2)	502 (1)	65 (1)
Si(11)	1697 (1)	6047 (2)	1496 (1)	74 (1)
Si(12)	1756 (1)	6101 (2)	788 (1)	70 (1)
Al(1)	567 (1)	8673 (1)	1178 (1)	42 (1)
Al(2)	633 (1)	10442 (2)	1465 (1)	47 (1)
Al(3)	-440 (1)	7702 (1)	1012 (1)	48 (1)
Al(4)	1497 (1)	7860 (2)	1051 (1)	46 (1)
C(1')	1182 (6)	4503 (11)	2571 (4)	180
C(2')	648 (7)	4443 (12)	2474 (4)	180
C(3')	261 (5)	4364 (10)	2592 (5)	180

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

definitely stable in air, in contrast to the starting material, $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$,¹⁵ and $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$.⁶ It was characterized by molecular weight, mass, infrared, and NMR spectroscopy. The mass spectrum exhibited the molecular

Table V. Selected Bond Distances (\AA) and Angles (deg) for $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_3\text{Al}$

Bond Distances			
Al(1)-N(2)	2.024 (6)	Al(1)-N(1)	2.018 (5)
Al(1)-N(5)	2.017 (5)	Al(2)-N(2)	1.901 (6)
Al(2)-N(1)	1.921 (6)	Al(1)-Al(3)	2.897 (3)
Al(1)-Al(2)	2.903 (3)	Al(3)-N(8)	1.854 (6)
Al(2)-N(3)	1.839 (6)	N(3)-Si(1)	1.747 (6)
Al(3)-N(7)	1.852 (7)	N(4)-Si(3)	1.732 (6)
Bond Angles			
N(2)-Al(1)-N(6)	96.3 (2)	N(5)-Al(1)-N(10)	94.7 (2)
N(2)-Al(1)-N(5)	88.2 (2)	N(6)-Al(1)-N(10)	87.1 (2)
N(5)-Al(1)-N(6)	82.0 (2)	Al(1)-N(6)-Al(3)	95.0 (2)
N(1)-Al(1)-N(2)	81.7 (2)	N(5)-Al(3)-N(6)	88.1 (2)
Al(1)-N(1)-Al(2)	95.2 (3)	N(2)-Al(2)-N(3)	109.9 (3)
Al(1)-N(5)-Al(3)	94.9 (2)	N(3)-Al(2)-N(4)	120.6 (3)
N(1)-Al(2)-N(2)	87.8 (3)	N(1)-Al(2)-N(4)	111.1 (3)
N(1)-Al(1)-N(6)	176.3 (2)	Si(1)-N(3)-Si(2)	114.5 (3)
N(5)-Al(1)-N(9)	176.0 (2)	Si(3)-N(4)-Si(4)	115.5 (3)
N(1)-Al(1)-N(5)	94.8 (2)		

ion at m/e 726 and a number of prominent ions derived from it, supporting further the dimer arrangement. No metastables were observed. Consequently, the actual fragmentation paths could not be established. The MS data and the molecular weight, determined by osmometry, show that $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ exists as a dimer in the gaseous state and in solution. The presence in the infrared spectrum of two sets of doublets 3415, 3396 and 3357, 3335 cm^{-1} in the ν_{NH} region together with an absence of absorption at 1120–1165 cm^{-1} eliminates the presence of HNSiMe_3 groups.¹⁹ In the ^1H NMR spectrum, two sharp, single resonances at δ 0.47 and 1.75 in the area ratio of 16.5:1 were observed, in reasonable agreement with the calculated value of CH_3 to H_2N protons of 18:1. The structure of 1, as illustrated in Figure 1, confirms the dimer arrangement, in agreement with the molecular weight measurements and mass spectral data. The planar four-membered Al_2N_2 ring is approximately square, as is evident from the bond lengths $\text{Al}(1)-\text{N}(1) = 1.944(5) \text{\AA}$ and $\text{Al}(1)-\text{N}(2) = 1.926(5) \text{\AA}$ and angles $\text{N}(1)-\text{Al}(1)-\text{N}(2) = 84.2(2)^\circ$ and $\text{Al}(1)-\text{N}(1)-\text{Al}(2) = 95.3(2)^\circ$. The planar dimeric structure is analogous to that of $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$,⁶ and similar to $[\text{Me}_2\text{AlNMe}_2]_2$,^{20,21} although the endocyclic Al-N bond lengths are shorter in 1 than the average (1.954,⁶ 1.958 \AA ^{20,21}) and are actually closer to those reported for six-membered $[\text{Me}_2\text{AlNH}_2]_3$,⁵ which were found to range between 1.921 and 1.942 \AA .

The exocyclic Al-N bond distances, which ranged from 1.836 (4) to 1.852 (4) \AA , are somewhat longer than those reported for other dimeric organoaluminum amides²² (1.798–1.827 \AA), most likely due to the bulky SiMe_3 groups. The 1.741- \AA N-Si and 1.868- \AA Si-C distances are directly comparable to those found in the (trimethylsilyl)amino-substituted boron compounds (1.736 and 1.854 \AA , respectively)¹⁹ and are in agreement with the 1.874- \AA Si-C average value reported for $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$.⁶ As expected for the ring system, the external $\text{N}(5)-\text{Al}(1)-\text{N}(6)$ angle in 1 of $120.0(2)^\circ$ is significantly greater than the internal angles. The $\text{Al}(1)-\text{Al}(2)$ separation in 1, 2.870 \AA , is slightly longer than in $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$, in agreement with a smaller internal angle in 1, caused by the bulky $(\text{Me}_3\text{Si})_2\text{N}$ groups.

(19) Paciorek, K. J. L.; Kratzer, R. H.; Kimble, P. F.; Nakahara, J. H.; Wynne, K. J.; Day, C. S. *Inorg. Chem.* 1988, 27, 2432.

(20) Laughlin, G. M.; Sim, G. A.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* 1972, 2197.

(21) Von Hess, H.; Hinderer, A.; Steinhauser, S. *Z. Anorg. Allg. Chem.* 1970, 377, 1.

(22) Ouzounis, K.; Riffel, H.; Hess, H.; Kohler, U.; Weidlein, J. *Z. Anorg. Allg. Chem.* 1983, 504, 67.

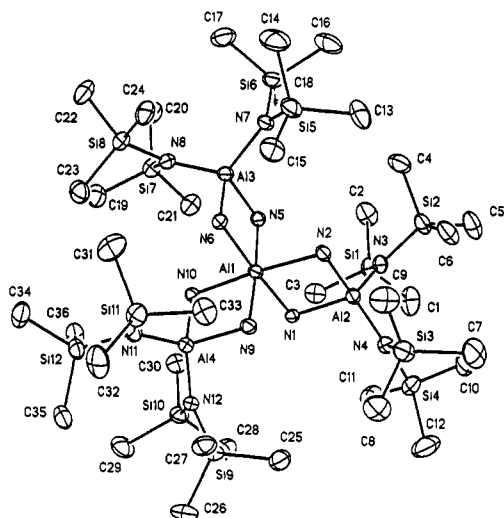
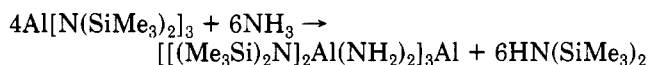


Figure 2. Thermal ellipsoid (probability level 20%) plot of 2. Hydrogens and solvent omitted for clarity.

Reaction of $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ with 2 mol of ammonia gave $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ (2), a colorless, crystalline, air-stable compound, characterized by elemental analysis, molecular weight, ^1H NMR and infrared spectroscopies, and single-crystal X-ray diffraction analysis. The overall process is summarized by

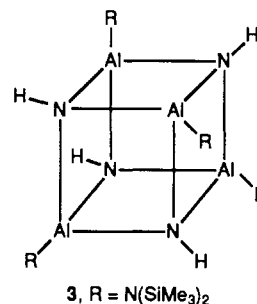


The mechanism of this reaction is unknown, but it has been established that 1 is not an intermediate in the formation of 2 since reaction of 1 with ammonia at room temperature resulted in a quantitative starting material recovery.

The structure of 2 given in Figure 2 is analogous to that of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$.⁷ 2 crystallizes as clear prisms in monoclinic space group $C2/c$. It has approximate noncrystallographic C_3 symmetry about the axis through the central Al atom, which is normal to the Al atoms plane (maximum deviation from a least-squares plane is 0.003 Å). All of the Al_2N_2 rings are planar with a maximum deviation from the plane of 0.004–0.006 Å. Average Al–N(H_2) distances are 2.021 (5) Å for the central aluminum atom and 1.909 (7) Å for the remaining Al–N(H_2) distances. The corresponding average distances in $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ are 2.020 (3) and 1.931 (7) Å.⁷ The long average 2.02-Å central Al(1)–N bond in 2, while longer than the typical Al–(NH_2) bond, is comparable to values for Al–N bonds with greater than four-coordinated Al. Examples are Al–N = 2.03 (1) Å in the bipyridine complex $[\text{AlCl}_2(\text{bpy})_2]\text{Cl}\cdot\text{CH}_3\text{CN}$ ²³ and Al–N = 1.96–2.02 Å in the phthalocyanine complex $\text{Al}(\text{Pc})\text{Cl}$.²⁴ The internal N–Al–N angles average 82.0 (4)° at the six-coordinated central Al and 88.0 (2)° at the four-coordinated Al atoms. Similar values of 82.9 (2)° and 87.7 (2)° were found for the SiMe_3 -substituted compound. For the $(\text{Me}_3\text{Si})_2\text{N}$ substituents, the atoms are nearly planar with the maximum deviations from the Al–N–Si(–Si) planes ranging from 0.003 to 0.08 Å. Average bond distances are as follows: Al–N = 1.850 (6) Å, N–Si = 1.742 (7) Å, C–Si = 1.87 (1) Å. The Al–N and N–Si distances are shortened due to N–Al and N–Si π bonding. Near intermolecular contacts are H–H contacts at van der Waals separation of 2.37 Å.

The structure is consistent with infrared and ^1H NMR spectroscopies and molecular weight data. The infrared absorptions at 3410 and 3330 cm^{-1} agree with the presence of the NH_2 bridging groups. The ^1H NMR spectrum shows two different nitrogen proton environments at 1.50, 1.44 ppm and 0.82, 0.76 ppm. This could be possibly due to the amino nitrogens being diastereomeric centers. The 8:1 ratio of the methyl protons to the nitrogen protons, although somewhat lower than the calculated value of 9:1 further confirms the arrangement.

Thermolysis Studies. Thermal transformation of the ammonolysis products into a higher molecular weight that was processible, i.e., either organic solvent soluble or fusible composition, was one of the objectives of this undertaking. The DSC of 1 exhibited a strong endotherm at 220 °C, corresponding to the melting point; no other endotherms or exotherms were observed up to 450 °C. A DSC rerun on a sample previously heated to 225 °C did not show the 220 °C endotherm, indicating decomposition. Pyrolysis of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ at 225 °C resulted in liberation of 2 mol of hexamethyldisilazane/mol of 1. The product failed to melt up to 220 °C, and no endotherm was present in its DSC up to 400 °C. On the basis of the nature of the starting material, in conjunction with the tendency of the aluminum compounds to form eight-membered arrangements,²⁵ and supported by the molecular weight and ^1H NMR data, it is believed that structure 3 is present here.



The elemental analyses data are very poor; this was also the case with the precursor, 1. The elemental composition of 3 is based largely on the production of $\text{HN}(\text{SiMe}_3)_2$ from the precursor 1, which corresponds exactly to the observed weight loss. The thermolysis reaction was repeated several times and found to be fully reproducible.

Attempts to transform $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$ to pure aluminum nitride were unsuccessful. Pyrolysis to 900 °C in vacuo gave only 10% of the expected hexamethyldisilazane. The production of methane (mole ratio of 3 to CH_4 = 1:7) indicates that silicon is retained in the residue, but it has not been determined if the silicon is in the form of silicon nitride and/or silicon carbide. The presence of aluminum nitride in the residue was shown by an infrared absorption at 720 cm^{-1} , in agreement with data reported for AlN .²⁶ Conducting the pyrolysis in an ammonia atmosphere, which was found to be effective in avoiding both carbon and silicon retention in the related boron compositions, was also unsuccessful. A ceramic yield of 20.23% would be expected for pure AlN ; the observed ceramic yield of 58% indicates the presence of other materials in addition to AlN . Apparently $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$ is not amenable to further reaction with ammonia.

The DSC of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ exhibited an endotherm at 196 °C corresponding to the melting point of 191 °C. A rerun of the sample previously heated to 250

(23) Bellavance, P. L.; Corey, E. R.; Corey, J. Y.; Hey, G. W. *Inorg. Chem.* 1977, 16, 462.

(24) Wynne, K. J. *Inorg. Chem.* 1984, 23, 4658.

(25) Jones, J. I.; McDonald, W. S. *Proc. Chem. Soc.* 1962, 366.

(26) Nyquist, R. A.; Kagel, R. O. *Infrared Spectra of Inorganic Compounds*; Academic Press: New York, 1971.

Table VI. Pyrolyses of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$

sample		conditions		residue		volatile products			TGA residue, ^c
mg	mmol	temp, °C	time, h	% ^a	theory ^b	total % ^a	HMDS, mmol	NH ₃ , mmol	%
760.7	0.652	200 ^d	20	27.1	14.05	72.9	3.44	none	21.7
30.6.6	0.263	204 ^e	15.5	27.0	14.05	73.0	1.36	0.54	21.8

^aThe percent is given with respect to the starting material employed. ^bThis value is calculated on the basis of the arrangement $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$ and the formation of aluminum nitride. ^cThe pyrolysis residue was subjected to TGA in nitrogen; the percent of residue is calculated with respect to the original sample. ^dEvacuated sealed ampule was employed. ^eThe sample was sealed with 0.54 mmol of ammonia.

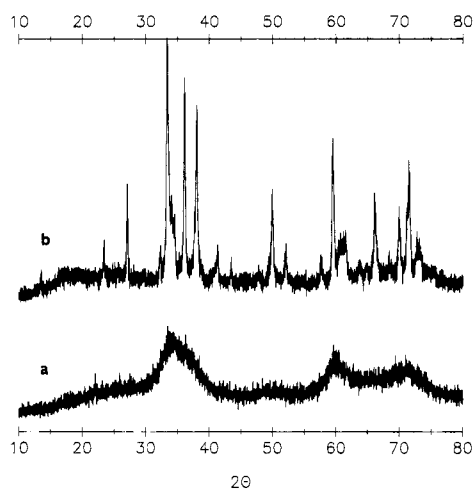


Figure 3. X-ray powder diffraction spectra from pyrolysis of $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$ (a) in N_2 1000 °C 8 h/8 h (b) followed by 1600 °C in N_2 4 h/4 h.

°C failed to show the endotherm, indicating that in the vicinity of ~195 °C, decomposition occurred. **2** was thus subjected to pyrolysis in vacuo and ammonia at 200 °C. The results of these tests are summarized in Table VI. Inasmuch as ammonia was recovered and the quantity of hexamethyldisilazane formed was the same in both experiments indicate that at this temperature ammonia has no effect on the decomposition process. The molar ratio of hexamethyldisilazane liberated to **2** was found to be 5:1. Due to the thermolysis product's insolubility in common organic solvents, structure determinations could not be made. However, it would appear from the reproducibility of the process that some specific arrangement is formed during the low-temperature thermolysis. Further pyrolysis under TGA conditions in N_2 gave a white residue, which exhibited in its infrared spectrum a very broad, weak absorption at ~900 cm^{-1} and a relatively strong, broad absorption at 730 cm^{-1} , characteristic of AlN.²⁶ The presence of either silicon carbide or silicon nitride and/or carbon is clearly indicated by the ceramic yield 21.8%, which is higher than the 14.06% calculated for AlN. For the composition $6\text{AlN}\cdot\text{Si}_3\text{N}_4$, the value is 22.0%. The pyrolysis at 900 °C of the thermolysis intermediate in a sealed, evacuated system gave a white-gray solid. From the composition of the low-temperature thermolysis product, $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$, formation of $6\text{AlN}\cdot\text{Si}_3\text{N}_4$ would require a $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6\cdot\text{CH}_4\cdot\text{NH}_3$ ratio of 1:6:0.33. The found ratio of 1:4.7:0.52 is in relatively good agreement. The powder X-ray pattern (Figure 3a) shows the material to be partially crystalline; annealing at 1600 °C (Figure 3b) resulted in the increased crystallization of both AlN and Si_3N_4 . From the diffraction pattern, the presence of AlN and $\beta\text{-Si}_3\text{N}_4$ admixed with a small amount (<5%) of Al_2O_3 and a trace of $\alpha\text{-Si}_3\text{N}_4$ is clearly evident. The formation of aluminum nitride-silicon nitride and aluminum nitride-silicon carbide ceramics having Al to Si in varying mole ratios has been reported.²⁷ In the case of

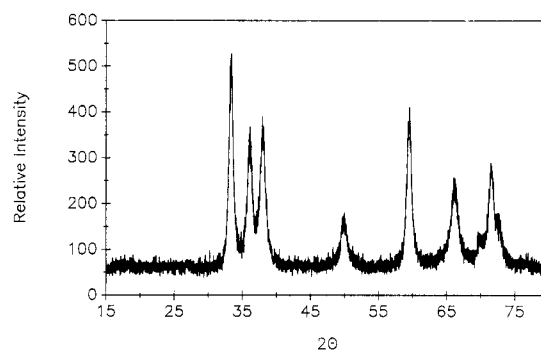


Figure 4. X-ray powder diffraction spectrum from pyrolysis of $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$ in NH_3 1000 °C 8 h/8 h.

$[(\text{Me}_3\text{Si})_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$,⁷ AlN-SiC was formed; the ratio of Al:Si was reported to be 5:1. The composition of the precursor, in our system, apparently predetermines the Al to Si ratio of 2:1, and the presence of bis(trimethylsilyl)amino instead of trimethylsilyl groups results in Si_3N_4 and not SiC production. The Al to Si ratio of 2:1 in the final ceramic (annealed at 1600 °C) was further confirmed by energy-dispersive X-ray analyses, which show the presence of aluminum and silicon in a 2.1:1 ratio.

When the intermediate $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$ was pyrolyzed in an ammonia stream at 1000 °C, partially crystalline AlN was formed. The absence of Si_3N_4 or SiC is evident from the powder X-ray pattern given in Figure 4.

On the basis of these investigations, the reaction of $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ with 1.5NH_3 resulting in **2** offers a potential precursor to both $6\text{AlN}\cdot\text{Si}_3\text{N}_4$ and AlN ceramics. There is a definite benefit in having a ceramic composition predetermined on the molecular level since this would ensure uniform properties, in particular in the case of coatings.

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Registry No. 1, 130326-27-1; 2, 130326-29-3; $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$, 25605-37-2; NH_3 , 7664-41-7; AlN, 24304-00-5.

Supplementary Material Available: Full listings of bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients (Tables SI-SX) for $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2$ and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$ (13 pages); listing of observed and calculated structure factors (Tables SVI-SXI) (57 pages). Ordering information is given on any current masthead page.

(27) Hackney, M. L. J.; Interrante, L. V.; Slack, G. A.; Schields, P. J. In *Ultrastructure Processing of Advanced Ceramics*; MacKenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; p 99.