to bridge in only one Mo complex, and the interactions are weak.[6] Ligands such as oxo and alkoxo exhibit a greater ability to donate electron density and bridge compared with siloxo, since a greater proportion of the O electron density in the siloxo group is locked into strong Si–O bonding interactions within the ligand, making it unavailable for bonding. It appears to us that the title compound crystallizes as a cubane, in part, because the strong bridging ability of the oxo groups in conjunction with the comparatively weaker bridging ability of the siloxo group prevents the formation of the bioctahedral structure.

Why should the cubane or bioctahedron form rather than some other more open structure? Representatives of open structures include the forementioned pyrazoylborate and the complex $Mo_4O_4(\mu_3\text{-}O)Cl_2(CH_3COO)_6$.[24] The structure of the latter molecule may be constructed from one of the simple dimer units depicted at the left in Figure 2 and two additional Mo-centered octahedra, each attached to one of the shared O vertices of the dimer. These vertices are the only ligand atoms shared among the Mo atoms. In the cubane and fused bioctahedral structures, the ratio of donor atoms:metal atoms is fixed at 4:1. Comparing the open structures with the bioctahedron and cubane, we find fewer ligand atoms occupying bridging positions in the open structures. If fewer atoms are bridging, a greater number of ligand atoms will be required to fill the resulting terminal sites and complete the octahedral coordination about each Mo atom. Hence, a larger ratio of donor atoms:metal atoms, 9:2, is observed in the open structures. If the bridging abilities of the ligand atoms are limited, a larger number of ligand atoms will be required, and the bioctahedron and cubane will not form. The ratio of donor atoms:metal atoms as dictated by the bridging and electron-donating abilities of the ligands affords the cubane structure of the title compound.

Acknowledgment. D.A.K. thanks the Alfred P. Sloan Research Foundation for a fellowship (1989–1991).

Supplementary Material Available: Table S-1, listing complete crystal and experimental data, Table S-2, giving positional parameters, Table S-3, listing *U* values, Table S-4, giving intramolecular interatomic distances, and Table S-5, listing intramolecular interatomic angles (16 pages); Table S-6, listing calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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Contribution from Ultrasystems Defense, Inc.,
16775 Von Karman Avenue, Irvine, California 92714

Novel Trimethylsilyl-Substituted Aminoboranes

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J. H. Nakahara, and R. H. Kratzer

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The major emphasis in the approaches to BN precursors has been centered on cyclics.[1] However, as demonstrated by Beck et al., reaction of simple adducts such as $Me_2S{\cdot}BHBr_2$ with ammonia provide alternate routes to BN.[2] Trimethylsilyl-substituted aminoboranes are also of potential interest in this application in view of their processibility, versatility, and the ease of (trimethylsilyl)amino group elimination. A number of (trimethylsilyl)amino-substituted boranes have been described.[3-10] We have prepared a bis((silylamino)boryl)amine, $[(Me_3Si)_2NBNHSiMe_3]_2NH$;[11] however, the feasibility of making longer chain B–N materials of this nature needed to be established. Shaw et al.[12] approached this problem by bridging N–B(Ph)–N with $(CH_2)_n$ units. The presence of carbon on nitrogen and boron in this system provides for carbon retention on any subsequent pyrolysis. In BN precursors a very important consideration is the avoidance of carbon substituents on boron. Earlier, Jenne and Niedenzu[13] and Nöth and co-workers[14,15] described a series of noncyclic boron-nitrogen compounds containing up to four boron atoms. However, in each of the compounds, at least some of the boron atoms were either alkyl- or aryl-substituted. Our goal was to prepare B–N chains free of B–C and N–C linkages. We wish now to report novel linear borylamines containing up to four boron atoms as well as intermediates containing free NH_2 substituents. The latter offer particularly suitable monomers for linear B–N polymer synthesis and borazine-ring-linking applications.

Experimental Section

General Procedures. Operations were carried out either in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass, or by using standard vacuum line procedures.[16] Infrared spectra were recorded: solids as double mulls (Kel-F oil No. 10 and Nujol); liquids as capillary films on a Perkin-Elmer Model 1330 infrared spectrophotometer. The mass spectra (EI) were obtained from a Du Pont Model 21-491B spectrometer. 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 3 ft × $^1/_8$ in. stainless steel column packed with 3% Dexsil 300 resin on 100/200 mesh Chromosorb W-AW. NMR spectra were recorded on a Varian VXR-200 spectrometer; for ^{11}B a 64.2-MHz operating frequency was employed. Me_4Si and $BF_3{\cdot}Et_2O$ were used as external standards for ^1H and ^{11}B NMR, respectively. Boron and nitrogen were determined by wet analysis; boron by base titration, nitrogen as NH_3 by using ion chromatography.

Materials. Ammonia (Matheson Gas Products) was purified by trap-to-trap distillation and dried over potassium, and BCl_3 by vacuum line fractional condensations; $(Me_3Si)_2NH$ (Aldrich Chemical Co.) was used as received; triethylamine (Aldrich Chemical Co.) was distilled from $LiAlH_4$. $(Me_3Si)_2NB(NH_2)NHSiMe_3$,[6] $(Me_3Si)_2NBCl_2$,[5] and $BCl_3{\cdot}NEt_3$[17] were prepared by literature procedures. All solvents were rigorously dried and degassed.

$(Me_3Si)_2NB[HNB(NHSiMe_3)N(SiMe_3)_2]_2$ (1). To a stirred solution of $(Me_3Si)_2NB(NH_2)NHSiMe_3$ (14.99 g, 54.4 mmol) in triethylamine (38 mL) was added dropwise, at room temperature, $(Me_3Si)_2NBCl_2$ (6.61 g, 27.3 mmol) over a period of 30 min; a white precipitate started to form immediately. Stirring was continued for 16 h at room temperature, followed by 6.5 h at 100 °C. After cooling, triethylamine hydrochloride, 4.15 g (55.4% yield), was filtered off. The excess triethylamine, unreacted starting materials, and byproducts were removed in vacuo by heating to 213 °C. Some of the product (13% of theoretical yield based on $(Me_3Si)_2NBCl_2$ employed) was present in the distillate as determined by GC. The product accounted for 87% of the 3.82 g of distillation residue, bringing the total yield of the material to 21.5%. Crystallization from Freon-113 gave 1.57 g of $(Me_3Si)_2NB[HNB(NHSiMe_3)N(SiMe_3)_2]_2$, mp 120–120.5 °C. Anal. Calcd for $C_{24}H_{76}N_7B_3Si_8$: N, 13.62; B, 4.50. Found: N, 13.93; B, 4.54. IR (cm^{-1}, NaCl plates): 3395 (w), 3360 (w), 3300 (m), 2950 (s), 2895 (m), 1410 (s, br), 1346 (s), 1260 (s), 1247 (s), 1143 (m), 1108 (s), 996 (s), 965 (sh),

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945 (s), 910 (m), 874 (m), 830 (s, br), 758 (s), 680 (s), 650 (w), 620 (m). MS (70 eV), *m/e* (relative intensity, ion): 719 (26.8%, M), 704 (14.6%, M − Me), 615 (11.7%, M − Me − H_2NSiMe_3), 445 (22.4%, M − HNB($NHSiMe_3$)$N(SiMe_3)_2$), 259 (100%, $(Me_3Si)_2NBNHSiMe_3$), 187 (10%, $H_2NBN(SiMe_3)_2$), 171 (12.8%, $BN(SiMe_3)_2$). ^1H NMR (C_6D_6): δ 0.30 (s), 3.55 (br) in the ratio 21.5:1 (theory 18:1, if $NH(SiMe_3)$ and bridging NH are unresolved). ^{11}B NMR: δ 34.8 (*h*/2 ~ 682 Hz).

$B[HNB(NHSiMe_3)N(SiMe_3)_2]_3$ (2). To a stirred refluxing solution of boron trichloride triethylamine adduct (5.09 g, 23.3 mmol) and triethylamine (7.08 g, 70.0 mmol) in benzene (15 mL) was added dropwise $(Me_3Si)_2NB(NH_2)NHSiMe_3$ (19.29 g, 70.0 mmol) over 1.5 h. Heating was then continued for another 2.5 h. Filtration gave 8.69 g (90.3% yield) of triethylamine hydrochloride. Removal of solvent from the filtrate gave 20.55 g of a thick slurry; washing with Freon-113 and then methanol resulted in isolation of a solid (6.05 g, 31.1% yield). Recrystallization from Freon-113 afforded 4.29 g (22.1% yield) of $B[NHB(NHSiMe_3)N(SiMe_3)_2]_3$, mp 128–130 °C. Anal. Calcd for $C_{27}H_{87}N_9B_4Si_9$: N, 15.11; B, 5.18. Found: N, 15.58; B, 4.76. IR (cm^{-1}, NaCl plates): 3348 (m–w), 3498 (m–w), 2955 (m), 2900 (m–w), 1430 (s), 1345 (s), 1280 (s), 1265 (s), 1250 (s), 1215 (m), 1180 (sh), 1128 (s), 973 (s), 946 (s), 875 (s), 836 (s, br), 790 (w), 755 (s), 684 (s), 630 (w), 615 (w). MS (70 eV), *m/e* (relative intensity, ion): 833 (18.7%, M), 818 (4.5%, M − Me), 575 (11.2%, M − $(Me_3Si)_2NBNSiMe_3$), 560 (16.9%, M − $NBN(SiMe_3)(NHSiMe_3)$), 259 (100%, $(Me_3Si)_2NBNHSiMe_3$), 187 (10.0%, $H_2NBN(SiMe_3)_2$), 171 (12.8%, $BN(SiMe_3)_2$). ^1H NMR: δ 0.30, 0.32 (s), 2.66 (s), 3.46 (s) in the ratio 27 (δ 0.30 and 0.32 combined):0.9:1 (theory 27:1:1). ^{11}B NMR: δ 31.4 (*h*/2 ~ 1364 Hz).

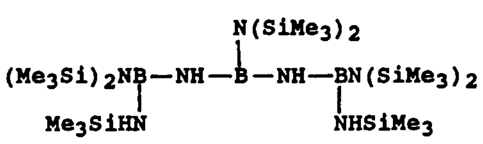
$(Me_3Si)_2NB(NH_2)_2$ (3) and $[(Me_3Si)_2NBNH_2]_2NH$ (4). To stirred liquid ammonia (~13 g held at −78 °C) was added, via an addition funnel, a solution of $(Me_3Si)_2NBCl_2$ (8.20 g, 33.9 mmol) in pentane (30 g) over a period of 1 h. Stirring at −78 °C was continued for 4 h. The mixture was then allowed to warm to room temperature overnight. The precipitated ammonium chloride (3.66 g, quantitative yield) was filtered off; the filtrate (following solvent removal in vacuo) gave 6.32 g of residue, which was separated into two portions by distillation in vacuo at 40–65 °C. The distillate, 3.88 g, bp 26–27 °C/0.001 mmHg, consisted of 80% of $(Me_3Si)_2NB(NH_2)_2$ corresponding to a 45% yield. This material was further purified by vacuum line fractionation through traps held at 0, −23, and −196 °C. The pure $(Me_3Si)_2NB(NH_2)_2$ was collected in the 0 °C trap. Anal. Calcd for $C_6H_{22}N_3BSi_2$: N, 20.67; B, 5.32. Found: N, 20.85; B, 5.31. IR (cm^{-1}, KBr plates): 3528 (m), 3435 (m), 2955 (s), 2895 (m), 1590 (s), 1445 (w), 1410 (w), 1360 (m), 1324 (s), 1285 (s), 1250 (s), 965 (s, br), 902 (m), 835 (s, br), 754 (m), 680 (m), 650 (w), 625 (w). MS (70 eV), *m/e* (relative intensity, ion): 203 (36.9%, M), 188 (100%, M − Me), 171 (86.0%, M − Me − NH_3), 130 (23.1%, $Me_3SiNSiMe$). ^1H NMR (C_6D_6): δ 0.18 (s), 1.63 (s) in the ratio 4.5:1 (theory 4.5:1). ^{11}B NMR: δ 31.9 (*h*/2 = 80.2 Hz).

$[(Me_3Si)_2NBNH_2]_2NH$ (1.89 g, 27% yield) comprised the distillation residue (95% purity based on GC). It was further purified by sublimation, mp 47–48°C. Anal. Calcd. for $C_{12}H_{41}N_5B_2Si_4$: N, 17.98; B, 5.55. Found: N, 17.25; B, 5.46. IR (cm^{-1}, KBr plates): 3525 (m), 3437 (m), 2955 (s), 2895 (m), 1594 (s), 1428 (s), 1403 (s), 1334 (s), 1300 (m), 1250 (s, br), 1153 (s), 965 (s, br), 837 (s), 755 (s), 680 (s), 650 (w), 624 (w). MS (70 eV), *m/e* (relative intensity, ion): 389 (14.1%, M), 374 (100%, M − Me), 357 (70.1%, M − Me − NH_3), 300 (11.6%, M − H_2NSiMe_3), 285 (77.1%, M − Me − H_2NSiMe_3), 269 (57.0%, M − Me − NH_3 − $NHSiMe_3$), 187 (36.3%, $H_2NBN(SiMe_3)_2$), 171 (26.0%, $BN(SiMe_3)_2$). ^1H NMR (C_6D_6): δ 0.24 (s), 2.31 (br), 2.84 (br) in the ratio 34:3.4:1 (theory 36:4:1). ^{11}B NMR: δ 33.0 (*h*/2 ~ 241 Hz).

Pyrolysis of $[(Me_3Si)_2NBNH_2]_2NH$. **4** (0.76 g, 1.95 mmol) was heated in vacuo at 200 °C for 20 h. A viscous liquid resulted. After opening to the vacuum system, the condensible volatiles (115 mg) were collected and then fractionated through −63 and −78 and into −196 °C cooled traps. $HN(SiMe_3)_2$ (93 mg, 0.59 mmol) was condensed in the −63 and −78 °C traps; NH_3 (22 mg, 1.29 mmol), in the −196 °C trap. The residue was analyzed by GC/MS; three borazines were identified: $[(Me_3Si)_2NBNH][(Me_3Si)HNBNH]_2$,[18] $[(Me_3Si)_2NBNH]_2[(Me_3Si)HNBNH]$,[19] and $[(Me_3Si)_2NBNH]_3$,[18] in the ratio 1:13:10.

Results and Discussion

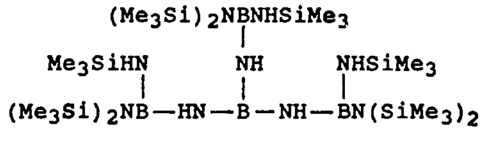
Reaction of $(Me_3Si)_2NBCl_2$ with $(Me_3Si)_2NB(NH_2)NHSiMe_3$ in a 1:2 ratio in the presence of triethylamine gave **1** in ~20% yield. The pure product was stable in air. The presence of a molecular ion in its mass spectrum and the fragmentation pattern fully support the above arrangement. The broad ^{11}B NMR resonance centered at 35 ppm is consistent with the data reported for related arrangements.[20] In the ^1H NMR spectrum only one NH resonance was observed. The relative ratio of the methyl protons to the nitrogen protons tends to indicate that this resonance is responsible for both the bridging NH and $NHSiMe_3$ groups. One would expect to observe two NH resonances, as in the case of the diborylamine compound.[11] The presence of $NHSiMe_3$ is shown by the strong infrared band at 1108 cm^{-1}. No pyrolysis studies were performed. However, since **1** could be analyzed by gas chromatography at 250 °C, it must be stable at least for a short period at this temperature. This is not surprising since amino(bis(trimethylsilyl)amino)boranes were found to be stable at 150–200 °C for several hours due to the shielding effect of the $(Me_3Si)_2N$ group.[10] On the other hand, at higher temperatures and in the presence of ammonia, the elimination of hexamethyldisilazane does occur.[21]



$$(Me_3Si)_2N\underset{\displaystyle Me_3SiHN}{\underset{|}{B}}-NH-\overset{\displaystyle N(SiMe_3)_2}{\overset{|}{B}}-NH-\underset{\displaystyle NHSiMe_3}{\underset{|}{B}}N(SiMe_3)_2$$

1

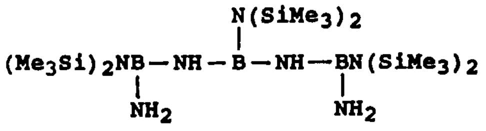
Compound **2** was obtained from the reaction of $BCl_3 \cdot NEt_3$ with $(Me_3Si)_2NB(NH_2)NHSiMe_3$ in a 1:3 ratio in the presence of triethylamine. The analytical data obtained for **2** are in full agreement with the assigned structure. In the ^1H NMR spectrum the NH protons are clearly resolved, and the observed ratios correspond closely with the theoretical values. The presence of a high-intensity molecular ion in its mass spectrum and the fragmentation pattern further confirm the arrangement. **2** was stable in air and exhibited high thermal stability, as evident by its elution from the GC column at 275 °C.



$$(Me_3Si)_2N\overset{\displaystyle Me_3SiHN}{\overset{|}{B}}-HN-\overset{\displaystyle \overset{\displaystyle (Me_3Si)_2NBNHSiMe_3}{\overset{|}{NH}}}{\overset{|}{B}}-NH-\overset{\displaystyle NHSiMe_3}{\overset{|}{B}}N(SiMe_3)_2$$

2

Inasmuch as the linear BN compounds can be prepared, and it is believed that the yields can be improved, the next step was to synthesize compounds containing free NH_2 groups amenable to condensation with either dihaloboranes or dihaloborazines. $(Me_3Si)_2NB(NH_2)_2$ (**3**) and $[(Me_3Si)_2NBNH_2]_2NH$ (**4**) were obtained by reacting $(Me_3Si)_2NBCl_2$ with a large excess of ammonia at −78 °C. We were unable to control conditions so as to obtain either **3** or **4** exclusively. Invariably, both materials were formed, but separation could be readily accomplished by distillation. There are a number of possible paths to **4**, namely, reaction of **3** with $(Me_3Si)_2NBCl_2$ or a mechanism involving an active intermediate such as $(Me_3Si)_2NB(NH_2)Cl$. There are no data available to postulate a specific mechanism. It is of interest that compound **5** was not observed. However, since the analyses were performed by GC/MS, such a material could have been retained



$$(Me_3Si)_2N\underset{\displaystyle NH_2}{\underset{|}{B}}-NH-\overset{\displaystyle N(SiMe_3)_2}{\overset{|}{B}}-NH-\underset{\displaystyle NH_2}{\underset{|}{B}}N(SiMe_3)_2$$

5

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[18] The borazine was identified by its mass spectrum (70 eV), *m/e* (relative intensity, ion): 414 (15.1%, M), 399 (100%, M − Me), 310 (18.4%, M − Me − $H_2NHSiMe_3$).

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by the column. In view of the high, >70%, combined yield of the isolated compounds **3** and **4**, this side reaction, if it occurred, took place only to a limited extent.

The analytical data obtained for $(Me_3Si)_2NB(NH_2)_2$ and $[(Me_3Si)_2NBNH_2]_2NH$ are in agreement with the assigned structures. Both compounds exhibited in their mass spectra a high-intensity molecular ion, and the breakdown patterns were consistent with the arrangements. In each case, a prominent ion was observed corresponding to loss of a methyl group and ammonia. Ions derived by loss of ammonia were absent in the mass spectra of **1** and **2**, which is to be expected due to the absence of NH_2 groups. Neither compound exhibited an infrared absorption at ~ 1100 cm^{-1}, confirming the absence of $NHSiMe_3$ groups; both had very strong bands in the vicinity of 1600 cm^{-1}, characteristic of a NH_2 deformation mode. The ^1H NMR of **3** showed two resonances at δ 0.18 (CH_3) and 1.63 (NH_2); for **4** three resonances were observed at δ 0.18 (CH_3), 2.31 (NH_2), and 2.84 (NH), confirming the presence of the three different NH protons. The ^{11}B NMR signal was broader in **4** than in **3**, which is to be expected. The chemical shifts, 31.8 and 33.0 ppm, respectively, are consistent with the literature data.[20]

Only preliminary thermal stability studies were performed on **4**. The material was recovered essentially unchanged when exposed to 150 °C for 20 h. However, after 20 h at 200 °C, no starting material was recovered. The two borazines $[(Me_3Si)_2NBNH]_2[(Me_3Si)HNBNH]$ and $[(Me_3Si)_2NBNH]_3$ were produced in approximately equal proportions, together with a small amount of $[(Me_3Si)_2NBNH][(Me_3Si)HNBNH]_2$.

Acknowledgment. Support of this research from the Strategic Defense Sciences Office through Contract N-00014-87-C-0713 from the Office of Naval Research is gratefully acknowledged. We thank Dr. G. K. S. Prakash of the University of Southern California for providing the NMR data and Dr. W. Krone-Schmidt and Ms. L. Lim for assisting with some of the syntheses.

Registry No. **1**, 130497-70-0; **2**, 130497-71-1; **3**, 62779-47-9; **4**, 130497-72-2; $(Me_3Si)_2NB(NH_2)NHSiMe_3$, 7266-80-0; $(Me_3Si)_2NBCl_2$, 6591-26-0; $BCl_3{\cdot}NEt_3$, 2890-88-2; NH_3, 7664-41-7; $[(Me_3Si)_2NBNH][(Me_3Si)HNBNH]_2$, 130497-73-3; $[(Me_3Si)_2NBNH]_2[(Me_3Si)HNBNH]$, 130497-74-4; $[(Me_3Si)_2NBNH]_3$, 113665-33-1.

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Complex of a Silyl Ether with a Dichloroaluminum Alkoxide. Reaction of the Bis(trimethylsilyl) Ether of *trans*-1,2-Cyclohexanediol with Aluminum Chloride

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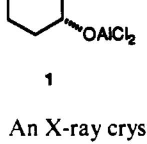
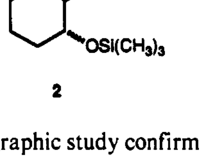
Received May 14, 1990

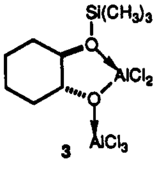
In attempting to prepare dichloroaluminum alkoxide **1**, a novel bidentate Lewis acid,[1] we added the bis(trimethylsilyl) ether **2**[2] of *trans*-1,2-cyclohexanediol to a suspension of 2 equiv of aluminum chloride in CH_2Cl_2 at 25 °C. This reaction yielded a crystalline compound that was not the expected product **1** of complete desilylation. Instead, its ^1H NMR spectrum showed a single trimethylsilyl signal shifted 0.56 ppm downfield from that of starting material **2**, and its elemental analysis confirmed that only 1 equiv of chlorotrimethylsilane had been lost. Structure **3** is consistent with these observations but includes two unusual features: coordination of a silyl ether by a Lewis acid[3] and a trans junction of five- and six-membered rings.



1



2



3

An X-ray crystallographic study confirmed this assignment and provided the structure shown in Figure 1. Crystallographic data

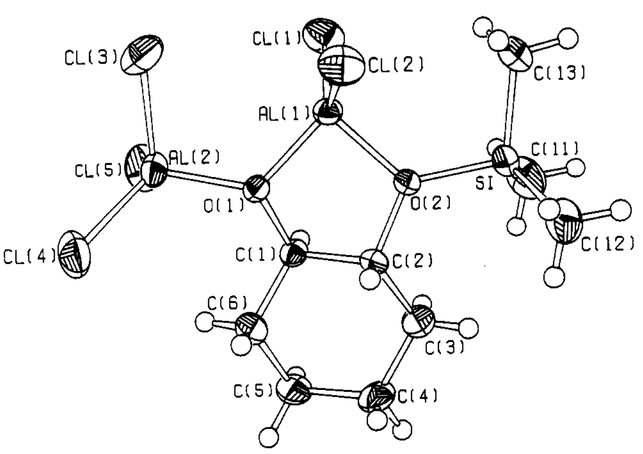


Figure 1. ORTEP drawing of the structure of the chloroaluminum alkoxide **3**. Non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability, and hydrogen atoms are shown as spheres of arbitrary size.

Table I. Crystallographic Data for the Chloroaluminum Alkoxide **3** and Experimental Parameters

formula	$C_9H_{19}Al_2Cl_5O_2Si$
fw	418.564
cryst syst	monoclinic
space group	$P2_1/c$
cell const	
a, Å	8.817 (2)
b, Å	13.729 (5)
c, Å	19.485 (5)
β, deg	126.63 (2)
cell volume (Å^3)	1892.8
Z	4
T (K)	190
ρ_{calcd}, g cm^{-3}	1.469
μ_{calcd}, cm^{-1}	9.20
radiation	graphite-monochromated Mo K$\bar{\alpha}$ (λ = 0.71069 Å)
cryst dimens, mm	0.28 × 0.36 × 0.70
scan width	1.00 + 0.35 tan θ
$2\theta_{max}$, deg	50.0
data collcn range	$\pm h,k,l$
no. of reflcns collcd	3598
no. of reflcns retained	2759 ($I \geq 3.00\sigma(I)$)
no. of params refined	208
goodness-of-fit	2.08
R	0.031
R_w	0.036

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(1) For references to related work on multidentate Lewis acids, see: Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955–958. Galeffi, B.; Simard, M.; Wuest, J. D. *Ibid.* **1990**, *29*, 951–954. Bélanger-Gariépy, F.; Hoogsteen, K.; Sharma, V.; Wuest, J. D. *Ibid.*, submitted for publication. Bachand, B.; Bélanger-Gariépy, F.; Wuest, J. D. *Organometallics* **1990**, *9*, 2860–2862.

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