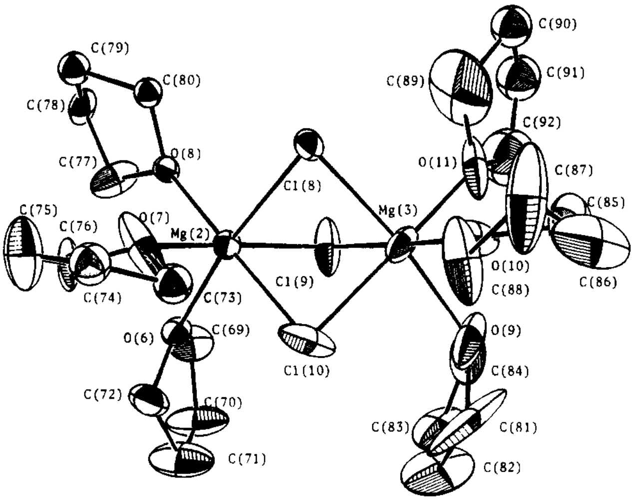

Figure 3. Magnesium dimer cation $[Mg_2Cl_3(THF)_6]^+$ as found in compound 2.

is attached to the bridging oxygen atom O(2) and also to the two chlorine atoms Cl(5) and Cl(6). These three atoms occupy a facial set of positions of an octahedron that is completed by the three THF ligands also attached to Mg(1). This unsymmetrical arrangement causes the bridging oxygen atom to form unequal bonds to the niobium atoms, with Nb(2)–O(2) = 1.971 (7) Å and Nb(3)–O(2) = 2.020 (8) Å. The two chlorine atoms Cl(5) and Cl(6) are roughly equal distances above and below the central Nb_4O_2 plane, viz., 1.53 and 1.67 Å.

Another feature of the marked asymmetry in this part of the anion is the presence of only one terminal Cl atom, Cl(4), on Nb(2), while there are two such atoms on Nb(3). This Cl(4) atom lies very close (0.14 Å) to the central Nb_4O_2 plane. Two of the THF ligands on the Mg(1) atom encroach on the regions above and below the central plane, so that it would not appear possible for Nb(2) to have had two terminal chlorine atoms without other changes having occurred.

It has previously been noted[3] that, in the symmetrical $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$ anion, the halves could be regarded formally as face-sharing bioctahedra, with the six eclipsed terminal positions occupied by Cl atoms and the three bridge positions by the central oxygen atom and two of the C–C bonds. In the present case, neither half of the molecule can be described in this way. In the Nb(3)–Nb(4) half, there is a distorted octahedron about one metal atom, Nb(4), but a distorted trigonal prism about the other, Nb(3). On the other side there is again one distorted octahedron, but there are only five coordination positions (in the sense we have been using this concept with regard to the $(PhC)_4$ groups) about the other, Nb(2). For what it is worth, a description of this arrangement as a trigonal bipyramid with O(1) and Cl(4) in axial positions can be given.

Concluding Remarks. The presently reported compounds emphasize further the point already evident in our previous studies. The reaction of PhCCPh with reduced solutions of niobium chloride has as its chief product the $Nb_2(PhC)_4$ unit (I), to which other ligands such as Cl, O, and THF then coordinate to fill either three or four addition positions about each Nb atom. These units, in turn, may remain as such (viz., the $[Nb_2Cl_3(PhC)_4(THF)_4]^+$ ion) or they may associate via shared ligands, either symmetrically (viz., the $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$ anion) or unsymmetrically, as in the two compounds described here. The details of what happens to the $Nb_2(PhC)_4$ unit seem quite varied and seem of much less importance than the formation and stability of that unit itself.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A-494.

Supplementary Material Available: Tables of anisotropic displacements and complete bond distances and angles for compounds 1 and 2 and stereoviews of unit cell contents for compound 1 (21 pages); tables of calculated and observed structure factors for compounds 1 and 2 (69 pages). Ordering information is given on any current masthead page.

Cleavage of Poly(diorganosiloxanes) by Trimethylaluminum

Allen W. Apblett and Andrew R. Barron*

Department of Chemistry and Materials Research Laboratory, Harvard University, Cambridge, Massachusetts 02138

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The interaction of $AlMe_3$ at elevated temperatures with poly(diorganosiloxanes), $(RMeSiO)_x$ (R = Me, n-$C_{18}H_{37}$, $-CH_2CH_2CF_3$, Ph), leads to rupture of the silicon–oxygen framework and yields the dimeric aluminum siloxides $[Me_2Al(OSiMe_2R)]_2$. The molecular structure of $[Me_2Al(OSiMe_2Ph)]_2$ has been confirmed by X-ray crystallography. The compound $[Me_2Al(OSiMe_2Ph)]_2$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 7.970 (3) Å, b = 24.563 (10) Å, c = 13.322 (4) Å, β = 105.05 (3)°, Z = 4, 2754 observed data, R = 0.0478, and R_w = 0.0639. At ambient temperatures the cyclic trisiloxane $(Me_2SiO)_3$ forms a highly fluxional 1:1 Lewis acid–base adduct with $AlMe_3$.

Introduction

It is widely known that reactions of $AlMe_3$ result in the leaching of silicon grease, primarily $(Me_2SiO)_x$, from joints and stopcocks.[1] In addition, we have observed the presence of an unidentified impurity in the reaction products, whose ^1H NMR spectrum consists of two peaks in a 3:2 ratio (δ 0.10 and 0.66, respectively).

In 1959 Jenkner reported[2] that the interaction of $(Me_2SiO)_x$ with 5% $AlEt_3$, at 175 °C, led upon hydrolysis to ethyl-substituted polysiloxanes, presumably via alkyl-

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ation of the Si–O–Si linkage. Although no aluminum siloxide compounds were isolated from this reaction, by Jenkner, they have been prepared by the reaction of $AlEt_3$ with $(MeHSiO)_x$ (eq 1).[3]

$$(MeHSiO)_x + AlEt_3 \rightarrow Et_2Al(OSiHMeEt) \qquad (1)$$

The interaction of $AlEt_3$ with $[Me_2SiO]_4$ and $(Me_3Si)_2O$ have also been reported to yield aluminum-containing species (eqs 2 and 3).[2]

$$(Me_2SiO)_4 + AlEt_3 \rightarrow Et_2Al(OSiMe_2)_3OSiMe_2Et \qquad (2)$$

$$(Me_3Si)_2O + AlEt_3 \rightarrow Et_2Al(OSiMe_3) + Me_3SiH + C_2H_4 \qquad (3)$$

In order to more fully understand the reactivity of aluminum alkyls with silicon grease, we have investigated the reaction of $AlMe_3$ with poly(diorganosiloxanes). The results of this investigation are reported herein.

Results and Discussion

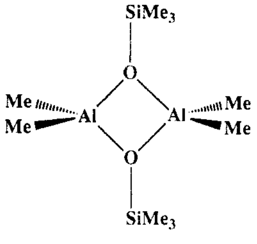
Reaction of $AlMe_3$ with silicon grease (Dow Corning), poly(dimethylsiloxane) oil (50 cP), or poly(dimethylsiloxane) rubber in refluxing toluene results in the formation of the dimeric aluminum siloxide compound $[Me_2Al(OSiMe_3)]_2$ (eq 4), which is readily isolated by vacuum sublimation, as colorless air-sensitive crystals.

$$(2/n)(Me_2SiO)_n + 2AlMe_3 \rightarrow \underset{1}{[Me_2Al(OSiMe_3)]_2} \qquad (4)$$

Compound 1 has been prepared previously by the reaction of alkali-metal trimethylsiloxides with $AlMe_2Cl$ (eq 5)[4] or substitution of the halide atoms of $Cl_2Al(OSiMe_3)$ with MeLi (eq 6).[5] An X-ray structural analysis[6] of 1 indicated that it is isomorphous with $[Me_2Si(NSiMe_3)]_2$; i.e., it has a dimeric structure, consisting of a planar Al_2O_2 ring, as has been commonly found for aluminum alkoxides (I).[7] We have determined that the dimeric nature of 1 is retained in pentane and benzene solution (see Experimental Section).

$$AlMe_2Cl + MOSiMe_3 \rightarrow 1 + MCl \qquad M = Li, Na \quad (5)$$

$$AlCl_2(OSiMe_3) + MeLi \rightarrow 1 + LiCl \qquad (6)$$



I

The reaction of $AlMe_3$ with other poly(diorganosiloxanes) occurs in a fashion analogous to that observed for $(Me_2SiO)_x$ to yield the appropriate aluminum siloxide compounds, 2–4 (eq 7).

$$(2/n)(RMeSiO)_n + 2AlMe_3 \rightarrow \underset{1-4}{[Me_2Al(OSiMe_2R)]_2} \qquad (7)$$

$$R = Me\ (1),\ n\text{-}C_{18}H_{37}\ (2),\ CH_2CH_2CF_3\ (3),\ Ph\ (4)$$

Compound 2 is obtained as white amorphous granules from THF/pentane (50:50) and 4 as colorless needles from pentane; 3 is a colorless distillable liquid. Compounds 2–4 are all, like 1, dimeric in solution and the gas phase (as determined by osmometry and mass spectroscopy, respectively). The dimeric nature of 4 in the solid state has been confirmed by X-ray crystallography (vide infra).

Table I. Heteroatom NMR Chemical Shifts[a]

compd	^{29}Si	^{17}O	^{27}Al
$[Me_2Al(OSiMe_3)]_2$ (1)	19.0	51.0 (90)	152.0 (2910)
$(Me_2SiO)_x$	−22.0	70.1 (170)	
$\{Me_2Al[OSiMe_2(n\text{-}C_{18}H_{37})]\}_2$ (2)	19.7	48.3 (360)	156.8 (9540)
$[(n\text{-}C_{18}H_{37})MeSiO]_x$	−22.7	50.2 (8050)	
$\{Me_2Al[OSiMe_2(CH_2CH_2CF_3)]\}_2$ (3)	19.4	48.0 (320)	155.2 (5470)
$[(CF_3CH_2CH_2)MeSiO]_x$	−22.2	58.1 (1430)	
$[Me_2Al(OSiMe_2Ph)]_2$ (4)	8.7	51.5 (240)	159.1 (8170)
$(PhMeSiO)_x$	−33.3	63.7 (1220)	
$Me_3Al[(OSiMe_2)_3]$ (5)	−5.4	71.1 (80)	160.8 (1955)
$(Me_2SiO)_3$	−9.6	70.5 (50)	
$(AlMe_3)_2$			154.9 (630)

[a] $W_{1/2}$ values in Hz are given in parentheses.

The structural similarity of the above compounds is reflected in the very small variation in the ^{17}O, ^{27}Al, and ^{29}Si NMR chemical shifts observed for the $Al(\mu\text{-}OSi)_2Al$ framework (see Table I). The only anomalous shift is the ^{29}Si NMR signal for compound 4, which is shielded by approximately 10 ppm due to the ring current of the pendant phenyl group. The equivalent shielding is observed in the corresponding polysiloxane.

Schmidbaur et al.[4] have attributed the deshielding of the silicon methyl protons of 1 (δ 0.10) with respect to those of $(Me_3Si)_2O$ (δ 0.04) as being due to the loss of the Si–O $d\pi$–$p\pi$ interaction, present in the latter compound, due to coordination of the oxygen to two aluminum atoms in 1. The consequence of this change is more apparent in the ^{29}Si NMR spectra; the resonances for 1 (δ 19.0) and 4 (δ 8.7) are shifted by ca. 11 ppm downfield from those of the corresponding disiloxanes, δ 6.8[8] and −1.8,[9] respectively. It should be noted, however, that the downfield displacement of the ^{29}Si NMR resonances (ca. 41 ppm) is significantly larger in the transformation from the poly(dialkylsiloxanes) to the aluminosiloxanes (see Table I).

The ^{17}O NMR signals for compounds 1–4 fall in a very narrow range (between δ 48.0 and 51.5), in contrast to the wide variation observed for the parent polysiloxanes. This may also be attributed to the reduced Si–O bond order in the aluminosiloxanes. The ^{27}Al NMR resonances for the aluminosiloxanes vary little from that of Me_3Al and are similar to those observed for dimeric dimethylaluminum alkoxides.[10] It is interesting to note that both quadrupolar nuclei (^{17}O and ^{27}Al) display resonances with line widths that are proportional to the steric bulk of the substituent on silicon.

The molecular structure of 4 is shown in Figure 1; selected bond lengths and angles are given in Table II. The structure consists of dimeric units with a planar Al_2O_2 ring system and the siloxy phenyl rings in the anti conformation. Th Al–O and Al–C distances in 4 (see Table I) are within the ranges reported previously: 1.7–2.0 Å[6,11] and 1.90–2.01 Å,[12] respectively. The Si–O distances [Si(1)–O(1) = 1.670 (2) Å, Si(2)–O(2) = 1.665 (2) Å] are toward the high end of the range previously observed for Si–O bonds,

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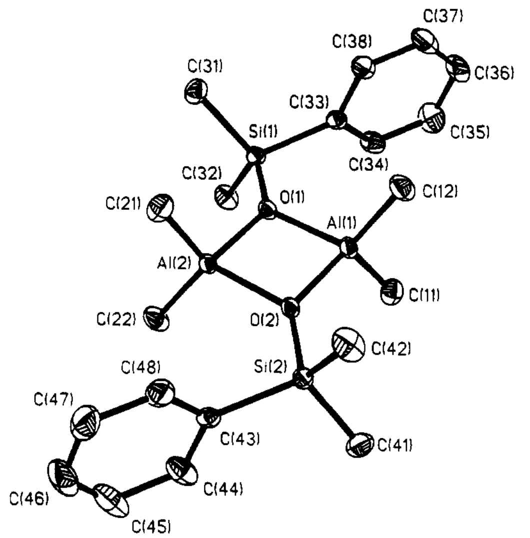

Figure 1. Structure of $[Me_2Al(OSiMe_2Ph)]_2$ (4). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $[Me_2Al(OSiMe_2Ph)]_2$

Al(1)–C(11)	1.949 (4)	Al(1)–C(12)	1.944 (5)
Al(1)–Al(2)	2.760 (2)	Al(1)–O(1)	1.850 (2)
Al(1)–O(2)	1.856 (2)	Al(2)–C(21)	1.958 (4)
Al(2)–C(22)	1.943 (5)	Al(2)–O(1)	1.852 (2)
Al(2)–O(2)	1.856 (2)	O(1)–Si(1)	1.670 (2)
Si(1)–C(31)	1.848 (3)	Si(1)–C(32)	1.850 (4)
Si(1)–C(33)	1.863 (4)	O(2)–Si(2)	1.665 (2)
Si(2)–C(41)	1.855 (4)	Si(2)–C(42)	1.848 (5)
Si(2)–C(43)	1.867 (4)		
C(11)–Al(1)–C(12)	121.1 (2)	C(11)–Al(1)–O(1)	110.9 (1)
C(12)–Al(1)–O(1)	113.2 (1)	C(12)–Al(1)–O(2)	109.6 (1)
C(11)–Al(1)–O(2)	112.2 (1)	O(1)–Al(1)–O(2)	83.7 (1)
C(21)–Al(2)–C(22)	121.4 (2)	C(22)–Al(2)–O(1)	110.7 (1)
C(21)–Al(2)–O(1)	110.3 (1)	C(21)–Al(2)–O(2)	111.9 (1)
C(22)–Al(2)–O(2)	112.6 (1)	O(1)–Al(2)–O(2)	83.6 (1)
Al(1)–O(1)–Al(2)	96.4 (1)	Al(1)–O(1)–Si(1)	129.5 (1)
Al(2)–O(1)–Si(1)	133.8 (1)	O(1)–Si(1)–C(31)	108.0 (1)
O(1)–Si(1)–C(32)	109.4 (2)	C(31)–Si(1)–C(32)	111.0 (2)
O(1)–Si(1)–C(33)	105.8 (1)	C(31)–Si(1)–C(33)	110.8 (2)
C(32)–Si(1)–C(33)	111.6 (2)	Al(1)–O(2)–Al(2)	96.1 (1)
Al(1)–O(2)–Si(2)	134.4 (1)	Al(2)–O(2)–Si(2)	129.1 (1)
O(2)–Si(2)–C(41)	108.9 (1)	O(2)–Si(2)–C(42)	108.7 (2)
C(41)–Si(2)–C(42)	111.4 (2)	O(2)–Si(2)–C(43)	106.0 (1)
C(41)–Si(2)–C(43)	111.0 (2)	C(42)–Si(2)–C(43)	110.7 (2)

1.612–1.660 Å,[13] but are not significantly different from those reported for alkoxysilanes and disiloxanes.[14] It is clear therefore that X-ray crystallography is not sufficiently sensitive to observe small changes in bonding between silicon and oxygen. We note that the core geometry of 4 is similar to that observed in $[Br_2Al(OSiMe_3)]_2$[15] and $[(Br_2Al)(OSiMe_2OSiMe_2O)]_2AlBr$.[16]

It is possible that the nature of the siloxane polymer end-blocking unit, $SiMe_3$ for the reactions discussed above, may play a role in the products obtained from the cleavage of the siloxane by $AlMe_3$. For example, the addition of AlR_3 to poly(organosiloxane)diols, $HO(R_2SiO)_xH$, results in the initial formation of $-SiOAlR_2$ end-blocked polymers.[17] In an effort to understand the mechanism for the cleavage of dialkylsiloxanes, we have investigated the interaction of $AlMe_3$ with the cyclic trisiloxane $(Me_2SiO)_3$, in which no end-blocking unit is present. The addition of 1 molar equiv of $AlMe_3$ to $(Me_2SiO)_3$ results in the formation of the 1:1 Lewis acid–base adduct $Me_3Al[(OSiMe_2)_3]$ (5).

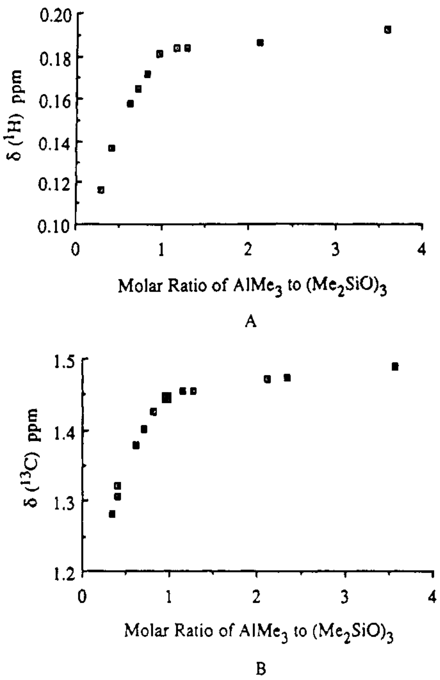

Figure 2. Silicon methyl ^1H (A) and ^{13}C (B) NMR shifts (δ) as a function of $AlMe_3/(Me_2SiO)_3$ molar ratio.

In order to investigate the formation of possible bis and tris complexes between $AlMe_3$ and $(Me_2SiO)_3$, the reaction has been monitored with use of ^1H and ^{13}C NMR spectroscopy at room temperature. The chemical shifts of the silyl methyls have been obtained as a function of the $AlMe_3$:$(Me_2SiO)_3$ molar ratio (Figure 2). The results show that upon increasing the molar ratio, there is a smooth shift of the resonances of the silyl methyl groups. The changes in chemical shifts level off at a molar ratio consistent with $Me_3Al[(OSiMe_2)_3]$.

The ^1H, ^{13}C, ^{17}O, and ^{29}Si NMR spectra of 5 (see Experimental Section and Table I) show only one type of $O-Si-Me_2$ and Al–Me environment from room trempetature down to −80 °C. This suggests that the $AlMe_3$ either is highly fluxional or is coordinated to all three trisiloxane oxygens. The latter would result in a six-coordinate aluminum center and is therefore discounted by the presence of a single broad resonance in the ^{27}Al NMR spectrum of 5 that is characteristic of a four-coordinate tetrahedral geometry around aluminum.

At $AlMe_3$:$(OSiMe_2)_3$ molar ratios greater than 1 there is only a single aluminum methyl resonance observed in the ^1H NMR spectrum, suggesting that free and coordinated $AlMe_3$ are in rapid exchange (eq 8).

Cooling such a solution to −60 °C results in the observation of signals due to free Al_2Me_6 and 5 (Figure 3). The observation, as low as −80 °C, of a single resonance of the silicon methyl groups is consistent with a highly fluxional complex in which the aluminum moves from one oxygen

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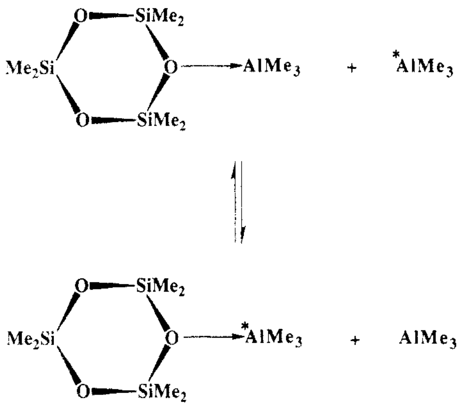
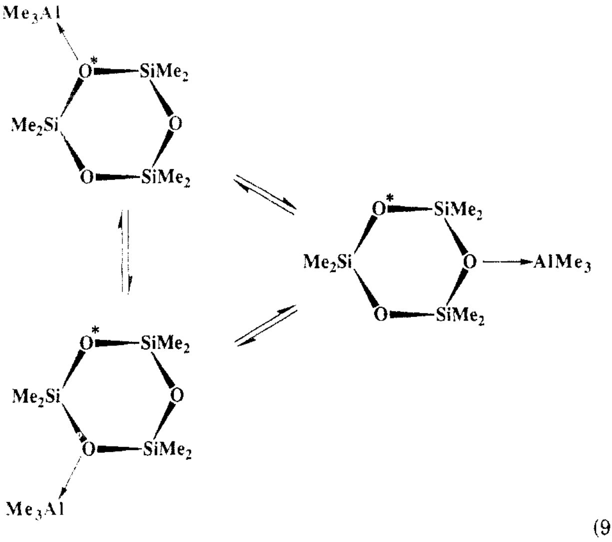


(8)

to the next around the cyclic trisiloxane ring (eq 9).



(9)

The molecular adduct **5** decomposes slowly at room temperature to give a mixture of **1** and a variety of cyclic and linear siloxanes, e.g., $(Me_2SiO)_x$ (x = 4, 6) and $Me_3SiO(SiMe_2O)_xSiMe_3$ (x = 2, 4). Refluxing $(Me_2SiO)_3$ with 3 equiv of $AlMe_3$ yields **1** quantitatively. The formation of **1**, as the only aluminum-containing moiety, from both linear and cyclic dimethylsiloxanes suggests that the identity of the polymer end group has a negligible role in the cleavage of poly(diorganosiloxanes) by trimethylaluminum.

Conclusion

The reaction of $AlMe_3$ with poly(diorganosiloxanes) leads to cleavage of the Si–O bond and alkylation at silicon. The mechanism of this reaction appears to involve the initial, facile coordination of aluminum to the siloxane oxygen atoms.

Experimental Section

All manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried, distilled, and degassed before use.

$AlMe_3$ was purchased as a 2 M solution in toluene from Aldrich and was used without further purification. $(Me_2SiO)_x$ (average molecular weight 3780, $SiMe_3$ terminated, Petrarch), $(PhMeSiO)_x$ (average molecular weight 2600, $SiMe_3$ terminated, Petrarch), $[(n\text{-}C_{18}H_{37})MeSiO]_x$ (average molecular weight 11 000, $SiMe_3$ terminated, Petrarch), $[(CF_3CH_2CH_2)MeSiO)]_x$ (molecular weight range 600–800, $SiMe_3$ terminated, Petrarch), and silicone grease (Dow Corning) were commercial products and were degassed in vacuo prior to use. Hexamethylcyclotrisiloxane, c-$(Me_2SiO)_3$ (Petrarch), was purified by sublimation at 25 °C and 0.1 mmHg. IR spectra (4000–600 cm^{-1}) were recorded on a Nicolet DX-5 FTIR spectrometer as neat liquids or as Nujol or Fluorolube mulls on KBr plates. ^1H and ^{13}C NMR spectra were obtained on a Bruker AM 500 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{17}O, ^{27}Al, and ^{29}Si NMR spectra (Table I) were recorded on a Bruker WM-300 spectrometer, and chemical shifts are reported versus H_2O, $[Al(H_2O)_6]^{3+}$, and Me_4Si ($CDCl_3$), respectively. Mass spectra were obtained by using a Kratos instrument operating at 70 eV. Melting points, boiling points, and thermogravimetric analyses were obtained on a Seiko 200 TG/DTA instrument. Molecular weight measurements were made in benzene and pentane, with use of an instrument similar to that described by Clark.[18]

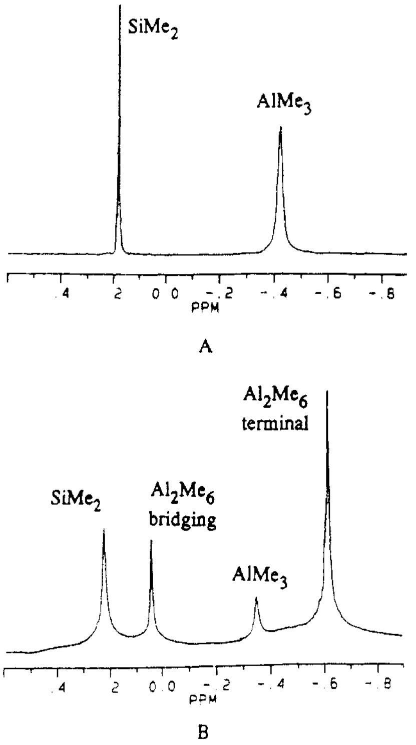


Figure 3. ^1H NMR spectra of $AlMe_3/(Me_2SiO)_3$ in a 2:1 molar ratio at 25 °C (A) and −60 °C (B).

$[Me_2Al(OSiMe_3)]_2$ (1). A solution of $AlMe_3$ (2 M) in toluene (2 mL, 40 mmol) was heated to reflux with either silicone grease or $(Me_2SiO)_x$ oil (50 cP) or rubber (2.96 g, 40 mmol). Dissolution of the siloxane was rapid, giving clear solutions within 15 min of refluxing. After 4 days the solutions were cooled to room temperature and transferred to a vacuum sublimator. The toluene was removed in vacuo, leaving a sticky, colorless solid. Sublimation at 45 °C and 0.1 Torr onto a water-cooled cold finger afforded colorless, rectangular crystals. The yields from poly(dimethylsiloxane) grease, oil, and rubber were 3.34 g (11.4 mmol, 57%), 3.98 g (13.6 mmol, 68%), and 3.59 g (12.3 mmol, 61%), respectively. Similarly, c-$(Me_2SiO)_3$ (2.22 g, 10 mmol) refluxed with $AlMe_3$ (15 mL of a 2 M solution in toluene) yielded **1** quantitatively (4.35 g, 14.9 mmol). Molecular weight: calculated for $C_{10}H_{30}Al_2O_2Si_2$, 292.48; found, 285 (benzene) and 291 (pentane). Mass spectrum: m/z 277 ($2M^+$ − Me), 131 (M^+ − Me). IR (Fluorolube and Nujol, cm^{-1}): 2961 (m), 2932 (m), 1411 (w), 1226 (s), 1197 (m), 1093 (s), 1020 (s), 848 (s), 821 (s), 802 (s), 760 (m), 699 (m), 666 (w), 604 (m). NMR (δ, C_6D_6): ^1H, 0.10 (9 H, s, $SiCH_3$), −0.66 (6 H, s, Al-CH_3); ^{13}C, 1.76 ($SiCH_3$), −7.90 (Al-CH_3).

$\{Me_2Al[OSiMe(n\text{-}C_{18}H_{37})]\}_2$ (2). $[(n\text{-}C_{18}H_{37})MeSiO]_x$ (6.25 g, ca. 20 mmol) and a solution of $AlMe_3$ in toluene (10 mL, 2 M, 20 mmol) were heated at reflux for 5 days. The volatiles were then removed in vacuo to give a white solid, which was recrystallized from 1:1 THF/pentane to give small white spherules: yield 7.13 g, 9.3 mmol, 93%; mp 50.7 °C. Molecular weight: calculated for $C_{44}H_{98}Al_2O_2Si_2$, 769.40; found, 759 (benzene). Mass spectrum: m/z 753 ($2M^+$ − Me), 515 ($2M^+$ − $C_{18}H_{37}$). IR (Fluorolube and Nujol, cm^{-1}): 2953 (m), 2917 (s), 2870 (w), 2848 (s), 1466 (m), 1406 (w), 1377 (w), 1255 (s), 1195 (s), 1170 (m), 1079 (br m), 1066 (br m), 1035 (br m), 988 (w), 967 (w), 912 (w), 843 (sh), 834 (s), 818

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(18) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

Table III. Summary of X-ray Diffraction Data

compd	$[Me_2Al(OSiMe_2Ph)]_2$
formula	$C_{20}H_{34}Al_2O_2Si_2$
space group	$P2_1/n$
a, Å	7.970 (3)
b, Å	24.563 (10)
c, Å	13.322 (4)
β, deg	105.05 (3)
V, $Å^3$	2518.5 (16)
Z	4
D(calcd), g cm^{-3}	1.099
cryst dimens, mm	0.42 × 0.32 × 0.35
temp, °C	-80 (1)
radiation	Mo Kα (0.71073 Å, graphite monochromator)
2θ limits, deg	4.0–45.0
no. of rflns collected	3670
no. of unique rflns	3286
no. of obsd data	2754
R	0.0478
R_w	0.0639
final residual, e $Å^{-3}$	0.27

(sh), 804 (m), 791 (s), 774 (w), 721 (s), 699 (s), 665 (m), 611 (s). NMR (δ, C_6D_6): ^1H, 1.21 [32 H, br m, $SiCH_2(\mathit{CH}_2)_{16}CH_3$], 0.82 [3 H, t, J(H–H) = 6.5 Hz, $SiCH_2(CH_2)_{16}\mathit{CH}_3$], 0.56 [2 H, br t, J(H–H) = 7.5 Hz, $Si\mathit{CH}_2(CH_2)_{16}CH_3$], 0.09 (6 H, s, $Si\mathit{CH}_3$), –0.71 (6 H, s, Al–CH_3); ^{13}C, 33.84, 32.39, 30.20, 30.02, 29.85, 29.73, 23.36, 23.13, 18.24, 14.36 [$Si(\mathit{C}H_2)_{17}\mathit{C}H_3$], 0.01 ($Si\mathit{C}H_3$), –7.84 (Al–$\mathit{C}H_3$).

$\{Me_2Al[OSiMe(CH_2CH_2CF_3)]\}_2$ (3). $[(CF_3CH_2CH_2)MeSiO]_x$ (9.37 g, ca. 60 mmol) and a solution of $AlMe_3$ in toluene (30 mL, 2 M, 60 mmol) were heated at reflux for 8 days. The volatiles were then removed in vacuo to yield a pale yellow liquid, which was distilled (90 °C, 0.1 Torr) to give a colorless liquid, yield 11.78 g, 25.8 mmol, 86%. Molecular weight: calculated for $C_{14}H_{32}Al_2F_6O_2Si_2$, 456.52; found, 449 (pentane). Mass spectrum: m/z 456 ($2M^+$), 359 ($2M^+ - CH_2CH_2CF_3$), 209 ($M^+ - F$), 131 ($M^+ - CH_2CH_2CF_3$). IR (Fluorolube and Nujol, cm^{-1}): 2956 (s), 2895 (sh), 2853 (w), 2825 (w), 1446 (m), 1421 (m), 1367 (m), 1316 (m), 1263 (s), 1210 (s), 1124 (s), 1064 (s), 1033 (m), 931 (m), 842 (m), 833 (m), 797 (w), 700 (br w), 666 (w). NMR (δ, C_6D_6): ^1H, 1.80 [2 H, m, J(H–H) = 7.5 Hz, J(H–F) = 10.2 Hz, $SiCH_2\mathit{CH}_2CF_3$], 0.71 [2 H, m, J(H–H) = 7.5 Hz, $Si\mathit{CH}_2CH_2CF_3$], –0.05 (6 H, s, $Si\mathit{CH}_3$), –0.61 (6 H, s, Al–CH_3); ^{13}C, 128.2 [q, J(C–F) = 283.6 Hz, $\mathit{C}F_3$], 28.14 [q, J(C–F) = 3.12 Hz, $\mathit{C}H_2CF_3$], 9.78 ($Si\mathit{C}H_2$), –0.76 ($Si\mathit{C}H_3$), –8.06 (Al–$\mathit{C}H_3$).

$[Me_2Al(OSiMe_2Ph)]_2$ (4). $(PhMeSiO)_x$ (8.17 g, ca. 60 mmol) and a solution of $AlMe_3$ in toluene (30 mL, 2 M, 60 mmol) were heated at reflux for 4 days. The volatiles were then removed in vacuo to give a colorless solid. Recrystallization from pentane (15 mL) yielded colorless needles: yield 9.01 g, 21.6 mmol, 72%; mp 46.9 °C; bp 180.4 °C. Molecular weight: calculated for $C_{20}H_{34}Al_2O_2Si_2$, 416.61; found, 420 (pentane). Mass spectrum: m/z 401 ($2M^+$ – Me), 339 ($2M^+$ – Ph), 193 (M^+ – Me). IR (Fluorolube and Nujol, cm^{-1}): 3071 (w), 3057 (w), 3015 (w), 2960 (m), 2933 (s), 2892 (m), 2823 (w), 1986 (w), 1964 (w), 1913 (w), 1891 (w), 1822 (w), 1776 (w), 1735 (w), 1664 (w), 1951 (m), 1488 (w), 1428 (s), 1409 (s), 1338 (w), 1307 (m), 1260 (s), 1193 (s), 1117 (s), 1018 (w), 999 (m), 922 (w), 827 (br s), 797 (br s), 738 (m), 689 (br s), 654 (m), 607 (m). NMR (δ, C_6D_6): ^1H, 7.52, 7.35 (5 H, m, $C_6\mathit{H}_5$), 0.45 (6 H, s, $Si\mathit{CH}_3$), –0.98 (6 H, s, Al–CH_3); ^{13}C, 135.96 (Si–C, Ph), 133.69 (o-C, Ph), 130.43 (p-C, Ph), 127.95 (m-C, Ph), –0.25 ($Si\mathit{C}H_3$), –8.32 (Al–$\mathit{C}H_3$).

$Me_3Al[(OSiMe_2)_3]$ (5). $AlMe_3$ (1 mL, 2 M, 2 mmol) in toluene was added to a preweighed quantity of $(Me_2SiO)_3$ (0.5–8 mmol) in toluene-d_8 (0.5 mL). The resultant solution was used to obtain ^1H, ^{13}C, ^{17}O, ^{27}Al, and ^{29}Si NMR spectra (see Table I and Figure 2). Removal of volatiles in vacuo resulted in the quantitative recovery of $(Me_2SiO)_3$. NMR [δ, $C_6D_5CD_3$, –80 °C, 1:1 $AlMe_3/(Me_2SiO)_3$]: ^1H, 0.23 (18 H, s, $Si\mathit{CH}_3$), –0.36 (9 H, s, Al–CH_3).

Table IV. Fractional Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^3 $Å^2$) for the Non-Hydrogen Atoms in $[Me_2Al(OSiMe_2Ph)]_2$

	x/a	y/b	z/c	U(eq)
Al(1)	–1857 (1)	3547 (1)	7276 (1)	27 (1)
C(11)	–3318 (5)	3402 (2)	5884 (3)	42 (1)
C(12)	–2740 (5)	3453 (2)	8495 (3)	46 (2)
Al(2)	1511 (1)	3917 (1)	7603 (1)	26 (1)
C(21)	2835 (5)	4013 (2)	9051 (3)	45 (1)
C(22)	2563 (5)	4043 (2)	6461 (3)	49 (2)
O(1)	342 (3)	3258 (1)	7439 (2)	27 (1)
Si(1)	942 (1)	2614 (1)	7330 (1)	27 (1)
C(31)	2807 (5)	2463 (2)	8447 (3)	41 (1)
C(32)	1537 (5)	2528 (2)	6086 (3)	43 (1)
C(33)	–973 (4)	2189 (1)	7375 (3)	29 (1)
C(34)	–2130 (5)	1992 (1)	6476 (3)	43 (1)
C(35)	–3589 (6)	1696 (2)	6520 (4)	59 (2)
C(36)	–3919 (6)	1587 (2)	7457 (4)	53 (2)
C(37)	–2789 (6)	1761 (2)	8351 (3)	53 (2)
C(38)	–1346 (5)	2062 (2)	8311 (3)	40 (1)
O(2)	–708 (3)	4208 (1)	7355 (2)	25 (1)
Si(2)	–1311 (1)	4857 (1)	7366 (1)	26 (1)
C(41)	–3049 (5)	4998 (2)	6167 (3)	47 (1)
C(42)	–2072 (6)	4978 (2)	8544 (3)	52 (2)
C(43)	671 (4)	5269 (1)	7402 (3)	29 (1)
C(44)	1038 (6)	5451 (2)	6499 (3)	48 (2)
C(45)	2535 (7)	5756 (2)	6528 (5)	68 (2)
C(46)	3633 (7)	5882 (2)	7447 (6)	79 (3)
C(47)	3327 (6)	5713 (2)	8357 (5)	72 (2)
C(48)	1847 (5)	5413 (2)	8329 (3)	49 (2)

Crystallography. A crystal data summary is given in Table III; fractional atomic coordinates are listed in Table IV. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with an LT-1 low-temperature device. Data collection was controlled by using the Nicolet P3 program.[19] Unit-cell symmetry was checked with the program XCELL. Raw diffractometer data were processed with the program XDISK. An empirical absorption correction was performed with the program PSICOR. The structure was solved by use of the SHELXTL-PLUS[20] package of programs. Drawings were produced by using the Nicolet program XP.

The unit cell was indexed by using 20 reflections obtained from a rotation photograph. A lattice determination from both the P3 program and XCELL suggested a monoclinic cell. Examination of the axial photographs confirmed this assignment. Systematic absences were consistent with the space group $P2_1$. The final unit cell parameters were obtained by a least-squares refinement of 50 selected reflections, including two Friedel pairs, in the range 15° < 2θ < 30°.

A total of 3670 reflections were collected in the range 4° < 2θ < 45°. Of these, 3286 were unique reflections and 2754 with $F_o > 5\sigma(F_o)$ were used in the structure solution. The intensities of three check reflections were measured after every 60 reflections; the intensities did not vary significantly during the data collection. A semiempirical absorption correction based on scans from six reflections in the range 16° < 2θ < 40° and Lorentz and polarization corrections were applied to the data.

Use of direct methods readily revealed the positions of the Al, Si, and O atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some but not all of the hydrogen atom positions. Therefore, all of the hydrogen atoms were placed in calculated positions $\{U_{iso}(H) = 1.2[U_{iso}(C)];\ d_{C-H} = 0.96$ Å$\}$ for refinement. The methyl groups were refined as rigid bodies with free rotation about the Al–C(methyl) and Si–C(methyl) bonds.

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Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (3 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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(19) *P3/R3 Data Collection Manual*; Nicolet Instrument Corp.: Madison, WI, 1987.

(20) *SHELXTL-PLUS Users Manual*; Nicolet Instrument Corp.: Madison, WI, 1988.