Preparation and Structure of Aluminum Derivatives of the Extremely Bulky Tris(trimethylsilyl)silyl Group. The Molecular Structure of the (Me₃Si)₃SiAl(C₆H₅)₂·THF Adduct

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The reaction of $R_{3-n}AlCl_n$ (n = 1-3; R = Me, Et) with $LiSi(SiMe_3)_3$·3THF affords the compound $(Me_3Si)_3SiAl(R_{3-n})Cl_{n-1}$·THF ($n$ = 3, 1; n = 1, R = Me, 4; R = Et, 5; n = 2, R = Et, 6) in high yield. $(Me_3Si)_3SiAlCl_2$·THF (1) reacts rapidly at -78 °C with alkyllithium reagents to produce the disubstituted organoaluminum complex $(Me_3Si)_3SiAlR_2$·THF (R = Ph, 2; R = n-Bu, 3) with the precipitation of LiCl. In addition, the reaction of R_3Al with $LiSi(SiMe_3)_3$·3THF yields the corresponding "ate" complex $[(Me_3Si)_3SiAlR_3]Li\cdot n$THF ($n$ = 2, R = Me, 7; n = 4, R = Et, 8). The structure of complex 2 has been determined from single-crystal X-ray diffraction studies. 2 crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 9.622 (3) Å, b = 13.135 (3) Å, c = 13.354 (3) Å, α = 78.75 (2)°, β = 82.00 (2)°, γ = 78.96 (2)°, and D_{calcd} = 1.03 g cm⁻³ for Z = 2. Least-squares refinement based on 2683 observed reflections with intensities $F_o \geq 2.5\sigma(F)$ in the range of 3° < 2θ < 52° converged at R = 5.6% (R_w = 5.1%). The observed bond distances are Al-Si = 2.479 (3) Å, Al-O = 1.927 (4) Å, and average Al-C = 1.986 (7) Å.

Introduction

The first silylaluminum derivative Al(SiMe₃)₃·OEt₂ was reported by Rosch in 1977.[1] Since that time a number of simple derivatives have been prepared[2] and several of their structures have been determined, including the amine,[3] various ether adducts,[3,4a] and "ate" complexes.[4a] These trimethylsilyl derivatives have shown normal behavior, relative to organoaluminum compounds, with the exception of the unsolvated parent Al(SiMe₃)₃, which appears to have an unusual structure in the solid state.[5] Janik et al.[6] have shown that Al(SiMe₃)₃ reacts with ammonia to yield the bridged dimer [(Me₃Si)₂AlNH₂]₂, but no organosilylaluminum derivative containing other ligands has been reported. Cowley et al.[7] have reported the synthesis and structures of the [(Me₃Si)₃Si]₂M(μ-Cl₂)Li(THF)₂ complexes (M = Ga or In) and in other work have shown that this bulky silyl ligand aids in the stabilization of a low valent tin derivative, [(Me₃Si)₃Si]₂Sn(μ-Cl)Li(THF)₃.[8] The [(Me₃Si)₃Si] group also has been shown to readily form derivatives of Zn, Cd, and Hg.[9]

There has been recent interest in the study of group 13 organometallic complexes as precursors for thin films with application toward the electronic industry. With these facts in mind we now wish to report the synthesis, characterization, and reactivities of tris(trimethylsilyl)silyl derivatives of aluminum.

Experimental Section

General Data. All manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Argon gas was purified by passing it through a series of columns containing De-ox catalyst (Alfa), phosphorous pentoxide, and calcium chloride. All solvents were distilled over sodium/benzophenone. ¹H and ¹³C NMR spectra were routinely recorded on a General Electric QE 300 NMR spectrometer. The chemical shifts are referenced to benzene-d_6 (δ = 7.15 ppm) which was degassed and distilled over Na/K alloy prior to use. Elemental analyses were performed by Midwest Microlab and/or Galbraith laboratories. The carbon and hydrogen analyses were performed by combustion analysis which may lead to carbide formation and incorrect results.[9] Silicon analysis was performed by ICP (inductively coupled plasma) and is well within experimental error while the lithium analysis was performed by atomic absorption spectroscopy. The aluminum chloride (EM), aluminum alkyls and alkyl halides (Aldrich) AlMe₃ (2.0 M), AlEt₃ (1.9 M), Al(i-Bu)₃ (1.9 M), 1.8 M Et₂AlCl, and 1.8 M EtAlCl₂ in toluene solution, Me₂AlCl (1.0 M) and 1.0 M MeAlCl₂ in hexane, 2.0 M phenyllithium solution in ether (Aldrich), and 2.5 M n-butyllithium solution in hexane (Aldrich) were all used as received. The LiSi(SiMe₃)₃·3THF was prepared as reported.[10]

Preparation of (Me₃Si)₃SiAlCl₂·THF (1). A solution of LiSi(SiMe₃)₃·3THF (11.96 g, 0.025 mol) in 100 mL of pentane was added dropwise to a stirred solution of Al₂Cl₆ (6.00 g, 0.045 mol). The reaction began immediately with formation of a milky white suspension. The reaction mixture was stirred at room temperature for 12 h after the addition was completed, then allowed to settle, and filtered. The volume was reduced under vacuum until crystal formation started and then cooled overnight in a refrigerator yielding a white microcrystalline solid precipitate. The solid was identified as 1: yield 60%; mp 150-151 °C. Anal. Calcd for C₁₃H₃₅AlCl₂OSi₄ (with 6% by weight LiCl): C, 35.24; H, 7.97; Cl, 20.82. Found: C, 35.12; H, 7.98; Cl, 20.69. In a second analysis after subsequent recrystallization to remove the LiCl (Anal. Calcd for C₁₃H₃₅AlCl₂OSi₄ (with 2% by weight LiCl): C, 36.64; H, 8.28; Cl, 18.31; Li, 0.33. Found: C, 36.61; H, 8.30; Cl, 18.83; Li, 0.57). ¹H NMR: δ 3.81 (b m, 4 H, THF), 1.03 (b m, 4 H, THF), 0.40 (s, 27 H, SiCH₃). ¹³C NMR: δ 73.0 (THF), 24.6 (THF), 3.6 (SiC).

Preparation of (Me₃Si)₃SiAl(C₆H₅)₂·THF (2). Phenyllithium (5.99 mL of a 2.0 M in ether solution, 11.98 mmol) was added dropwise to a solution of 1 (2.50 g, 5.99 mmol) in 100 mL of pentane at -78 °C. The reaction was stirred for 1 h under these conditions, then the cold bath was removed and the reaction was stirred for another 1 h as it warmed to room temperature. The yellow solution was then allowed to settle and filtered. The volume of the solution was reduced to afford a white crystalline solid. The solid was identified as 2: yield 85%; mp 174-176 °C. Chemical analyses of 2 were performed by both Midwest Microlab (Anal. Calcd for C₂₅H₄₅AlOSi₄: C, 59.94; H, 9.07. Found: C, 49.83, 51.54; H, 8.68, 8.76) and by Galbraith Laboratories (Anal. Calcd

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for C$_{25}$H$_{45}$AlOSi$_4$: C, 59.94; H, 9.07; Si, 22.43. Found: C, 45.83; H, 8.09; Si, 22.27). ^{1}H NMR: δ 7.85–7.28 (m, 10 H, C$_6$H$_5$), 3.64 (b m, 4 H, THF), 1.03 (b m, 4 H, THF), 0.37 (s, 27 H, SiCH$_3$). ^{13}C NMR: δ 149.4 (ipso-C), 138.3 (ortho-C), 127.9, 127.6, 72.9 (THF), 24.9 (THF), 4.5 (SiC).

Preparation of (Me$_3$Si)$_3$SiAl(C$_6$H$_5$)$_2$·THF (2a). The procedure was the same as for **2** except that only 1 equiv of phenyllithium was used. Upon workup, only the disubstituted product **2** and unreacted **1** were observed.

Preparation of (Me$_3$Si)$_3$SiAl((CH$_2$)$_3$CH$_3$)$_2$·THF (3). *n*-Butyllithium (1.00 mL of a 2.5 M solution in hexane (2.50 mmol) was added dropwise to a solution of **1** (0.52 g, 1.25 mmol) in 100 mL of pentane at –78 °C. The reaction mixture was stirred for 1 h at –78 °C, the cold bath was removed, and the reaction was allowed to stir for another 1 h, then allowed to settle, and filtered. The pentane was removed under vacuum affording a viscous oil. The oil was identified as **3**, yield 74%. ^{1}H NMR: δ 3.56 (b m, 4 H, THF), 1.60 (m, 12 H, (CH$_2$)$_3$), 1.10 (b m overlapping m, 10 H, THF, CH$_3$), 0.4 (s, 27 H, SiCH$_3$). ^{13}C NMR: δ 71.7 (THF), 29.7 and 29.30 (AlC$_\beta$, AlC$_\gamma$), 24.9 (THF), 14.2 (AlC$_\delta$), 13.9 (AlC$_\alpha$), 4.4 (SiC).

Preparation of (Me$_3$Si)$_3$SiAl((CH$_2$)$_3$CH$_3$)$_2$·THF (3a). The procedure was the same as in **3** except that only 1 equiv of *n*-butyllithium was used. Upon workup, only the disubstituted product **3** and unreacted **1** were observed.

Preparation of (Me$_3$Si)$_3$SiAlMe$_2$·THF (4). Me$_2$AlCl (1.42 mL, 1.42 mmol) was added dropwise to a stirred solution of LiSi(SiMe$_3$)$_3$·3THF (0.67 g, 1.42 mmol) in 100 mL of pentane. After the reaction mixture was stirred for 3.5 h at room temperature, it was allowed to settle and filtered. The solvent was removed under vacuum leaving a white solid. The solid was identified as **4** and recrystallized from pentane at –78 °C: yield 81%; mp 122–124 °C. ^{1}H NMR: δ 3.48 (b m, 4 H, THF), 1.05 (b m, 4 H, THF), 0.39 (s, 27 H, SiCH$_3$), –0.35 (s, 3 H, AlCH$_3$). ^{13}C NMR: δ 71.3 (THF), 24.8 (THF), 4.3 (SiC), –4.9 (AlC).

Preparation of (Me$_3$Si)$_3$SiAlEt$_2$·THF (5). The procedure is the same as described for **4** using LiSi(SiMe$_3$)$_3$·3THF (0.62 g, 1.32 mmol) and Et$_2$AlCl (0.73 mL, 1.32 mmol). After the reaction mixture was stirred for 3 h at room temperature, it was allowed to settle and filtered. The solvent was removed under vacuum leaving a white solid. The solid was identified as **5** and recrystallized from pentane at –78 °C: yield 78%; mp 128–129 °C. ^{1}H NMR: δ 3.52 (b m, 4 H, THF), 1.32 (t, 6 H, AlCH$_2$CH$_3$), 1.06 (b m, 4 H, THF), 0.40 (s, 27 H, SiCH$_3$), 0.22 (q, 4 H, AlCH$_2$CH$_3$). ^{13}C NMR: δ 71.7 (THF), 24.9 (THF), 10.2 (AlC$_\beta$), 4.4 (SiC), 3.6 (AlC$_\alpha$).

Preparation of [(Me$_3$Si)$_3$SiAl(Et)Cl·THF (6). The procedure is the same as described for **4** using 2 equiv of LiSi(SiMe$_3$)$_3$·3THF (1.13 g, 2.40 mmol) and EtAlCl$_2$ (1.20 mL, 2.40 mmol). After the reaction mixture was stirred for 12 h at room temperature, it was allowed to settle and filtered. The solid was identified as **6** and recrystallized from pentane at –78 °C °C: yield 83%; mp 198–200 °C. ^{1}H NMR δ 3.7 (b m, 4 H, THF), 1.30 (t, 3 H AlCH$_2$CH$_3$), 1.03 (b m, 4 H, THF), 0.41 (s, 27 H, SiCH$_3$), 0.24 (q, 2 H, AlCH$_2$CH$_3$). ^{13}C NMR: δ 72.1 (THF), 24.7 (THF), 9.0 (AlC$_\beta$), 4.0 (SiC), 1.3 (AlC$_\alpha$).

Preparation of [(Me$_3$Si)$_3$SiAlMe$_3$]Li·2THF (7). To a stirred solution of LiSi(SiMe$_3$)$_3$·3THF (0.67 g, 1.42 mmol) in 100 mL of pentane was added dropwise AlMe$_3$ (0.71 mL, 1.42 mmol). The reaction started immediately with the formation of a milky white precipitate. After the mixture was stirred for h at room temperature, it was allowed to settle and the supernatant solution decanted off leaving a white solid. The solid was vacuum dried and identified as **7**: yield 88%; decomposes 65 °C. ^{1}H NMR: δ 3.30 (b m, 8 H, THF), 1.26 (b m, 8 H, THF), 0.56 (s, 27 H, SiCH$_3$), –0.39 (s, 3 H, AlCH$_3$). ^{13}C NMR: δ 68.5 (THF), 25.4 (THF), 4.7 (SiC), –5.6 (AlC).

Preparation of [(Me$_3$Si)$_3$SiAlEt$_3$]Li·4THF (8). The procedure is the same as described for **7** using LiSi(SiMe$_3$)$_3$·3THF (0.89 g, 1.89 mmol) and AlEt$_3$ (1.0 mL, 1.89 mmol). After the reaction mixture was stirred for 4 h at room temperature, it was allowed to settle and the supernatant solution decanted off leaving a white solid. The solid was vacuum dried and identified as **8**: yield 80%; decomposes 65 °C. Anal. Calcd for C$_{30}$H$_{72}$AlLiO$_4$Si$_4$: C, 56.02, H, 11.28. Found: C, 55.95; H, 10.69. ^{1}H NMR: δ 3.32 (b m, 16 H, THF), 1.49 (b m overlapping t, 25 H, THF,

Table I. Experimental Parameters for the X-ray Diffraction Study of (Me$_3$Si)$_3$SiAl(C$_6$H$_5$)$_2$•THF (2)

compd	(Me$_3$Si)$_3$SiAl(C$_6$H$_5$)$_2$·THF
formula	C$_{25}$H$_{45}$AlOSi$_4$
mol wt, amu	500.96
cryst color	colorless
cryst system	triclinic
space group	P$\bar{1}$
Z	2
cell const constrained from 25 high-angle reflctns	
a, Å	9.622 (3)
b, Å	13.135 (3)
c, Å	13.354 (3)
α, deg	78.75 (2)
β, deg	82.00 (2)
γ, deg	78.96 (2)
V, Å^3	1615.7 (7)
d(calcd), g cm^{-3}	1.03
radiatn type	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å) with a graphite monochromator
temp, °F	80
type of data collectn	$\theta/2\theta$ scan
2θ scan range, deg	3–52
octants used	+h, ±k, ±l; h, 0–12; k, –15 to +15; l, –15 to +15
scan rate, deg/min	variable 2–5
std reflctns	3 measd per every 100 reflctns, the max dev was 7%
no. of data collected	6755
scan width	1.3–1.3
bkgd/scan ratio	0.50
no. of unique reflctns	6357
obsd reflctns with $F_o \geq 2.5\sigma(F)$	2683
linear absorptn coeff (μ), cm^{-1}	1.91
$F(000)$	544 electrons
absorptn correctn	none applied
no. of parameters refined	285
obsd/parameter ratio	9.4:1
R	5.6%
R_w	5.1%
g^a	0.002 98
overall shift/esd	0.000
max shift/esd	0.001
residual electron density, e/Å^3	0.24, 1.75 Å away from C25

$^a w^{-1} = \sigma^2(F_o) + g(F_o)^2$.

AlCH$_2$CH$_3$), 0.58 (s, 27 H, SiCH$_3$), 0.27 (q, 6 H, AlCH$_2$CH$_3$). ^{13}C NMR: δ 68.6 (THF), 25.4 (THF), 12.3 (AlC$_\beta$), 5.3 (Si–C), 4.1 (AlC$_\alpha$).

Structure Determination and Refinement of (Me$_3$Si)$_3$SiAl(C$_6$H$_5$)$_2$·THF (2). Crystals of **2** were grown from a pentane/Et$_2$O solution at –20 °C over a period of 2 days. A crystal suitable for X-ray diffraction was mounted in a thin-walled capillary tube in the drybox, plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed on a Nicolet R3 diffractometer for data collection. The crystal and X-ray data collection parameters are listed in Table I.

Compound **2** crystallized in the triclinic crystal system and was assigned to the space group P$\bar{1}$ (No. 2) on the basis of statistical data from SHELXTL[11] direct method outputs and subsequently confirmed after refinement and convergence. Unit cell parameters were derived from the least-squares fit of the angular settings of 25 reflections with 20° < 2θ < 30°. Data reduction by SHELX[12] direct method routines produced a partial solution for the space group P$\bar{1}$. This partial solution was used as the input to a Fourier synthesis, and all of the heavy atom positions were determined from the difference map. The aluminum atom was found to be in the general position of this space group since there are only

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Table II. Atomic Positional Parameters for
$(Me_3Si)_3SiAl(C_6H_5)_2 \cdot THF$

atom	x	y	z	$U_{eq}{}^a$ Å^2
Al1	0.3023 (2)	0.6548 (1)	0.6655 (1)	0.0529 (6)
Si1	0.2181 (2)	0.7813 (1)	0.7856 (1)	0.0500 (6)
Si2	0.2780 (2)	0.9477 (1)	0.7147 (1)	0.0704 (7)
Si3	−0.0319 (2)	0.7973 (1)	0.8067 (1)	0.0683 (7)
Si4	0.2900 (2))	0.7329 (1)	0.9518 (1)	0.0695 (7)
O1	0.4896 (3)	0.5823 (2)	0.6956 (3)	0.065 (2)
C1	0.1771 (7)	1.0141 (4)	0.6026 (5)	0.111 (3)
C2	0.4729 (6)	0.9334 (4)	0.6658 (5)	0.099 (3)
C3	0.2400 (7)	1.0378 (4)	0.8132 (5)	0.106 (3)
C4	−0.1003 (6)	0.8056 (5)	0.6793 (4)	0.095 (3)
C5	−0.0872 (6)	0.6774 (4)	0.8935 (4)	0.089 (3)
C6	−0.1251 (6)	0.9172 (4)	0.8624 (5)	0.104 (3)
C7	0.3007 (8)	0.5858 (4)	0.9961 (4)	0.110 (3)
C8	0.4693 (6)	0.7659 (6)	0.9608 (5)	0.119 (4)
C9	0.1616 (6)	0.8018 (4)	1.0474 (4)	0.087 (3)
C10	0.2043 (5)	0.5311 (4)	0.6835 (4)	0.054 (2)
C11	0.1581 (5)	0.5008 (4)	0.6012 (4)	0.065 (2)
C12	0.0991 (6)	0.4101 (5)	0.6111 (5)	0.077 (3)
C13	0.0849 (6)	0.3463 (4)	0.7031 (6)	0.079 (3)
C14	0.1302 (7)	0.3718 (5)	0.7860 (5)	0.101 (3)
C15	0.1869 (7)	0.4627 (5)	0.7764 (4)	0.084 (3)
C16	0.3359 (6)	0.7208 (4)	0.5197 (4)	0.059 (2)
C17	0.4708 (6)	0.7229 (4)	0.4652 (4)	0.072 (3)
C18	0.4912 (8)	0.7695 (5)	0.3638 (5)	0.087 (3)
C19	0.3775 (9)	0.8176 (5)	0.3100 (5)	0.094 (4)
C20	0.2400 (9)	0.8177 (5)	0.3600 (5)	0.093 (3)
C21	0.2219 (7)	0.7703 (4)	0.4624 (5)	0.077 (3)
C22	0.6008 (6)	0.6264 (4)	0.7269 (5)	0.088 (3)
C23	0.7352 (6)	0.5550 (5)	0.6995 (5)	0.098 (3)
C24	0.6935 (6)	0.4518 (4)	0.6980 (5)	0.084 (3)
C25	0.5492 (6)	0.4802 (4)	0.6649 (5)	0.093 (3)

$^a U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i{}^* a_j{}^* \bar{a}_i \cdot \bar{a}_j$.

two molecules in the unit cell ($Z = 2$). Isotropic least-squares refinement of these coordinates indicated large thermal motions associated with a few of the carbon atoms of the phenyl rings and the tris(trimethylsilyl)silyl group. Full-matrix least-squares refinement of positional and thermal parameters for non-hydrogen atoms was carried out by the minimizing function $\sum(w|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structural factors, respectively. The weighting scheme used on the last cycle was $w = 2.1902/\sigma^2(F_o) + 0.000\,298(F_o)^2$. The scattering factors for neutral carbon and aluminum was used.[13] All the hydrogen atoms were placed in calculated positions with a C–H bond distance of 1.08 Å and assigned an isotropic thermal parameter approximately 1.2 times the thermal parameter of the carbon atom to which it was bound. All hydrogen atom positional parameters were held fixed from subsequent refinement. A few additional cycles of refinement of the data led to convergence with $R = 5.6\%$ and $R_w = 5.1\%$. The final difference Fourier map showed a maximum residual electron density of 0.24 e/Å^3, 1.75 Å away from the C25 atom with an overall shift/error of 0.000.
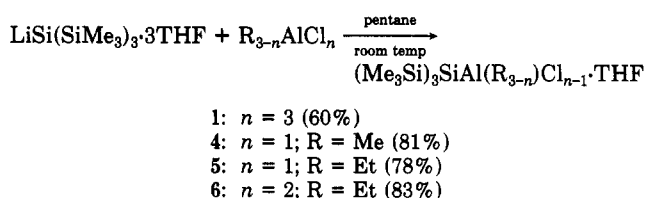
Results and Discussion

Synthesis. The initial preparation of the mixed organosilylaluminum compounds was carried out by the reaction of $LiSi(SiMe_3)_3 \cdot 3THF$ with $R_{3-n}AlCl_n$ and represents a very convenient and simple route to these substituted complexes as shown in Scheme I. With $n = 1$ or 3 readily separated products were obtained; with $n = 2$ a mixture of products was obtained when the ratio of reactants was 1:1 which could not readily be separated under the conditions used; however, when the ratio of $LiSi(SiMe_3)_3 \cdot 3THF$ to $EtAlCl_2$ was approximately 2:1, $(Me_3Si)_3SiAl(Et)Cl \cdot THF$ was obtained in high yield.
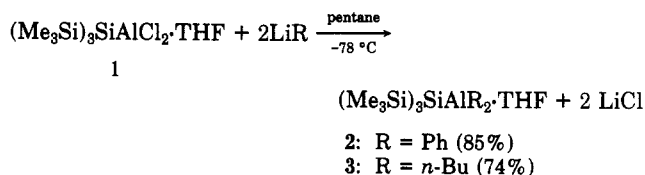
(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor D. Reidel, Dordrecht).

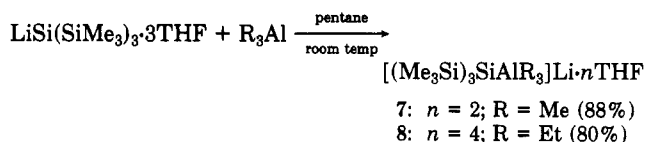(14) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1988**, *27*, 4335.

Scheme I

$$LiSi(SiMe_3)_3 \cdot 3THF + R_{3-n}AlCl_n \xrightarrow[\text{room temp}]{\text{pentane}}$$

$$(Me_3Si)_3SiAl(R_{3-n})Cl_{n-1} \cdot THF$$

1: $n = 3$ (60%)
4: $n = 1$; R = Me (81%)
5: $n = 1$; R = Et (78%)
6: $n = 2$; R = Et (83%)

Scheme II

$$(Me_3Si)_3SiAlCl_2 \cdot THF + 2LiR \xrightarrow[-78\,°C]{\text{pentane}}$$

1

$$(Me_3Si)_3SiAlR_2 \cdot THF + 2\,LiCl$$

2: R = Ph (85%)
3: R = n-Bu (74%)

Scheme III

$$LiSi(SiMe_3)_3 \cdot 3THF + R_3Al \xrightarrow[\text{room temp}]{\text{pentane}}$$

$$[(Me_3Si)_3SiAlR_3]Li \cdot nTHF$$

7: $n = 2$; R = Me (88%)
8: $n = 4$; R = Et (80%)

Compound 1 was reacted with alkyllithium reagents, LiR (R = Me, n-Bu, Ph), to study its substitution patterns. The reaction proceeded smoothly with nonsterically hindered alkyllithium reagents (Scheme II) with only the isolation of the disubstituted organosilylaluminum complex, even if only 1 equiv of the alkyllithium was used. This suggests a much higher and thermodynamic stability for the disubstituted product over the monosubstituted or a significant increase in the reactivity of the monosubstituted intermediate. When the reaction was attempted under the same conditions or at room temperature with bulky substituents (i.e. t-Bu or $(Me_3Si)_2N$), there was no sign of reaction. This is presumably due to the steric interactions between the different groups bound to the aluminum center and the incoming ligand, prohibiting the reaction from occurring. In addition, the reaction of compound 1 with alkali-metal derivatives (i.e. MeLi, MeONa, or t-BuOK), not soluble in pentane, did not proceed since there was no driving force for the reaction, precipitation of MCl where M = alkali metal.

Since the preceding reactions occurred without the formation of an "ate" type complex, we were interested in finding a simple and convenient route for the synthesis of this novel class of compounds. This can be accomplished by the addition of the R_3Al to a solution of $LiSi(SiMe_3)_3 \cdot 3THF$ in pentane, affording the corresponding "ate" complex as a precipitate (Scheme III). The reaction is straight forward with R = Me or Et; however, with R = i-Bu, the reaction affords a mixture of products. This can be explained by the reaction first forming the desired "ate" complex but then, due to its instability, further reacting with itself.

Characterization. The characterization of the silylaluminum compounds was accomplished by using ^{1}H and ^{13}C NMR, chemical reactions, and elemental analysis. Some difficulty associated with the combustion analysis of organoaluminum compounds leads to unsatisfactory results in many cases for carbon and hydrogen analyses. Analysis for silicon on the same sample of compound 2 yielded excellent results.

The analytical data of 1 always indicates there is a small amount of LiCl which cannot be removed even with subsequent recrystallizations. This was confirmed by lithium analysis. The lithium chloride was not believed to be
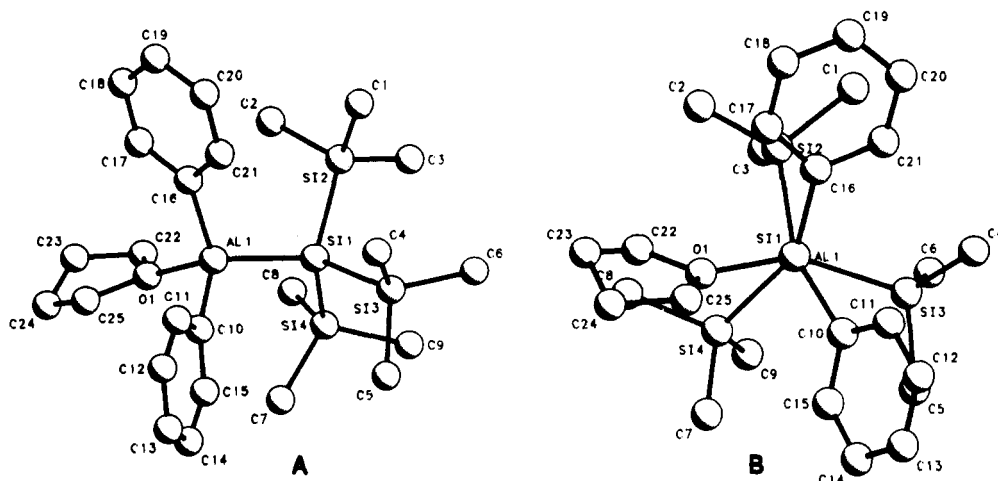
Figure 1. Two views of (Me₃Si)₃SiAl(C₆H₅)₂·THF (2) with the atoms labeled. Hydrogens are omitted for clarity. (A) General view of the molecule. (B) A projection along the Al–Si1 bond showing the eclipsed configuration.

Table III. Bond Lengths (Å) and Angles (deg) for
(Me₃Si)₃SiAl(C₆H₅)₂·THF

Bond Lengths			
Al1–Si1	2.479 (3)	O1–C25	1.466 (8)
Al1–O1	1.927 (4)	C10–C11	1.39 (1)
Al1–C10	1.990 (6)	C10–C15	1.39 (1)
Al1–C16	1.981 (7)	C11–C12	1.392 (9)
Si1–Si2	2.351 (2)	C12–C13	1.35 (1)
Si1–Si3	2.356 (2)	C13–C14	1.37 (1)
Si1–Si4	2.349 (3)	C14–C15	1.38 (1)
Si2–C1	1.876 (8)	C16–C21	1.407 (9)
Si2–C2	1.884 (6)	C16–C17	1.400 (9)
Si2–C3	1.890 (8)	C17–C18	1.38 (1)
Si3–C4	1.884 (8)	C18–C19	1.37 (1)
Si3–C5	1.883 (7)	C19–C20	1.40 (1)
Si3–C6	1.889 (7)	C20–C21	1.39 (1)
Si4–C7	1.895 (7)	C22–C23	1.492 (9)
Si4–C8	1.882 (7)	C23–C24	1.49 (1)
Si4–C9	1.887 (7)	C24–C25	1.473 (9)
O1–C22	1.453 (8)		

Bond Angles			
Al1–Si1–Si2	111.1 (1)	O1–C22–C23	104.4 (6)
Al1–Si1–Si3	105.29 (9)	O1–C25–C24	105.8 (6)
Al1–Si1–Si4	117.49 (9)	C1–Si2–C2	106.7 (3)
Al1–O1–C22	126.9 (3)	C1–Si2–C3	107.8 (3)
Al1–O1–C25	121.6 (4)	C2–Si2–C3	108.9 (3)
Al1–C10–C11	122.1 (5)	C4–Si3–C5	107.1 (3)
Al1–C10–C15	123.4 (5)	C4–Si3–C6	107.7 (3)
Al1–C16–C17	124.3 (5)	C5–Si3–C6	108.0 (3)
Al1–C16–C21	121.2 (5)	C7–Si4–C8	107.5 (3)
Si1–Al1–O1	108.1 (2)	C7–Si4–C9	108.0 (3)
Si1–Al1–C10	117.3 (2)	C8–Si4–C9	105.9 (3)
Si1–Al1–C16	114.6 (2)	C10–Al1–C16	112.6 (3)
Si1–Si2–C1	112.2 (2)	C10–C11–C12	122.8 (7)
Si1–Si2–C2	109.9 (2)	C10–C15–C14	122.9 (7)
Si1–Si2–C3	111.2 (2)	C11–C12–C13	120.5 (8)
Si1–Si3–C4	110.2 (2)	C12–C13–C14	119.0 (7)
Si1–Si3–C5	110.2 (2)	C13–C14–C15	120.4 (8)
Si1–Si3–C6	113.4 (2)	C16–C17–C18	123.0 (6)
Si1–Si4–C7	110.0 (3)	C16–C21–C20	123.4 (6)
Si1–Si4–C8	113.3 (3)	C17–C18–C19	121.0 (7)
Si1–Si4–C9	111.9 (2)	C18–C19–C20	118.7 (8)
Si2–Si1–Si3	108.47 (9)	C19–C20–C21	119.4 (7)
Si2–Si1–Si4	108.1 (1)	C22–O1–C25	110.0 (4)
Si3–Si1–Si4	105.9 (1)	C22–C23–C24	106.0 (5)
O1–Al1–C10	99.1 (2)	C23–C24–C25	104.1 (5)
O1–Al1–C16	102.5 (2)		

Table IV. Selected Bond Distances in
Organosilylaluminum Derivatives

compound	Al–Si, Å	ref
Al(SiMe₃)₃·OEt₂	2.46, 2.47, 2.48	4a
Na[Al(SiMe₃)₄]	2.47, 2.48, 2.49, 2.49	4a
Na[Al(SiMe₃)₄]·2toluene	2.44, 2.44, 2.46, 2.74	4a
[Al(SiMe₃)₃]₂·TMEDA	2.47	3
[(Me₃Si)₂AlNH₂]₂	2.47, 2.48	6
[(Me₃Si)₂Al(NH₂)]₃Al	2.47, 2.47, 2.49	14
(Me₃Si)₃SiAl(C₆H₅)₂·THF	2.48	this work

is present, only one form is observed, indicating that rapid exchange occurs between bound and unbound THF.

The number of THF molecules strongly coordinated to complexes **7** and **8** differ in number as determined from the ¹H NMR spectra with two molecules associated with **7** and four with **8**. In the latter compound the four THF molecules will fully occupy the four sites around the Li⁺ ion. In complex **7** coordination to additional groups must be presumed to complete the coordination of the Li⁺ ion with the most likely interaction to the methyl groups. This type of interaction has been observed in crystal structures of several organoaluminates.[4] The difference in the coordination of the lithium in complexes **7** and **8** may be accounted for on the basis of the increased steric interaction on the replacement of the methyl group by the ethyl group which prohibits the close approach of the Li⁺ ion which is needed for bonding to occur.

Structure. Two views of the molecular unit of **2** determined by single-crystal X-ray diffraction studies are shown in Figure 1 with selected bond distances and bond angles listed in Table III. The geometry around the Al atom can be described as distorted tetrahedral with bond angles of Si–Al–O = 108.1°, Si–Al–C(16) = 114.6°, Si–Al–C(10) = 117.3°, C(10)–Al–O = 99.1°; C(16)–Al–O = 102.5°, and C(10)–Al–C(16) = 112.6°.

A comparison of the coordination around the Al atom in the (Me₃Si)₃SiAlPh₂·THF adduct with that observed in other organoaluminum derivatives shows that all of the bond distances and angles fall into the typical ranges observed for these types of derivatives (see Table IV). The one unusual feature of this structure is depicted in Figure 1B, a projection along the Al–Si1 bond, which shows that the substituents bonded to the Al atom and the Si1 are far removed from the expected staggered configuration. The dihedral angles are all relatively small with values of (a) 33.5 (2)° for the O–Al···Si1–Si4 angle, (b) 40.0 (2)° for C1–Al···Si1–Si3, and (c) 21.8 (2)° for C16–Al···Si1–Si2. One may also note that the SiMe₃ groups are all oriented so that

present in a discrete complex because multiple recrystallizations reduced its content.

In compounds **1–6** the ¹³C chemical shifts of the THF moiety are significantly altered from free THF which indicates that the THF molecules remains coordinated to the aluminum atom in solution. If a small excess of THF

the methyl groups will minimize the interactions with the phenyl rings or the THF moiety. This is consistent with some modest steric crowding and, further, may lead to increased energy barriers for rotation of the various groups.

The high reactivity of these compounds indicates possible utility as precursors for organosilane deposition in thin films. This has important applications in the production of semi- and superconducting materials. We are now exploring this general synthesis for mixed organosilylaluminum compounds and are investigating the NMR properties both in solution and in the solid state.

Complexes of the Allylic Diorganotriarsinidene Ligand, η^3-RAsAsAsR. Syntheses and Crystal Structures of Cp*Mo(CO)₂(η^3-PhAsAsAsPh) and Cp*W(CO)₂(η^3-MeAsAsAsMe)

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Sealed-tube reactions of [Cp*M(CO)₂]₂ (Cp* = η^5-C₅Me₅; M = Mo or W) with the cyclopolyarsines, *cyclo*(AsR)$_n$ (R = Me, n = 5; R = Ph, n = 6), in toluene at 150–170 °C produce the new complexes Cp*M(CO)₂(η^3-RAsAsAsR) (1, M = Mo, R = Ph; 2, M = W, R = Me), which are strict isoelectronic and isolobal analogues of π-allyl complexes. As such they constitute the first examples of π-allyl complexes formed without carbon atoms. 1 and 2 have been crystallographically characterized. 1: monoclinic, P2₁/c, a = 20.287 (6) Å, b = 9.047 (2) Å, c = 13.835 (3) Å, β = 95.39 (2)°, V = 2528.0 (8) Å³, Z = 4, R = 5.84%. 2: monoclinic, P2₁/c, a = 12.607 (4) Å, b = 8.613 (2) Å, c = 16.998 (5) Å, β = 96.21 (2)°, V = 1835.0 (10) Å³, Z = 4, R = 5.33%. All As–As bond distances in both structures are statistically identical; at 2.361 (2) Å, the distance is intermediate between As–As single and double bonds, in keeping with the approximate bond order of 1.5 expected for an allylic analogue. Formation of these allylic complexes is not found when [CpMo(CO)₃]₂ replaces [Cp*Mo(CO)₂]₂ in reactions of similar initial As/metal ratios. Rather the closed, tetrahedrane analogues CpMo(CO)₂(η^3-As₃) and [CpMo(CO)₂]₂(μ,η^2-As₂) are found in which all of the original organic substitution has been lost by disproportionation (2RAs → R₂As + As).

Introduction

Isolobal analogies have proved to be especially useful in the development of transition-metal/main-group hybrid cluster chemistry. In previous reports[1,2] we have shown that an As atom, as an analogue of the CH group, can form complexes containing the As₂ group in structures closely related to known acetylene complexes, and the *cyclo*-As₅ group, functioning as a cyclopentadienide analogue, can form triple-decker "sandwich" complexes.[3] In an elegant demonstration of the limits to which these analogies can be extended, Scherer and co-workers have shown that the *cyclo*-P₅ group has clear η^5-cyclopentadienyl functionality in forming the ferrocene-like complex (η^5-P₅)Fe(η^5-C₅Me₅).[4]

Acetylenic analogues also offer the intriguing possibility of providing insight into the mechanisms for metal-based cyclooligomerization reactions through the isolation of As analogue intermediates. One such As analogue intermediate is [(η^5-C₅H₅)₂Mo₂(CO)₂(μ_2,η^2-As₂)₂] which we have isolated and structurally characterized;[2] this diacetylene analogue has been proposed as a cyclooligomerization intermediate, but never isolated.[5] Furthermore, rings and chains of RAs units (isolobally related to CH₂ groups) form complexes with analogues among organic structures such as trishomocubane.[6,7] We have now further extended these analogies to the formation of the first examples of all-arsenic, π-allyl analogue complexes containing the RAsAsAsR group, specifically, [(η^5-C₅Me₅)M(CO)₂(η^3-RAsAsAsR)] (M = Mo or W and R = Me or Ph). We herein report the synthesis and crystal structures of 1 (M = Mo, R = Ph) and 2 (M = W, R = Me). We are aware of no other structures containing an allyl analogue group composed entirely of non-carbon atoms.[8] Appel and co-

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