angles to be substantially smaller than 109.5° (O–V–O, 81.6 and 83.2°). With two of the phenolate oxygen atoms drawn back in the bridging interaction to Li, the angle between the remaining two V–O bonds opens up to 118.5 and 114.4° for the two independent complexes. Another consequence of the bridging interaction to Li^+ is that the V–O bonds involved in the bridges are approximately 0.1 Å longer than the terminal ones. The distorted tetrahedral structure of **2** relaxes to a nearly perfect tetrahedral geometry in **3**[19] when the lithium cation is separated from the anion by treatment with 12-crown-4. Whereas there are no particularly short V···H interactions in **3**, complex **2** has some rather small V···H separations (minimum 2.39 Å), indicative of agostic interactions.

Solution magnetic susceptibility data for compounds **1** (2.90 μ_B), **2** (2.75 μ_B), and **3** (2.72 μ_B) are consistent with a d^2 electronic configuration. The solution electronic absorption spectra of **2**[17] and **3**[19] are characteristic of tetrahedral V(III), reminiscent of that reported for VCl_4^- in $CsAlCl_4$.[24] Similar spectra have been reported for $[V(mes)_3(R)]^-$ (mes = mesityl; R = phenyl, *o*-tolyl, Me, CPh_3, mes).[25] A dramatic color change from green to blue occurs upon dissolving **2** in coordinating solvents such as THF, presumably as a result of solvating the lithium ion and thereby removing it from direct contact with the $V(DIPP)_4^-$ unit. The light green color of **1** is consistent with other examples of six-coordinate V(III) species.[26] While under certain conditions EPR spectra have been observed for octahedral[27a] and tetrahedral[27b] V(III) species, solutions of the novel phenolate complexes are EPR-silent at room temperature and 77 K at X-band frequency.

Cyclic voltammetry of compounds **2** and **3** display two quasi-reversible waves tentatively assigned to V^{III}/V^{IV} and V^{IV}/V^V redox couples, as well as irreversible waves corresponding to phenolate oxidation.[28] Reduction to V(II) apparently is not accessible under these conditions, within the solvent window. On the other hand, chemical reduction of **2** with a Na/Hg amalgam proceeds slowly and gives rise to a hexane-soluble product, which possesses an EPR spectrum consistent with an $S = {}^3/_2$ species. Confirmation of this latter product as a vanadium(II) phenolate complex awaits further investigation.

In conclusion, three novel vanadium(III) phenolate complexes have been prepared and characterized by X-ray crystallography, magnetic, spectroscopic, and electrochemical methods. These compounds represent the first examples of mononuclear homoleptic four- and six-coordinate vanadium(III) phenolate species. Accessibility of a lower oxidation level in the case of **2** has been demonstrated. Further investigations into reactivity of **1–3** and their reduced analogs are under way.

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Registry No. **1**, 117226-81-0; **2**, 117226-83-2; **3**, 117226-84-3; $VCl_3 \cdot 3THF$, 19559-06-9; $[V_2Cl_3(THF)_6]^+$, 89172-47-4.

Supplementary Material Available: For **1–3**, fully labeled ORTEP drawings and tables of positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles (38 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of California
Berkeley, California 94720

Wolf Christian A. Wilisch
Michael J. Scott
William H. Armstrong*

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(24) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p 400.

(25) (a) Seidel, W.; Kreisel, G. *Z. Anorg. Allg. Chem.* **1976**, *426*, 150–154. (b) Kreisel, G.; Scholz, P.; Seidel, W. *Z. Anorg. Allg. Chem.* **1980**, *460*, 51–55.

(26) For example, $V(cat)_3^{3-}$ is a similar light green color. See ref 21.

(27) (a) Foner, S.; Low, W. *Phys. Rev.* **1960**, *120*, 1585–1588. (b) Ham, F. S.; Ludwig, G. W. In *Paramagnetic Resonance*, Lowe, W., Ed.; Academic: New York, 1963; Vol. 1, p 163.

(28) Cyclic voltammetry: Potentials (V) were measured vs. Ag/Ag^+, q-r = quasi-reversible, irrev = irreversible. **1** (CH_3CN, 0.1 M Et_4NClO_4): +1.56 (q-r), +0.87 (q-r), –0.77 (irrev). **2** (CH_2Cl_2, 0.1 M Bu_4NPF_6): +1.67 (q-r), +0.28 (q-r), +1.22 (irrev). **3** (CH_3CN, 0.1 M Et_4NClO_4): +1.64 (q-r), +0.52 (q-r), +1.08 (irrev).

Articles

Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131

Formation and Molecular Structure of the Novel Six-Coordinate Aminoalane Complex $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$

J. F. Janik, E. N. Duesler, and R. T. Paine*

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Reaction of $[(CH_3)_3Si]_3Al \cdot O(C_2H_5)_2$ and NH_3 in a 1:2 ratio results in the formation of $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$. The compound was characterized by elemental analysis, mass, infrared, and NMR spectroscopic data, and a single-crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 13.981$ (2) Å, $b = 14.064$ (2) Å, $c = 23.025$ (2) Å, $\beta = 106.2$ (1)°, $Z = 4$, $V = 4347$ (1) Å^3, and $\rho = 0.98$ g cm^{-3}. Least-squares refinement gave $R_F = 9.56\%$ and $R_{wF} = 7.37\%$ on 2504 reflections with $F \geq 3\sigma(F)$. The molecular structure shows a central six-coordinate, pseudooctahedral Al atom bonded to three bidentate aminosilyl aluminum ligands, $\{[(CH_3)_3Si]_2Al(NH_2)_2^-\}$. The average central $Al-N(H)_2$ distance is 2.020 (5) Å, and the average $Al-N(H)_2$ distance in the ligand units is 1.932 (5) Å. Pyrolysis of this molecular species provides a mixture of AlN and SiC.

Introduction

The reactions of trialkylaluminum compounds and NH_3 have been studied by Wiberg,[1] and more recently, the reactions of $(CH_3)_3Al$ and $(C_2H_5)_3Al$ have been reinvestigated by Interrante and co-workers[2] and by Tebbe and Bolt.[3] The 1:1 stoichiometric

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(1) Wiberg, E., work discussed by: Bahr, G. *FIAT Review of German Science 1939–1946*; Dieterichsche Verlagsbuchhandlung: Wiesbaden, BRD, 1948; Inorganic Chemistry, Part II.

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

(3) Baker, R. T.; Bolt, J. D.; Chowdhry, U.; Klabunde, U.; Reddy, G. S.; Roe, C.; Staley, R. H.; Tebbe, F. N.; Vega, A. J. *Mater. Res. Soc. Symp. Proc.*, in press.

0020-1669/88/1327-4335$01.50/0

combinations are found to initially produce adducts, $R_3Al{\cdot}NH_3$, which, upon heating, release alkane, RH, below 100 °C with the formation of a trimeric aminoalane $[R_2AlNH_2]_n$, $n = 3$. These molecular alane products are reported to release an additional equivalent of alkane below 200 °C with apparent formation of solid, polymeric iminoalanes, $[RAlNH]_n$. The latter compounds have not been well-characterized in part because they are very insoluble in common organic solvents. Nonetheless, these compounds have been found to serve as useful preceramic reagents for formation of AlN and AlN composites.[2,3] Further, it has been noted that combination of the iminoalane with excess R_3Al results in the formation of a liquid material that can be processed into AlN fibers.[3]

In a general search for molecular precursors to ceramic composites, we have recently reported[4] on reactions of the silylalane $[(CH_3)_3Si]_3Al$ and NH_3 utilizing stoichiometric ratios of 1:1 and 1:3. In the former case, a dimeric molecular product, $\{[(CH_3)_3Si]_2AlNH_2\}_2$, was isolated in high yield, characterized, and processed into a solid-state mixture of AlN and SiC. In the presence of 3 equiv of ammonia, only 2 equiv of NH_3 were consumed by $(Me_3Si)_3Al$. The resulting insoluble polymeric product could not be fully characterized; however, a formula $[(CH_3)_2SiAl(NH_2)_2]_n$ was proposed on the basis of the composition of evolved gaseous byproducts and limited spectroscopic data. Pyrolysis of this product also produced mixtures of AlN and SiC with different Al/Si compositions relative to the pyrolysis product obtained from the 1:1 reaction. During the course of that initial study, we also observed the formation of a second, organic-solvent-soluble product when the 1:1 reactant ratio was not carefully adhered to in NH_3; however, the species was not successfully isolated. We report here on the isolation of that product, its characterization, and its formation of AlN/SiC upon pyrolysis.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulations of all reagents and reaction products. Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer from solution cells and KBr pellets. Mass spectra were obtained from a Finnegan mass spectrometer by using a heated solids probe. NMR spectra were recorded on Varian FT-80A and JEOL GSX-400 NMR spectrometers. All NMR samples were sealed in 5-mm tubes with deuteriated lock solvent, and the spectra (^{13}C, ^{1}H) were referenced with $(CH_3)_4Si$. Elemental analyses were performed by R. Ju of UNM Analytical Services Laboratory and by Galbraith Laboratories.

Materials. Ammonia was obtained from Matheson Gas Products, purified by trap to trap distillations, and dried over sodium. $[(CH_3)_3Si]_3Al{\cdot}O(C_2H_5)_2$ was prepared as described in the literature.[5] All solvents were rigorously dried with appropriate drying agents and degassed. Solvent transfers were accomplished by vacuum distillation.

Reaction of $[(CH_3)_3Si]_3Al{\cdot}Et_2O$ and NH_3 in a 1:2 Ratio. $[(CH_3)_3Si]_3Al{\cdot}O(C_2H_5)_2$ (4.7 mmol, 1.49 g) was placed in a 100-mL Schlenk flask in a nitrogen-filled glovebag. Ammonia (4.6 mmol) was condensed into the flask at −196 °C. The mixture was warmed to 25 °C and stirred for 2 days. The volatiles were removed, and additional ammonia (4.6 mmol) was added. After 6 days at 25 °C, the volatiles were removed and combined with the volatiles collected in the first stage of the reaction (gas composition: $(CH_3)_3SiH$ and NH_3). The remaining solid was combined with 30 mL of dry hexane, and the majority of the solid dissolved. The solution was filtered, and the filtrate and residue were analyzed. The insoluble residue was washed with hexane and dried, and elemental analyses and infrared spectra were obtained. The filtrate was evaporated, leaving 0.67 g of colorless solid product, yield 89% based upon formation of $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$. Anal. Calcd for $Si_6Al_4N_6C_{18}H_{66}$: C, 33.61; H, 10.34; N, 13.07. Found: C, 33.22; H, 9.97; N, 12.37. It was soluble in hydrocarbons, benzene, $(C_2H_5)_2O$, and $(C_2H_5)_3N$. The compound is recovered unchanged from each solvent. The compound decomposes without melting.[6] Infrared spectrum (cm^{-1}, KBr): 3371 (s), 3317 (s), 2940 (s), 2886 (s), 2807 (sh), 1520 (m), 1454 (m), 1431 (m), 1390 (sh), 1252 (m), 1238 (m), 1060 (m), 848 (s), 826 (s), 806 (s), 729 (m), 676 (s), 655 (s), 615 (s), 582 (s), 462 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 1.8 (CH_3Si). ^{1}H NMR (C_6D_6): δ 0.36 (CH_3Si).

Table I. Summary of Crystallographic Data for $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$

chem formula: $Al_4Si_6N_6C_{18}H_{66}$	space group: *C2/c*
fw: 643.2	$T = 20\ (2)$ °C
$a = 13.981\ (2)$ Å	$\bar{\lambda} = 0.71069$ Å
$b = 14.064\ (2)$ Å	$\rho_{calcd} = 0.98$ g cm^{-3}
$c = 23.025\ (2)$ Å	$\mu = 2.9$ cm^{-1}
$\beta = 106.2\ (1)°$	transmissn coeff: 0.874–0.933
$V = 4347\ (1)$ Å^3	$R_F = 9.56\%$
$Z = 4$	$R_{wF} = 7.37\%$

Pyrolysis of $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$. $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$ (1.6 mmol, 1.03 g) was loaded into a quartz tube, which was evacuated, and the closed tube was heated to 600 °C for 24 h. The tube was cooled, and the volatiles were removed and identified as $(CH_3)_3SiH$, and CH_4. The amount of faintly gray solid retained was 0.3 g. This solid was pyrolyzed in a quartz tube at 930 °C for 80 h, and a small amount of residual gas was evolved. The remaining solid was then treated at 930 °C for 6 h with NH_3 and was characterized by powder X-ray diffraction, SEM, and energy-dispersive X-ray analysis.

Crystal Structure Determination for $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$. Single crystals were obtained as colorless prisms from a saturated hexane solution stored at 0 °C. A suitable crystal, 0.23 × 0.35 × 0.35 mm, was mounted in a glass capillary and sealed. The crystal was centered on a Syntex P3/F automated diffractometer, and determinations of the crystal class, orientation matrix, and cell parameters were obtained in a standard fashion.[7] The data were collected at 20 °C in the ω scan mode (2θ = 2–50°) by using Mo Kα radiation (scan rate, variable 5–30° min^{-1}; scan range, [$\omega(0) - 0.9°$] to [$\omega(0) + 0.9°$]), a scintillation counter and pulse-height analyzer. Details of the data collection are summarized in Table I. Inspection of the data set indicated space group *C2/c* or its noncentric counterpart, *Cc*, and lattice constants were obtained from a least-squares fit to automatically centered settings for 25 reflections ($12.35° < 2\theta < 35.78°$). A small absorption correction based upon 360 Ψ scans was applied to the data; agreement factors for the azimuthal scans before and after the absorption correction were 2.14% and 1.94%, respectively. The data were corrected for Lorentz and polarization effects, redundant data averaged (R_{merge} = 2.53%), and space group extinct reflections removed. No signs of crystal decay were observed.

All calculations were performed on a Syntex R3/SHELXTL structure determination system.[8] Neutral-atom scattering factors and anomalous dispersion terms were used for all non-hydrogen atoms during the refinements. The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$. From a total of 3848 independent reflections, 2504 were observed above the $3\sigma(F)$ level, and these were used in the structure solution and refinement. The structure was solved by direct methods. The best *E* map gave trial positions for the four Al atoms, and the positions for the remaining non-hydrogen atoms were provided in a subsequent difference Fourier map. Refinement of the positional and anisotropic thermal parameters gave convergence at R_F = 11.16% and R_{wF} = 11.21%. The hydrogen atoms were calculated by using the riding model (C–H vector fixed in direction and length (0.96 Å) but not position) with U_{iso} set to 1.2 times the last U_{equiv} of their parent atom. This led to a final least-squares refinement convergence with R_F = 9.56% and R_{wF} = 7.37% for 155 variables and 2504 reflections. A final difference Fourier synthesis showed no unusual features, with the maximum peak height being 0.5 eÅ^{-3}. The anisotropic thermal parameters for the methyl carbon atoms C(7), C(8), and C(9) on Si(3) are large, and a difference map was searched without success for multiple sites. The acentric space group *Cc* was employed for an alternate solution, but the refinement did not converge. Tables of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters and complete listings of bond distances and angles are available in the

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

(5) Rösch, L. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 480. Rösch, L.; Altman, G. *J. Organomet. Chem.* **1980**, *195*, 47.

(6) Attempts to obtain a mass spectrum of the compound from a sample heated in a solids probe showed a highest mass ion at *m/e* 610.

(7) Programs used for centering reflections, autoindexing, refinement of cell parameters and axial photographs are those described in: Sparks, R. A. *Nicolet P3/R3 Operations Manual*; Syntex Analytical Instruments: Cupertino, CA, 1978.

(8) The SHELXTL package of programs for calculations and plots is described in: Sheldrick, G. M. *SHELXTL Users Manual, Revision 3*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses scattering factors and anomalous dispersion terms taken from: *International Tables of X-Ray Crystallography*; Kynoch: Birmingham, England, 1968; Vol. IV. Discrepancy indices are defined as follows: $R_F = [\sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF} = [\sum(w|F_o| - |F_c|)^2/\sum wF_o]^{1/2}$ and the goodness of fit GOF = $[w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO is the number of observations and NV is the number of variables.

Table II. Non-Hydrogen Atom Positional Parameters and Their Esd's for $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$

atom	*x/a*	*y/b*	*z/c*
Al(1)	0.00000	0.27495 (14)	0.25000
N(1)	−0.0545 (3)	0.3827 (3)	0.2895 (2)
N(2)	−0.0511 (3)	0.1750 (3)	0.2966 (2)
N(3)	0.1224 (3)	0.2678 (3)	0.3217 (2)
Al(2)	0.00000	0.48196 (15)	0.25000
Si(1)	0.13133 (14)	0.57844 (11)	0.31905 (8)
C(1)	0.1647 (5)	0.6826 (4)	0.2767 (3)
C(2)	0.2509 (5)	0.5123 (4)	0.3534 (3)
C(3)	0.0897 (6)	0.6317 (5)	0.3825 (3)
Al(3)	0.06655 (14)	0.17647 (12)	0.36517 (8)
Si(2)	0.14264 (16)	0.01638 (13)	0.37520 (9)
C(4)	0.0420 (7)	−0.0746 (5)	0.3485 (4)
C(5)	0.2063 (7)	−0.0189 (5)	0.4535 (3)
C(6)	0.2274 (8)	−0.0079 (7)	0.3296 (5)
Si(3)	0.03095 (15)	0.24743 (13)	0.45611 (8)
C(7)	−0.0986 (7)	0.2264 (8)	0.4568 (4)
C(8)	0.0346 (8)	0.3788 (5)	0.4601 (3)
C(9)	0.1130 (9)	0.2110 (8)	0.5279 (3)

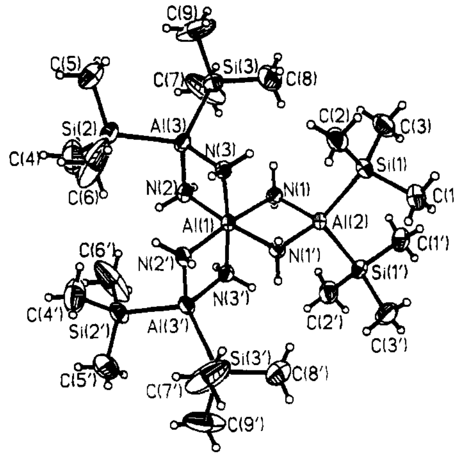

Figure 1. Molecular structure and labeling scheme (25% thermal ellipsoids) for $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$. A 2-fold axis passes through Al(1) and Al(2).

supplementary material. Nonhydrogen atom positional parameters are summarized in Table II.

Results and Discussion

During our initial studies[4] of the reactions of $[(CH_3)_3Si]_3Al$ and NH_3, the appearance of additional resonances in the ^{13}C and ^1H NMR spectra of $\{[(CH_3)_3Si]_2AlNH_2\}_2$, when this dimeric molecule was prepared under conditions where there was a slight excess of NH_3 over a 1:1 reactant ratio, led us to suspect the formation of a second molecular product. Indeed, combination of $[(CH_3)_3Si]_3Al{\cdot}O(C_2H_5)_2$ and NH_3 in a 1:2 ratio produced a second colorless crystalline product shown to be $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$ (**1**) by elemental analysis, spectroscopic data and, most convincingly, by a single-crystal X-ray diffraction analysis. The chemistry is summarized by

$$4[(CH_3)_3Si]_3Al{\cdot}O(C_2H_5)_2 + 6NH_3 \rightarrow Al\{(NH_2)_2Al[Si(CH_3)_3]_2\}_3 + 6(CH_3)_3SiH + 4O(C_2H_5)_2$$

Further variations in reactant stoichiometry confirmed that the optimum yield of **1** resulted with a reactant ratio of 1:1.5. Trimethylsilane was quantitatively recovered from the reaction mixtures, and a small amount of an insoluble white solid was obtained when the amount of ammonia was greater than 1.5 equiv. The insoluble product was identified by elemental analysis and infrared spectroscopy to be the same insoluble material obtained from reactions reported previously[4] where excess NH_3 was employed.

The molecular structure of **1** is shown in Figure 1, and selected interatomic bond distances and angles are summarized in Table III. The structure can be considered to contain a central aluminum ion Al(1) bonded equivalently to the amide nitrogen atoms of three formal bidentate ligands, $\{[(CH_3)_3Si]_2Al(NH_2)_2^-\}$. The six amide nitrogen atoms surrounding Al(1) form a pseudooctahedral coordination polyhedron. The average $Al(1)-N(H)_2$ distance, 2.020 Å (range 2.022 (4)–2.017 (5) Å) is significantly longer than the average $Al-N(H)_2$ distance in the $\{[(CH_3)_3Si]_2Al(NH_2)_2^-\}$ groups, 1.932 Å [Al(2)–N(1), Al(3)–N(2), Al(3)–N(3) range 1.936 (4)–1.923 (5) Å]. The average $Al(1)-N(H)_2$ distance also is longer than the typical range of distances found in other aluminum amides, 1.91–1.97 Å. Examples include $\{[(CH_3)_3Si]_2AlNH_2\}_2$, 1.953 (2) and 1.956 (2) Å;[4] $[(CH_3)_2AlN(CH_3)_2]_2$, 1.958 (5) Å;[9] $[(CH_3)_2AlNH_2]_3$, 1.935 (5);[10] and $[H_2AlN(CH_3)_2]_3$, 1.93 (3) Å.[11] The average $Al-N(H)_2$ distance in the ligands, on the other hand, is more typical of the Al–N internal ring distances found in dimeric and trimeric aminoalane rings. The average N–Al(1)–N bite angle is 82.9 (2)° while the remaining average of the adjacent N–Al(1)–N bond angles in the central octahedron is 92.7 (2)°. The internal N–Al–N angles in the bidentate ligands are 87.7 (3) and 87.6 (3)°. These angles compare favorably with the N–Al–N angle in $\{[(CH_3)_3Si]_2AlNH_2\}_2$, 86.9 (1)°, and both are larger than those typically found in Al–NH rings containing alkyl fragments on the Al atom. The nonequivalent Al–Si bond distances range from 2.472 (2) to 2.492 (3) Å, and these compare favorably with the distances in $[(Me_3Si)_2AlNH_2]_2$, 2.472 (1) Å, and $(Me_3Si)_3Al{\cdot}TMEDA$, 2.472 Å. The factor responsible for the one long Al(3)–Si(3) distance (2.492 Å) is not obvious.

Table III. Selected Bond Distances (Å) and Angles (deg) for $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$

	Bond Distances		
Al(1)–N(1)	2.022 (4)	Al(1)–N(2)	2.017 (5)
Al(1)–N(3)	2.022 (3)	Al(2)–N(1)	1.935 (4)
Al(3)–N(2)	1.936 (4)	Al(3)–N(3)	1.923 (5)
Al(1)–Al(2)	2.911 (3)	Al(1)–Al(3)	2.905 (2)
Al(2)–Si(1)	2.472 (2)	Al(3)–Si(2)	2.473 (3)
Al(3)–Si(3)	2.492 (3)		
	Bond Angles		
N(1)–Al(1)–N(2)	92.8 (2)	N(2)–Al(1)–N(1′)	174.6 (2)
N(1)–Al(1)–N(3)	90.5 (2)	N(3)–Al(1)–N(3′)	174.3 (2)
N(2)–Al(1)–N(3)	82.9 (2)	N(3)–Al(1)–N(1′)	93.7 (2)
N(1)–Al(1)–N(1′)	83.0 (2)	N(3)–Al(1)–N(2′)	93.2 (2)
Al(1)–N(1)–Al(2)	94.7 (2)	N(2)–Al(1)–N(2′)	91.6 (3)
Al(1)–N(3)–Al(3)	94.8 (2)	Al(1)–N(2)–Al(3)	94.6 (2)
N(1)–Al(2)–N(1′)	87.6 (3)	N(2)–Al(3)–N(3)	87.7 (2)

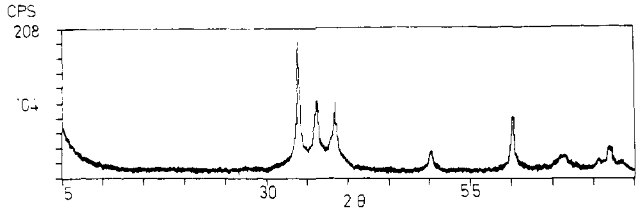

Figure 2. X-ray diffraction powder pattern for the pyrolysis product from $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$.

The spectroscopic data collected for **1** are consistent with the solid-state structure. In particular, the ^1H and ^{13}C NMR spectra show equivalent trimethylsilyl proton and carbon environments, and the infrared spectra show absorptions at 3371 and 3317 cm^{-1} that can be assigned to the bridging amide NH_2 stretches and absorptions at 2940 and 2886 cm^{-1} that are assigned to C–H stretches for the methyl groups. The spectra are very similar to those for $\{[(CH_3)_3Si]_2AlNH_2\}_2$ except that the ^1H resonance for the amide groups was not detected in **1**.

Pyrolysis of **1** was studied as previously described for $\{[(CH_3)_3Si]_2AlNH_2\}_2$.[4] Samples were heated in two stages in a quartz tube under vacuum. At 600 °C, $(CH_3)_3SiH$ and CH_4 were

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

(10) Czekaj, C. L.; Hackney, M. L.; Sigel, G. A.; Interrante, L. V. *Mater. Res. Soc. Symp. Proc.*, in press.

(11) Semenko, K. N.; Loblouski, E. B.; Dovsinskii, A. L. *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 696.

4338 *Inorg. Chem.* **1988**, *27*, 4338–4343

collected and identified, and at 930 °C, very small amounts of $(CH_3)_3SiH$, CH_4, and H_2 were found in the off-gas. The remaining light gray solid was heated at 930 °C under a stream of ammonia. The resulting solid is still slightly gray, and the color suggests the presence of residual carbon. A powder X-ray pattern for this material is shown in Figure 2. The pattern is essentially identical with the patterns for the isostructural pure phases of AlN and 2H-SiC, and the diffraction lines are shifted slightly to larger 2θ values from those of pure AlN.[12] Energy-dispersive X-ray analyses unambiguously show the presence of aluminum and silicon in an approximate 5:1 ratio.

On the basis of these results and the findings from our earlier studies of the pyrolysis of $\{[(CH_3)_3Si]_2AlNH_2\}_2$,[4] it appears that aluminum nitride containing small amounts of SiC is obtained from pyrolysis of these molecular aminosilylaluminum precursors. At this time, additional detailed processing studies of these precursors under a variety of conditions and extensive microstructure characterization of the resulting ceramic products are in progress.

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Registry No. $[(CH_3)_3Si]_3Al{\cdot}Et_2O$, 75441-10-0; $(CH_3)_3SiH$, 993-07-7; $\{[(CH_3)_3Si]_2Al(NH_2)_2\}Al$, 117251-56-6; CH_4, 74-82-8; AlN, 24304-00-5; SiC, 409-21-2.

Supplementary Material Available: Tables SI–SV, giving a full description of experimental data for the X-ray analysis, anisotropic temperature factors, hydrogen atom positional parameters, and all bond distances and bond angles (7 pages); Table SVI, giving calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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(12) The diffraction lines displayed by the mixture have the following values [2θ, deg (*hkl*)]: 33.816 (100), 36.090 (002), 38.375 (101), 50.110 (102), 60.100 (110), 71.367 (200), 72.124 (112). Close examination of the diffraction patterns does not reveal evidence for the presence of low-temperature α-SiC as might be expected; however, the relatively small amount of silicon in the sample, as evidenced by X-ray analysis, makes identification of a specific SiC phase difficult. Parallel studies of the system $[(CH_3)_3Si]_3Al/PH_3$ reveal formation of AlP and SiC. In this case, the binaries are not isostructural, and the powder X-ray diffractions of the separate components do not severely overlap. We observe SiC with diffuse diffraction lines, and the majority of the SiC is amorphous.

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Substitution Reaction of Hexachlorocyclotriphosphazene with Trimethylaluminum

Logan A. Jackson* and Paul J. Harris

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The reaction of hexachlorocyclotriphosphazene with trimethylaluminum yields the fully substituted hexamethylcyclotriphosphazene and a ring-opened linear phosphazene salt. The substitution pathway that yields the fully substituted cyclic product was determined by monitoring the reactions of several methylchlorocyclotriphosphazenes with trimethylaluminum with the use of gas chromatography and ^{31}P NMR spectroscopy. The reaction was found to proceed via both geminal and nongeminal substitution pathways, depending on the species undergoing substitution. The degree of ring opening that occurred was observed to decrease with increasing methyl substitution of the phosphazene ring. The new products prepared were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental analysis.

Introduction

The preparation of highly alkylated phosphazenes is an area of concentrated interest. The most thoroughly examined means of synthesis of highly alkylated phosphazenes involves the reaction of halophosphazenes with organometallic reagents.[1] The studies of the reaction of organometallic reagents with chlorocyclotriphosphazenes have produced a wide variety of mono- and dialkylated cyclic chlorotriphosphazenes.[2–7] However, complete replacement of the chlorine atoms of the cyclic trimeric phosphazene ring with alkyl substitutents has not yet been achieved by direct substitution reactions with organometallic reagents. Studies of the reaction of cyclic chlorophosphazenes with various organometallic reagents have been used as models for similar reactions with the poly(dichlorophosphazene) polymer.[8] The reactions of organometallic reagents with poly(dichlorophosphazene) have resulted in substitution, but these reactions are also accompanied by cleavage of the phosphazene chain.[9,10]

The reactions of organometallic reagents with chlorocyclotriphosphazenes are some of the most complex in main-group chemistry. The substitution pathway has not always been well-defined and in many cases involves complex intermediates. The reactions of Grignard reagents with chlorocyclotriphosphazenes are found to yield bicyclophosphazenes, while these reactions in the presence of an organocopper reagent are found to proceed via a metal–halogen-exchange pathway to yield mono- and dialkylated chlorocyclotriphosphazenes.[2,4] Reactions with simple organolithium reagents have primarily been found to result in cleavage of the phosphazene ring.[14,15] Recently, the reaction of methyl-

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(1) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119.
(2) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(3) Allcock, R. H.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(4) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(5) Harris, P. J.; Williams, K. B.; Fisher, B. L. *J. Org. Chem.* **1984**, *49*, 406.
(6) Harris, P. J.; Schwalke, M. A.; Lui, V.; Fisher, B. L. *Inorg. Chem.* **1983**, *22*, 1812.
(7) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256.
(8) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(9) Allcock, H. R.; Chu, C. T. W. *Macromolecules* **1979**, *12*, 551.
(10) MacCallum, J. R.; Tanner, J. *J. Polym. Sci., Part A* **1968**, *6*, 3163.
(11) Lui, C. F.; Evans, R. L. U.S. Patent 3169933, 1965; *Chem. Abstr.* **1965**, *63*, 704e.
(12) Allcock, H. R.; Harris, P. J.; Desorcie, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2814.
(13) Allcock, H. R.; Harris, P. J.; Desorcie, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 852.
(14) Biddlestone, M.; Shaw, R. A. *Phosphorus Relat. Group V Elem.* **1973**, *3*, 95.
(15) Harris, P. J.; Fadeley, C. L. *Inorg. Chem.* **1983**, *22*, 561.

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