chloride ion. $[Re_2Cl_9]^-$ can be reduced to the dimeric rhenium(IV,III) complex, $[Re_2Cl_9]^{2-}$, at a glassy-carbon electrode in a reversible electrode reaction. Like $[Re_2Cl_9]^-$, $[Re_2Cl_9]^{2-}$ exhibits only limited stability in basic melt at room temperature and slowly converts to a mixture of $[ReCl_6]^{2-}$ and the dimeric rhenium(III) complex, $[Re_2Cl_8]^{2-}$. However, this metamorphosis is considerably slower than that involving $[Re_2Cl_9]^-$. $[Re_2Cl_9]^{2-}$ can be reduced electrochemically to $[Re_2Cl_8]^{2-}$ in a one-electron irreversible electrode reaction.

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Synthesis and Reactions of [Bis(trimethylsilyl)amido]aluminum Compounds

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The reaction of $LiN(SiMe_3)_2$ with $AlCl_3{\cdot}NEt_3$ and solid aluminum chloride produced $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$, $AlCl[N(SiMe_3)_2]_2$, and $Al[N(SiMe_3)_2]_3$. $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ failed to react with hexamethyldisilazane; no trimethylchlorosilane was eliminated on pyrolysis. Pyrolysis of $AlCl[N(SiMe_3)_2]_2$ gave methane as the major volatile product, not the expected trimethylchlorosilane. Treatment of $[AlCl_2NHSiMe_3]_2$ with triethylamine did not lead to a simple complex. $[(Me_3Si)_2NAlNSiMe_3]_2$ was obtained from the reaction of $[AlCl_2NHSiMe_3]_2$ and $LiN(SiMe_3)_2$. Exposure of $[(Me_3Si)_2NAlNSiMe_3]_2$ to ammonia led to liberation of 1.5 mol of $HN(SiMe_3)_2$; thermolysis of the ammonolysis product was investigated. Reaction of boron trichloride with $Al[N(SiMe_3)_2]_3$ resulted in trimethylboron formation and some boron incorporation, accompanied by tetramethylsilane elimination and methyl group replacement by chlorine.

Introduction

(Trimethylsilyl)amino-substituted boron compounds were found to lead to processible boron nitride precursors[1-3] amenable, among other things, to fiber production. In view of the chemical similarities of boron and aluminum, it was of interest to extend those concepts to aluminum. The advantages of having (trimethylsilyl)amino substituents are the absence of metal–carbon bonds and the ease of formation and volatility of the potential leaving groups, namely Me_3SiCl, $(Me_3Si)_2NH$, and the intermediate Me_3SiNH_2. Furthermore, such an approach provides a possibility of synthesizing precursors of AlN·BN ceramics.

Initial investigations were directed at preparing aluminum analogues of $(Me_3Si)_2NBCl_2$ and $(Me_3Si)_2NB(Cl)NHSiMe_3$, utilizing the methods of Wells and Collins.[4] This approach was not successful; however, when $LiN(SiMe_3)_2$ was used, a series of bis(trimethylsilyl)amino-substituted aluminum compounds were prepared. We report here the syntheses and reactions of the products formed.

Experimental Section

General Procedures. Operations were carried out either in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo. Infrared spectra were recorded: solids as double mulls (Kel-F oil No. 10 and Nujol); liquids as capillary films; gases in 10-cm cells, on a Perkin-Elmer Model 1330 infrared spectrophotometer. 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 × $^1/_8$ 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 JEOL FX90Q broad-band spectrometer, using either C_6D_6 or $CDCl_3$ as solvent and TMS as an external standard. Thermal gravimetric analyses (TGAs) were carried out in nitrogen from room temperature to 1000 °C at 10 °C/min with a Du Pont 990/951 system. Vacuum-line techniques were utilized where applicable; volatile products were separated by fractional condensation and measured and identified by a combination of volume measurement, quantitative infrared spectral analysis, and GC/MS. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Materials. Ammonia (Matheson Gas Products) was purified by trap-to-trap distillation and dried over potassium. The $AlCl_3{\cdot}HN(SiMe_3)_2$ complex,[5,6] $[AlCl_2NHSiMe_3]_2$,[5,6] and $LiN(SiMe_3)_2$[7] were prepared by known procedures. $AlCl_3{\cdot}NEt_3$ was prepared in hexane from triethylamine and aluminum chloride and recrystallized from benzene/heptane; mp 121–122 °C (lit.[8] 121.6–122.1 °C). Aluminum chloride, anhydrous, 99.99% (Gold Label; used without further purification), and $(Me_3Si)_2NH$ were obtained from Aldrich Chemical Co. All solvents were rigorously dried and degassed before use.

Treatment of $AlCl_3{\cdot}HN(SiMe_3)_2$ with Triethylamine. A mixture of $AlCl_3{\cdot}HN(SiMe_3)_2$ (1.0 g, 3.4 mmol) and triethylamine (1.72 g, 17.0 mmol) in benzene (5 mL) was refluxed for 20 h under nitrogen bypass. No precipitate was formed; the reaction mixture was evaporated in vacuo. The volatiles consisted of benzene, triethylamine, and $(Me_3Si)_2NH$. The solid residue (0.80 g) consisted of $AlCl_3{\cdot}NEt_3$ complex, as determined from comparison of its infrared spectrum with that of an authentic sample.

Reaction of the $AlCl_3{\cdot}NEt_3$ Complex with $LiN(SiMe_3)_2$. To a stirred solution of $AlCl_3{\cdot}NEt_3$ (1.40 g, 6.0 mmol) in benzene (5 mL) was added the lithium salt (1.00 g, 6.0 mmol) in benzene (10 mL) over a period of 10 min. After standing at room temperature for 3 days, the cloudy solution was evaporated in vacuo. The residue (2.26 g) was treated with benzene. The insoluble LiCl (240 mg, 96% yield) was filtered off. The solid (1.99 g, 92.6% yield) recovered after benzene removal was crystallized from hexane, giving 1.44 g (67.0% yield; mp 104–106 °C) of $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$. Another recrystallization from hexane gave 0.66 g (mp 105–106 °C). Anal. Calcd for $C_{12}H_{33}AlCl_2N_2Si_2$: C, 40.10; H, 9.25; Al, 7.51; Cl, 19.73; N, 7.79. Found: C, 39.60; H, 9.02; Al, 7.21; Cl, 20.2; N, 7.91. Infrared spectrum (cm^{-1}, KBr plates): 2988 (m), 2950 (m), 2900 (m), 1452 (m), 1398 (w), 1388 (w), 1253 (s), 1178 (m), 1167 (w), 1156 (m), 1082 (m), 1031 (m), 1006 (w), 900 (s, br), 865 (s, br), 841 (s, br), 766 (m), 731 (m), 713 (m), 678 (m), 667 (m), 620 (w), 490

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(s), 470 (s), 395 (s). Mass spectrum (70 eV), *m/e* (relative intensity, ion): 343 (2.5%, M − Me), 242 (4.7%, M − Me − NEt_3), 198 (12.4%, M − $N(SiMe_3)_2$), 169 (14.8%, M − $N(SiMe_3)_2$ − Et), 161 (20.3%, $HN(SiMe_3)_2$), 146 (100%, $Me_3Si(Me_2Si)NH$). ^1H NMR (C_6D_6): δ 0.41, 0.43 (18 H, CH_3Si), 0.82 (9 H, CH_3), 2.63 (6 H, CH_2).

Reaction of Aluminum Chloride with $LiN(SiMe_3)_2$ in a 1:2 Mole Ratio. To a stirred solution of the lithium salt (6.0 g, 35.9 mmol) in benzene (35 mL) was added aluminum chloride (2.40 g, 18.0 mmol) over a 1-h period. The next day a fine precipitate, 2.00 g (LiCl expected, 1.58 g), was filtered off. Solvent removal from the filtrate afforded $AlCl[N(SiMe_3)_2]_2$ as a yellow liquid, 6.29 g. Distillation at 0.001 mmHg gave 0.26 g (bp 57–58 °C), 3.45 g (bp 60–63 °C), and 0.78 g (bp 67–71 °C); fractions 1 and 2 (53.9% yield) exhibited identical infrared spectra; the material crystallized on standing (mp 30–31 °C). Anal. Calcd for $C_{12}H_{36}AlClN_2Si_4$: C, 37.61; H, 9.47; Al, 7.04; Cl, 9.25; N, 7.31. Found: C, 37.10; H, 9.59; Al, 7.30; Cl, 9.41; N, 7.81. Infrared spectrum (cm^{-1}, capillary film, KBr plates): 2950 (m), 2895 (w), 1441 (w, br), 1400 (w, br), 1251 (s), 1195 (w, sh), 1054 (w), 1045 (w), 922 (s, br), 895 (s, br), 860 (s), 836 (s), 757 (m), 672 (m), 613 (w), 520 (s), 373 (m). Mass spectrum (70 eV), *m/e* (relative intensity, ion): 382 (6.7%, M), 367 (44.5%, M − Me), 347 (68.5%, M − Cl), 275 (100%, $(Me_3Si)_2NAlNHSiMe_3$), 259 (38.7%, M − Me − Me_3SiCl), 187 (23.2%, $(Me_3Si)_2NAl$). ^1H NMR (C_6D_6): δ 0.23, 0.25 (CH_3Si).

Reaction of Aluminum Chloride with $LiN(SiMe_3)_2$ in a 1:3 Mole Ratio. To a stirred solution of the lithium salt (5.0 g, 29.9 mmol) in benzene (25 mL) was added aluminum chloride (1.33 g, 9.97 mmol) over a period of 20 min. Stirring at room temperature was continued for 3 days; the precipitated LiCl (1.19 g, 93% yield) was filtered off. Removal of the solvent in vacuo afforded a solid (5.36 g). Dissolution in pentane resulted in an additional 40 mg of LiCl. Fractional crystallization of the pentane-soluble material from Freon-113 gave 2.07 g (40.8% yield) of $Al[N(SiMe_3)_2]_3$ (mp 215–217 °C). Anal. Calcd for $C_{18}H_{54}AlN_3Si_6$: C, 42.55; H, 10.71; Al, 5.31; N, 8.27; MW, 508.15. Found: C, 42.05; H, 10.40; Al, 5.53; N, 8.52; MW, 470 (pentane vapor pressure depression at 16 °C). Infrared spectrum (cm^{-1}, KBr plates) 2971 (s), 2955 (s), 2908 (m), 1440 (w), 1403 (w), 1291 (m), 1250 (s, br), 900 (s, br), 857 (s, br), 830 (s, br), 757 (s), 673 (s), 618 (m), 475 (w), 382 (m). Mass spectrum (70 eV), *m/e* (relative intensity, ion): 507 (9.2%, M), 492 (68.4%, M − Me), 404 (33.6%, M − 2Me − $SiMe_3$), 347 (47.2%, M − $N(SiMe_3)_2$), 275 (70.2%, $(Me_3Si)_2NAlNHSiMe_3$), 202 (100%, $(Me_3Si)_2NAlNH$). ^1H NMR ($CDCl_3$): δ 0.24 (CH_3Si).

Reaction of $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ with $(Me_3Si)_2NH$. A mixture of the complex (669.5 mg, 1.86 mmol) and $(Me_3Si)_2NH$ (1.20 g, 7.43 mmol) was heated in a sealed, evacuated ampule at 110 °C for 18.5 h. No noncondensable volatiles were detected; the condensable volatiles (1.16 g) consisted essentially of $(Me_3Si)_2NH$ mixed with trace amounts of trimethylsilane and Me_3SiCl. The infrared spectrum of the residue was identical with that of the starting material, $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$.

Pyrolysis of $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$. The complex (491.6 mg, 1.37 mmol) was heated in an evacuated ampule at 170 °C for 17.5 h. A total of 24.2 mg (0.24 mmol) of condensable volatiles was obtained; the major component was triethylamine admixed with traces of ethylene, trimethylsilane, and tetramethylsilane. A small quantity ~0.13 mmol, of methane was produced. The residue, on the basis of infrared spectral analysis, consisted largely of the starting material.

Pyrolysis of $AlCl[N(SiMe_3)_2]_2$. The chloro compound (780.7 mg, 2.04 mmol) was heated in a sealed, evacuated ampule at 150 °C for 85.5 h. The noncondensable volatiles consisted essentially of methane (1.22 mmol); Me_3SiCl (0.11 mmol) was identified in the condensable volatiles. The residue, a thick viscous liquid, was not characterized.

Reaction of $[AlCl_2NHSiMe_3]_2$ with Triethylamine. A mixture of $[AlCl_2NHSiMe_3]_2$ (1.05 g, 2.82 mmol), triethylamine (0.58 g, 5.73 mmol), and toluene (5 mL) was stirred at room temperature for 16 h in a closed system. Present in the condensable volatiles were triethylamine (2.37 mmol), $(Me_3Si)_2NH$ (1.36 mmol), Me_3SiCl (0.11 mmol), and toluene. The residue (1.14 g), a viscous liquid, was not characterized.

Preparation of $[(Me_3Si)_2NAlNSiMe_3]_2$. At room temperature, to a stirred solution of $LiN(SiMe_3)_2$ (25.0 g, 149 mmol) in benzene (100 mL) was added $[AlCl_2NHSiMe_3]_2$ (14.2 g, 38.1 mmol) in benzene (150 mL) over a period of 1.75 h. After the mixture was stirred for 24 h, the precipitated LiCl (7.67 g) was filtered off. Removal of solvent in vacuo yielded 22.1 g of solid residue. Crystallization twice from Freon-113 gave 13.1 g (62.7% yield) of $[(Me_3Si)_2NAlNSiMe_3]_2$ (mp 192–194 °C). Anal. Calcd for $C_{18}H_{54}Al_2N_4Si_6$: C, 39.37; H, 9.91; Al, 9.83; N, 10.20; MW, 549.14. Found: C, 38.98; H, 9.98; Al, 9.66; N, 10.6; MW, 600 (by vapor pressure depression at 0 °C in pentane, 3.6 wt %). Infrared spectrum (cm^{-1}, KBr plates): 2951 (s), 2898 (m), 1440 (w), 1397 (w), 1252 (s), 1242 (s), 1017 (s, br), 963 (s, br), 901 (s, br), 827 (s, br), 771 (s), 753 (s), 695 (s), 672 (s), 629 (m), 612 (m), 477 (w), 365 (w). Mass spectrum (70 eV) *m/e* (relative intensity, ion): 548 (20.4%, M), 533 (100%, M − Me), 461 (22.0%, M − $NSiMe_3$), 445 (24.2%, M − $SiMe_3$ − 2Me), 373 (11.7%, M − $N(SiMe_3)_2$ − Me). ^1H NMR (C_6D_6): δ 0.25 (18 H, $(CH_3)_3Si$), 0.28 (36 H, $[(CH_3)_3Si]_2N$).

Reaction of $[(Me_3Si)_2NAlNSiMe_3]_2$ with Ammonia. $[(Me_3Si)_2NAlNSiMe_3]_2$ (10.10 g, 18.4 mmol) in hexane (48.68 g) was allowed to react with ammonia (0.67 g, 39.6 mmol) for 1 h at 0 °C. Specifically, with use of the vacuum-line assembly, the measured quantity of ammonia, in an ampule, was allowed to warm from −196 °C (by removing the liquid-nitrogen trap) to room temperature, and as the ammonia was volatilized, it was absorbed by the reaction mixture held at 0 °C. Subsequently, the reaction mixture was warmed to room temperature and stirred for 16 h. The volatiles were removed in vacuo, initially at room temperature and finally at 85 °C. The heating was necessary to remove the last traces of $(Me_3Si)_2NH$ and hexane. The volatile condensables, in addition to hexane, consisted of ammonia (3.07 mmol, 7.7% recovery) and $(Me_3Si)_2NH$ (3.66 g, 22.7 mmol, 82.4% yield). The resultant solid was treated with Freon-113 (45 mL), and the small quantity of insoluble material was removed by filtration. The filtrate on evaporation gave 5.76 g (93% yield) of $-[Me_3SiNAl(NH_2)N(SiMe_3)AlNHSiMe_3-]_n$ (mp 195–215 °C). Anal. Calcd for $C_9H_{30}Al_2N_4Si_3$: C, 32.50; H, 9.09; Al, 16.23; N, 16.85; MW, 332.59. Found: C, 31.27; H, 9.13; Al, 15.72; N, 16.90; MW, 2300 (by vapor pressure depression in pentane, 3.4 wt %). Infrared spectrum (cm^{-1}, KBr plates): 3383 (m), 3330 (w), 3282 (m), 2947 (s), 2895 (m), 1435 (w, br), 1400 (w, br), 1250 (s), 1111 (s, br), 922 (s), 887 (s), 832 (s), 755 (s), 724 (m), 674 (m). ^1H NMR (C_6D_6): δ −0.44 (br, 1 H, NH), 0.22 (s, 9 H, CH_3), 0.35 (s, 9 H, CH_3), 0.40 (s, 9 H, CH_3), 0.87 (br, 2 H, NH_2). The TGA (to 1000 °C at 10 °C/min, in nitrogen atmosphere) showed a ceramic yield of 43.2% (calculated for pure AlN 24.65%).

Pyrolysis of $-[Me_3SiNAl(NH_2)N(SiMe_3)AlNHSiMe_3-]_n$ (1.84 g, 5.54 mmol) was heated in vacuo at 200 °C for 24 h; the volatiles evolved at this stage (175 mg) were composed of ammonia and $(Me_3Si)_2NH$. Heating at 278–280 °C for 21 h gave an additional 280 mg of condensable volatiles for a total weight loss of 24.7%. The combined condensable volatiles were composed of $(Me_3Si)_2NH$ (3.18 mmol) and ammonia (0.63 mmol). Involatile residue infrared spectrum (cm^{-1}): 3380 (w), 3295 (w), 2943 (s), 2890 (m), 1430 (w), 1400 (w), 1248 (s), 1107 (w), 1050 (w), 927 (s, br), 883 (s, br), 830 (s, br), 756 (s), 722 (m), 671 (m). A portion of the above product exhibited 32.5% weight loss under TGA conditions (total weight loss (including the thermolysis at 200–280 °C) 51.7%; calculated for pure AlN production, weight loss 75.35%). Another portion of the above thermolysis product (336.3 mg) was heated in a tube furnace in an ammonia atmosphere (500 mmHg): 280–540 °C, 0.3 h; 540–755 °C, 1.25 h; 755–990 °C, 1.5 h. The residue was black and granular: ceramic yield 177.3 mg, 52.7%. The ceramic yield starting with $-[Me_3SiNAl(NH_2)NSiMe_3AlNHSiMe_3-]_n$ was 37.7% (calculated for pure AlN 24.65%).

Reaction of Boron Trichloride with $Al[N(SiMe_3)_2]_3$. A mixture of $Al[N(SiMe_3)_2]_3$ (260 mg, 0.513 mmol) and boron trichloride (85.0 mg, 0.726 mmol) was heated in vacuo in a sealed ampule at 100 °C for 24 h. The condensable volatiles consisted of Me_3B (0.11 mmol), Me_4Si (0.64 mmol), and Me_3SiCl (0.17 mmol). The involatile residue, a thick viscous liquid, was not characterized.

Results and Discussion

Reaction of the $AlCl_3{\cdot}NEt_3$ complex with $(Me_3Si)_2NH$, both in refluxing benzene and at 80 °C in the absence of a solvent, gave only the unreacted starting materials. This is contrary to what has been reported for the corresponding boron complex.[4] Treatment of $AlCl_3{\cdot}HN(SiMe_3)_2$ with triethylamine resulted in the formation of the triethylamine complex and liberation of $(Me_3Si)_2NH$, instead of the desired dehydrohalogenation products. In view of the above, the triethylamine complex was next allowed to react with $LiN(SiMe_3)_2$ in a 1:1 molar ratio and gave $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ in a 67% yield, i.e.

$$AlCl_3{\cdot}NEt_3 + LiN(SiMe_3)_2 \rightarrow AlCl_2N(SiMe_3)_2{\cdot}NEt_3 + LiCl$$

$AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ was characterized by elemental analysis and mass and NMR spectroscopies. The mass spectrum exhibited a $(M - CH_3)^+$ ion at *m/e* 343 and other ions consistent with the structure. The ^1H NMR spectrum showed the methyl triplet (δ 0.82) and methylene quartet (δ 2.63) of the triethylamine and the trimethylsilyl proton resonance (δ 0.41, 0.43).

$AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ was extremely moisture sensitive. Exposure of an infrared sample to the atmosphere for approximately 1 min resulted in extensive hydrolysis, as shown by comparison of the infrared spectra of the unexposed and exposed materials. In the latter, bands between 2700 and 2500 cm^{-1} indicated the formation of triethylamine hydrochloride.

Treatment of aluminum chloride with an equimolar amount of the lithium salt did not give the dichloro compound, i.e.

$$AlCl_3 + LiN(SiMe_3)_2 \rightarrow AlCl_2N(SiMe_3)_2 + LiCl$$

The only product obtained (30% yield) was $AlCl[N(SiMe_3)_2]_2$. The monochloro compound was formed in a 53.9% yield when we employed a 1:2 mole ratio of $AlCl_3$ to the lithium salt. The mass spectrum of $AlCl[N(SiMe_3)_2]_2$ showed a molecular ion at *m/e* 382, as well as high-intensity ions at *m/e* 367 (M – Me) and *m/e* 347 (M – Cl).

The trisubstituted compound, $Al[N(SiMe_3)_2]_3$ was isolated in a 73% yield by the reaction

$$AlCl[N(SiMe_3)_2]_2 + LiN(SiMe_3)_2 \rightarrow Al[N(SiMe_3)_2]_3 + LiCl$$

Direct interaction of $AlCl_3$ with the lithium salt, in a 1:3 mole ratio, afforded $Al[N(SiMe_3)_2]_3$ in a 41% yield.

The spectroscopy data for $Al[N(SiMe_3)_2]_3$ are consistent with the structure. The mass spectrum gave a molecular ion at *m/e* 507, as well as a high-intensity ion at *m/e* 347 [M – $N(SiMe_3)_2$]. The ^1H NMR spectrum showed a single trimethylsilyl proton environment (δ 0.24).

Both the disubstituted and the trisubstituted materials were moisture-sensitive, and a short exposure to the atmosphere resulted in hydrolysis. $Al[N(SiMe_3)_2]_3$ was prepared by Pump, Rochow, and Wannagat[9] by reaction of $(Me_3Si)_2NH$ with lithium aluminum hydride. These authors reported a melting point >500 °C; hydrolysis or the presence of residual salts could be responsible for the observed absence of melting.

Neither the monochloro compound, $AlCl[N(SiMe_3)_2]_2$, nor the trisubstituted material, $Al[N(SiMe_3)_2]_3$, formed adducts with triethylamine. This finding supports the conclusions of Wiberg, Baumeister, and Zahn[10] regarding the steric effects of bis(trimethylsilyl)amino groups on aluminum. Inasmuch as the complex $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ on reaction with an excess of $LiN(SiMe_3)_2$ gave the tris compound, it is obvious that the presence of triethylamine does not hinder the substitution process. Triethylamine could not be replaced in $AlCl_2N(SiMe_3){\cdot}NEt_3$ by hexamethyldisilazane.

The propensity for trimethylhalosilane elimination, well documented for the boron analogues,[11,12] was also found to apply to aluminum compounds,[5,6] namely, $AlCl_3{\cdot}HN(SiMe_3)_2$ and $[AlCl_2NHSiMe_3]_2$. It was anticipated that, in the case of $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$, triethylamine and Me_3SiCl would be liberated, giving a cyclic derivative, $[AlClNSiMe_3]_x$. Exposure at 170 °C gave approximately 15% of the expected triethylamine mixed with small quantitites of trimethylsilane, tetramethylsilane, and methane. In the mass spectrum of $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$, a number of high-mass fragments retained the triethylamine portion, also indicating that the complex is not readily dissociated.

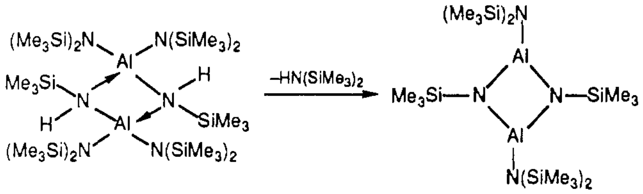
Pyrolysis of $AlCl[N(SiMe_3)_2]_2$ was investigated next. The absence of triethylamine in this material eliminated its potential interference. The product expected here was the dimer:

$$2AlCl[N(SiMe_3)_2]_2 \rightarrow [(Me_3Si)_2NAlNSiMe_3]_2 + 2Me_3SiCl$$

At 150 °C, the major volatile material formed was methane; Me_3SiCl amounted only to 5.6% of theory. The formation of methane points to a condensation reaction involving the methyl groups on silicon.

The symmetrical dissociation of aluminum chloride dimer upon reaction with Lewis bases under formation of neutral donor–acceptor complexes is well established.[13] Since $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ was formed in a good yield and since in $AlCl_3{\cdot}HN(SiMe_3)_2$ the hexamethyldisilazane is readily replaced by triethylamine, it was expected that a related complex, $AlCl_2NHSiMe_3{\cdot}NEt_3$, would result from the reaction of $[AlCl_2NHSiMe_3]_2$ with triethylamine. The reaction consumed slightly more than 1 mol of triethylamine and was accompanied by the liberation of 0.5 mol of $(Me_3Si)_2NH$ and a trace of Me_3SiCl. This finding shows that what occurs is not simply a cleavage of coordinative bridges and establishment of a coordinative bond with triethylamine. In the infrared spectrum of the product, the presence of ammonium chloride was shown by the bands at 3142, 2985, and 1412 cm^{-1}; the new absorption at 3270 cm^{-1} indicated the formation of additional NH linkages. On the basis of these results, we postulate that the initial process likely involves the evolution of Me_3SiNH_2, which decomposes into $(Me_3Si)_2NH$ and ammonia. Reaction of the ammonia produced with the chlorine substituents likely results in the formation of the new NH moieties and ammonium chloride.

The dimer $[AlCl_2NHSiMe_3]_2$ provides a potential starting material for the synthesis of aluminum compounds having the $NHSiMe_3$ substituent, i.e., $(Me_3Si)_2NAl(Cl)NHSiMe_3$, $[(Me_3Si)_2N]_2AlNHSiMe_3$, or $(Me_3Si)_2NAl(NHSiMe_3)_2$. The corresponding boron analogues have been described.[4,14] Reaction of $[AlCl_2NHSiMe_3]_2$ with an equimolar quantity of $LiN(SiMe_3)_2$ resulted in the recovery of some $[AlCl_2NHSiMe_3]_2$ and a mixture of products that could be neither separated nor characterized. Employing a 1:2 ratio of $[AlCl_2NHSiMe_3]_2$ to the lithium salt afforded a 62.7% yield of $[(Me_3Si)_2NAlNSiMe_3]_2$. An intramolecular process, depicted as follows, is most likely responsible for the production of the four-membered ring compound:



The dimer arrangement is based on the measured molecular weight and the mass spectral breakdown pattern, in particular the high-intensity molecular ion, *m/e* 548. For several ions, listed as follows, the corresponding metastable ions were observed, and thus the fragmentation paths have been substantiated: 548$^+$ (M) → 533$^+$ + Me (*m** 520); 533$^+$ → 518$^+$ + Me (*m** 503); 533$^+$ → 461$^+$ + $NSiMe_2$ (*m** 399); 533$^+$ → 445$^+$ + $SiMe_4$ (*m** 371). The ^1H NMR spectrum showed two trimethylsilyl proton environments on the ring nitrogens (δ 0.25) and the exocyclic nitrogens (δ 0.28).

The dimer formation therefore follows the processes observed for the boron analogue, which produced exclusively the four-membered-ring compound[11,15,16] rather than a trimer or tetramer. Thus, the ring size is governed by entropy (favoring the larger number of product molecules, namely dimers rather than trimers or tetramers), ring strain, and substituent-caused steric factors.[17,18]

$[(Me_3Si)_2NAlNSiMe_3]_2$ was found to be very moisture sensitive, shown by the appearance of absorption at 3285 cm^{-1} in the IR spectrum (ascribed to NH) after a short exposure to the atmosphere. Reaction with ammonia gave material for which the following formula is proposed, i.e.

$$[(Me_3Si)_2NAlSiMe_3]_2 \xrightarrow{1.5NH_3} -[Me_3SiNAlNHSiMe_3NSiMe_3AlNH_2-]_n + 1.5HN(SiMe_3)_2$$

The general arrangement, although it is unknown whether it is a cyclic or a linear structure, is based in part on that of the starting material, $(Me_3Si)_2NH$ evolved, ammonia consumed,

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elemental composition, and infrared and ^{1}H NMR spectral data. The three bands in the N–H stretch region of the infrared spectrum in conjunction with the absorption at 1111 cm^{-1} (found to be characteristic of the NHSiMe$_3$ group)[19] support the presence of two types of amino hydrogens. The ^{1}H NMR spectrum shows three different methyl proton environments with the two very close together, δ 0.40 and 0.35, being assigned to the trimethylsilyl groups on the ring nitrogens. Protons on nitrogen are known to produce broad NMR peaks at varied locations. The signals at –0.44 and 0.87 ppm are ascribed to the NH protons. Their relative ratio, 1:2, is in agreement with the assignments; however, the ratio of the methyl protons to the nitrogen protons, 25.7:1, is much higher than the calculated value of 9:1. This could be due to peak broadening of the NH protons. The molecular weight of 2300 indicates the compound exists in solution in a polymeric form. Difficulty was experienced in solvent removal, and efforts to obtain crystals for X-ray structure determination were unsuccessful. The material exhibited only a single endotherm in the differential scanning calorimetry analysis at ~275 °C. No endotherm was observed within the melting range. Thermolysis at 280 °C gave $(\mathrm{Me_3Si})_2\mathrm{NH}$ and ammonia; the ratio of the starting material to $\mathrm{HN(SiMe_3)_2}$ to $\mathrm{NH_3}$ was found to be 1:0.6:0.1. From the above ratios, the large decrease in the infrared 1110-cm^{-1} absorption, and the retention of the doublet at 3380 and 3290 cm^{-1}, one is tempted to speculate that condensation took place via the NHSiMe$_3$ substitutents.

Pyrolysis up to 1000 °C of the low-temperature thermolysis product, using TGA, resulted in a black, shiny residue, pointing to carbon retention in agreement with the high ceramic yield. Conducting the final pyrolysis in a tube furnace, under an ammonia atmosphere, at 280–990 °C, gave a 37.7% ceramic yield, which is higher than the 24.65% calculated for pure AlN production.

One of the objectives of this investigation was to prepare precursors for BN·AlN ceramics. Reaction of $\mathrm{Al[N(SiMe_3)_2]_3}$ with BCl$_3$, on the basis of literature data,[20–22] offered a potential approach, i.e.

$$\mathrm{BCl_3 + Al[N(SiMe_3)_2]_3 \rightarrow Cl_2BN(SiMe_3)Al[N(SiMe_3)_2]_2 + Me_3SiCl}$$

Unreacted starting materials were recovered at 50 °C; at 71 °C partial reaction took place; at 100 °C all BCl$_3$ was consumed and Me$_3$SiCl, Me$_4$Si, and Me$_3$B were liberated. The isolation of the last two compounds shows that exchange between methyl and chloro groups occurred. Formation of $\mathrm{(CH_3)_x(Cl)_ySiN}$ units is proposed on the basis of the reactions of $\mathrm{N(SiMe_3)_3}$ and $\mathrm{[(Me_3Si)_2NBNSiMe_3]_2}$ with boron trichloride.[23] The ratio of $\mathrm{Al[N(SiMe_3)_2]_3}$:Si liberated:B incorporated:Me liberated:Cl liberated (in Me$_3$SiCl) was found to be 1:1.5:1.2:1.9:0.3. The methyl group calculation includes all the methyl groups from Me$_3$B and one from Me$_4$Si. From the above ratio, we calculate that the formation of N–B–N bridges takes place to the extent of ~20%. Therefore, the resultant system contains BCl and SiCl linkages and consequently should be amenable to reactions with $(\mathrm{Me_3Si})_2\mathrm{NH}$ and ammonia and lead to potential candidate precursors to ceramics containing B, Al, and Si.

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Fluorinated Three- and Four-Nitrogen Compounds and Their Reactions

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Insertion of trifluoroacetonitrile into the nitrogen–chlorine bond of $\mathrm{CF_3(C_2F_5)NN(Cl)C_2F_5}$ gives $\mathrm{CF_3(C_2F_5)NN(C_2F_5)N{=}C(Cl)CF_3}$ in low yield. Polyfluorodiazanes containing an ether functionality $\mathrm{CF_3(C_2F_5)NN{=}C(CF_3)OR_f}$ [$\mathrm{R_f = CH_2CF_3, CH(CF_3)_2}$] are prepared by reacting $\mathrm{CF_3(C_2F_5)NN{=}C(Cl)CF_3}$ with $\mathrm{LiOR_f}$. Chlorine fluoride adds readily to the carbon–nitrogen double bond in $\mathrm{CF_3(C_2F_5)NN{=}C(CF_3)OR_f}$ to give $\mathrm{CF_3(C_2F_5)NN(Cl)CF(CF_3)OR_f}$. Photolysis of the latter compounds results in the formation of tetrazanes $\mathrm{[CF_3(C_2F_5)NNCF(CF_3)OR_f]_2}$. The tetrazane $\mathrm{[CF_3(C_2F_5)NN(C_2F_5)]_2}$ when heated with polyfluoroolefins ($\mathrm{CF_2{=}CFCl, CFCl{=}CFCl, CF_2{=}CH_2, CF_2{=}CFH}$) forms $\mathrm{CF_3(C_2F_5)NN(C_2F_5)CX_2CY_2N(C_2F_5)N(C_2F_5)CF_3}$.

Introduction

At first glance, with the exception of compounds of carbon, it would appear that molecules containing catenated atoms of other elements are relatively unstable. While there is no element that can compete with carbon in numbers of catenated atoms, it should be noted that it is possible to prepare stable catenated species of other elements, especially if fluorine atoms or fluorinated groups or other electronegative species are present in the molecule; e.g., compare $\mathrm{CF_3O_nCF_3}$ (n = 1–3) and $\mathrm{O_nF_2}$ (n = 1, 2, 4, and perhaps 5 and 6) or $\mathrm{CF_3S_nCF_3}$ (n = 1–6), $\mathrm{HS_nH}$ (n = 1–6), and $\mathrm{Cl\,S_nCl}$ (n = 1–100). Thus, it is expected that stable catenated nitrogen compounds should exist, since $\mathrm{(CF_3)_3N}$ and $\mathrm{CF_3N_2CF_3}$ are both extremely stable molecules.

We[1] and others[2,3] have been able to synthesize highly stable perfluoroalkyl-substituted tetrazanes $\mathrm{(R_f)_2NN(R_f)N(R_f)N(R_f)_2}$. The earlier syntheses[3] were accomplished in low yield by the photolysis of diazanes, e.g., $\mathrm{R_fN{=}NR_f \xrightarrow{h\nu} [(R_f)_2NNR_f]_2}$, or from the photolysis or thermolysis of a halogen (Cl$_2$ or Br$_2$) with $\mathrm{[(CF_3)_2NN(CF_3)]_2Hg}$.[2] The former reaction is assumed to proceed

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