Silicon–Metal Bonded Compounds. 17. The Synthesis and Crystal Structure of Bis[tris(trimethylsilyl)aluminum]–Tetramethylethylenediamine and of Bis(trimethylsilyl)magnesium–Tetramethylethylenediamine

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Two new (trimethylsilyl)metal–tetramethylethylenediamine complexes, bis[tris(trimethylsilyl)aluminum]-tetramethylethylenediamine (I) and bis(trimethylsilyl)magnesium–tetramethylethylenediamine (II), have been prepared by exchange of TMEDA with previously reported $Al(SiMe_3)_3{\cdot}THF$ and $Mg(SiMe_3)_2{\cdot}DME$ adducts. They were shown by NMR spectroscopy to be the 2:1 and 1:1 complexes, respectively. The crystal structures of I and II were determined by single-crystal X-ray diffraction techniques. I crystallized in the monoclinic space group $P2_1/n$ with cell dimensions $a = 9.495$ (8) Å, $b = 16.973$ Å, $c = 13.710$ (6) Å, and $\beta = 93.37$ (5)°. The structure of II was determined in the monoclinic space group $P2_1/c$ with cell dimensions of $a = 14.359$ (19) Å, $b = 9.309$ (10) Å, $c = 17.060$ (20) Å, and $\beta = 110.85$ (9)°. I contains two, four-coordinate, Al atoms with three Si–Al bonds with an average length of 2.47 Å. The fourth position is occupied by an N atom from the TMEDA molecule at 2.069 Å that serves as a bridge to the second $Al(SiMe_3)_3$ unit. In II the Mg atom is four-coordinate bound to two Si atoms at 2.63 Å and to two N atoms in the chelating TMEDA moiety at 2.19 Å.

Introduction

There are only a few quantitative studies on main-group silylmetal derivatives with the total structural studies limited to the mercury derivatives $Hg(SiMe_3)_2$,[1] $Hg(SiPh_3)_2$,[2] $Si(Me)_2HgSi(Me)_2CH_2Si(Me)_2HgSi(Me)_2$-$HgSi(Me)_2CH_2$,[2] $Li_2[Hg(SiMe_2Ph)_4]$,[3,4] $Li_2[Hg(SiMe_3)_4]$, and $[Mg_4(OME)_6(DME)_2][Hg(SiMe_2Ph)_3]_2$[5] (OME = $MeOCH_2CH_2O^-$, DME = $MeOCH_2CH_2OMe$), to the hexamer $(LiSiMe_3)_6$[6] and its tetramethylethylenediamine (TMEDA) adduct $(LiSiMe_3)_2{\cdot}(TMEDA)_3$,[7] and finally to the single magnesium species $Mg(SiMe_3)_2{\cdot}DME$.[8] The structure of $Al(SiMe_3)_3{\cdot}OEt_2$ also has been studied but no details of this structure have appeared.[9]

The data available show considerable parallel to the results obtained for the corresponding carbon derivatives but also show that there are some unusual differences. For example, in the series of silylmercury derivatives that have been studied two-, three-, and four-coordinate mercury atoms[1,3,4,5] have been observed, whereas, for the simple organomercury systems, the anionic three- and four-coordinate species are not stable. A second major difference appears to occur between the interaction silyl- and organolithium derivatives with base. The hexameric silyl derivative $(LiSiMe_3)_6$[6] reacts with TMEDA to yield $(LiSiMe_3)_2{\cdot}(TMEDA)_3$ with complete destruction of the aggregate producing an extremely reactive species with the trimethylsilyl moiety coordinated to a single lithium atom. In the corresponding saturated organolithium derivatives, TMEDA is not a sufficiently strong base to disrupt the lithium aggregate completely, leaving a tetrameric structure bridged by TMEDA molecules for *n*-butyllithium[10] and dimers for those which are more sterically hindered[11] or unable to carry sufficient negative charge to form simple ion pairs.[12]

In this paper we report the preparations of two new (trimethylsilyl)metal addition compounds, bis[tris(trimethylsilyl)aluminum]-tetramethylethylenediamine (I) and bis(trimethylsilyl)magnesium–tetramethylethylenediamine (II) and their crystal structures. These are compared with the known silylmetal complexes and related organometallic species.

Experimental Section

Preparation of Compounds. All of the main-group silylmetal derivatives are highly reactive and require exclusion of oxygen and any source of H^+ such as water. As a result, all studies were carried out by using Schlenk, high vacuum, or inert atmosphere box techniques. The solvents *n*-pentane, cyclopentane, and ether as well as tetramethylethylenediamine (TMEDA) were stirred and refluxed overnight over CaH_2 or $LiAlH_4$ and then distilled into storage vessels on the vacuum line for use as needed. The 1,2-dimethoxyethane (DME) was stirred over Na chips for 3 days and distilled just prior to use.

$Hg(SiMe_3)_2$ was prepared by the procedure described by Rösch et al.[13] and recrystallized from pentane. $Al(SiMe_3)_3{\cdot}THF$ was

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(1) Albright, M. J.; Schaaf, T. F.; Butler, W. M.; Hovland, A. K.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6261.

(2) Bleckman, I.; Soliman, M.; Reuter, K.; Neumann, W. P. *J. Organomet. Chem.* **1976**, *108*, C18.

(3) Ilsley, W. H.; Sadurski, E. A.; Schaaf, T. F.; Albright, M. J.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1980**, *190*, 257.

(4) Ilsley, W. H.; Albright, M. J.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1980**, *19*, 3577.

(5) Sadurski, E. A.; Ilsley, W. H.; Thomas, R. D.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7761.

(6) Ilsley, W. H.; Schaaf, T. F.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3769. Schaaf, T. F.; Butler, W.; Glick, M. D.; Oliver, J. P. *Ibid.* **1974**, *96*, 7593.

(7) Tecle', B.; Ilsley, Wm. H.; Oliver, J. P. *Organometallics* **1982**, *1*, 875.

(8) Claggett, A. R.; Ilsley, Wm. H.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1797.

(9) Rösch, L.; Altnau, G.; Erb, W.; Pickardt, J.; Bruncks, N. *J. Organomet. Chem.* **1980**, *197*, 51.

(10) Köster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1.

(11) Zerger, R. P.; Stucky, G. D. *J. Chem. Soc., Chem. Commun.* **1973**, 44.

(12) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111* 3157.

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Table I. Experimental Data from the X-ray Diffraction Study on $[Al(SiMe_3)_3]_2 \cdot TMEDA$ and $Mg(SiMe_3)_2 \cdot TMEDA$

	I	II
mol formula	$Al_2Si_6N_2C_{24}H_{70}$	$MgSi_2N_2C_{12}H_{34}$
mol wt	609.3	286.9
cryst dimens, mm^3	0.25 × 0.25 × 0.60	0.2 × 0.4 × 0.9
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
cell dimens[a]		
a, Å	9.495 (8)	14.359 (19)
b, Å	16.973 (8)	9.309 (10)
c, Å	13.710 (6)	17.060 (20)
β, deg	93.37 (5)	110.85 (9)
V, $Å^3$	2206 (2)	2131 (4)
Z	4 (the assymetric unit is half the molecule)	4
D_{calcd}, g cm^{-3}	0.917	0.894
radiation	Mo $K\bar{\alpha}$ (λ = 0.710 69 Å)	
monochromator	graphite	
2θ range, deg	$4 < 2\theta < 45$	$4 < 2\theta < 40$
scan type	$\theta - 2\theta$; moving crystal-moving counter	
scan speed, deg min^{-1}	variable 2.0–5.0	
scan width, deg	$[2\theta(Mo\ K\alpha_1) - 1.1] \rightarrow [2\theta(Mo\ K\alpha + 1.1]$	
bkgd measurement	stationary crystal–stationary counter at beginning and end of 2θ, each for one-fourth the time taken for the 2θ scan	
std rflctns	3 measured every 97 reflections; no significant deviation from the mean was observed	
unique data	3179	2229
unique data with $Fo^2 > 3\sigma(Fo^2)$	1467	1036
abs coeff μ, cm^{-1}	3.88	1.79
F_{000}	676	640
R_F	0.050	0.065
R_{wF}	0.063	0.089

[a] Lattice parameters were obtained with the use of an auto indexing program and a least-squares fit to the setting angles at the unresolved Mo $K\bar{\alpha}$ components of 30 selected reflections.

prepared by the procedure described by Rösch[14] by reaction of $Hg(SiMe_3)_2$ with Al powder in a slurry using 90/10 pentane to THF as the solvent. $Mg(SiMe_3)_2 \cdot DME$ was prepared as previously described[8] by shaking excess magnesium turnings with $Hg(SiMe_3)_2$ in DME. In each case the resulting product was recrystallized before subsequent use in the preparation of the TMEDA complexes. I was prepared as follows: 0.72 g (2.3 mmol) of $Al(SiMe_3)_3 \cdot THF$ was placed in a reaction vessel and dissolved in 10 mL of *n*-pentane. The vessel was attached to the vacuum system and evacuated. Then, approximately a five-fold excess (~12 mmol) of TMEDA was distilled into the vessel from the vacuum system. The vessel was closed off and allowed to warm gradually to room temperature and stand for 2 h with occasional shaking until no further visible change occured (the color changed from pale yellow to light green). The reaction vessel was attached to the vacuum system and the solvent removed. Pumping was continued for several hours (vacuum ~10^{-5} torr) leaving a white crystalline material. This was purified by placing the crude material in one arm of an "H vessel" equipped with a fine glass frit and distilling in just enough *n*-pentane to dissolve the product. The solution was then filtered through the frit to remove the small amount of insoluble material present. The vessel then was placed in a freezer (−20 °C) and allowed to stand for several days. Gradually colorless needle-shaped crystals formed, and the solvent then was decanted off. The recrystallization process was repeated a second time yielding 0.58 g (0.92 mmol) of $[Al(SiMe_3)_3]_2 \cdot TMEDA$; 80% yield, based on $Al(SiMe_3)_3 \cdot THF$. A benzene solution of this gave a proton NMR spectrum consisting of three lines, δ 0.32 ($I \simeq 27$), δ 2.05 ($I \simeq 6$), and δ 1.38 ($I = 2$) corresponding to reaction 1.

$$2Al(SiMe_3)_3 \cdot THF + TMEDA \rightarrow 2THF + [AlSiMe_3)_3]_2 \cdot TMEDA \quad (1)$$

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(Al(SiMe_3)_3)_2 \cdot TMEDA$

atom	x/a	y/b	z/c	B_{eq}, $Å^2$
Al	0.9254 (2)	0.3453 (1)	0.8247 (1)	4.4 (1)
Si(1)	0.6682 (2)	0.3462 (1)	0.8431 (1)	6.3 (1)
Si(2)	0.9903 (2)	0.4293 (1)	0.6870 (1)	6.3 (1)
Si(3)	1.0109 (2)	0.2086 (1)	0.8083 (1)	6.6 (1)
N	1.0203 (6)	0.3938 (3)	0.9505 (3)	5.2 (1)
C(1.1)	0.5783 (9)	0.3125 (10)	0.7273 (8)	15.0 (5)
C(2.1)	0.6027 (11)	0.2719 (8)	0.9282 (10)	15.6 (5)
C(3.1)	0.5863 (10)	0.4378 (6)	0.8750 (13)	14.7 (4)
C(1.2)	0.8973 (12)	0.3897 (6)	0.5744 (5)	11.8 (3)
C(2.2)	0.9387 (11)	0.5345 (5)	0.6921 (5)	10.0 (3)
C(3.2)	1.1766 (11)	0.4290 (9)	0.6588 (9)	15.9 (5)
C(1.3)	0.9077 (10)	0.1664 (5)	0.6983 (6)	10.3 (3)
C(2.3)	0.9776 (12)	0.1392 (4)	0.9105 (7)	10.9 (3)
C(3.3)	1.1993 (10)	0.1983 (5)	0.7827 (9)	12.9 (4)
C(1)	0.9803 (11)	0.3487 (4)	1.0358 (5)	8.2 (2)
C(2)	1.1741 (9)	0.3890 (5)	0.9464 (6)	8.4 (3)
C(3)	0.9725 (6)	0.4767 (3)	0.9555 (4)	5.1 (1)

[a] Standard deviations in parentheses refer to the least significant digit(s). [b] B_{eq} is the isotropic equivalent obtained from the six anisotropic thermal parameters.

II was synthesized in a similar manner by placing 3.2 mmol of pure $Mg(SiMe_3)_2 \cdot DME$ in a reaction vessel and dissolving it in 10 mL of cyclopentane. The reaction vessel was evacuated, and approximately a 10-fold excess (32 mmol) of TMEDA was distilled into the vessel from the vacuum system. The reaction vessel was then warmed slowly to room temperature and allowed to stand for 3 h until no further change occurred, yielding a light brown solution. The solvent was removed on the vacuum system, giving an off-white solid product which was pumped on for several hours. This material was crystallized in the same manner as I from *n*-pentane yielding 0.64 g (2.1 mmol; 66% yield based on $Mg(SiMe_3)_2 \cdot DME$) of colorless crystalline needles of II after three crystallizations. The ^1H NMR spectrum of a benzene solution gave three signals; δ 0.45 ($I \simeq 9$), δ 1.84 ($I \simeq 3$), δ 1.62 ($I \simeq 2$) corresponding to the formation of II via eq 2.

$$Mg(SiMe_3)_2 \cdot DME + TMEDA \rightleftharpoons Mg(SiMe_3)_2 \cdot TMEDA + DME \quad (2)$$

X-ray Crystallographic Studies. Data Collection. Single crystals of both I and II were mounted in thin-walled capillary tubes in the drybox under an argon atmosphere, plugged with grease, removed, and flame sealed. In each case the crystals were mounted on a Syntex $P2_1$ four-circle diffractometer equipped with a Mo $K\bar{\alpha}$ (λ = 0.710 69 Å) source with the radiation diffracted from a highly oriented graphite crystal in the parallel mode with a θ–2θ scan in bisecting condition. The specific conditions and unit cell dimensions are given in Table I.

Structure Determination. The structure of I was solved by direct methods[15] (program MULTAN) phasing on 170 *E*'s normalized according to parity groups with magnitude greater than 1.2. The solution of highest figure of merit was used to calculate an *E* map from which the Al, Si(1), Si(2), Si(3), and N atoms were located. The carbon atoms were located in a subsequent difference Fourier synthesis (FORDAP).[16] After isotropic least-squares refinement (ORFLS)[16] of the heavy atoms, calculated hydrogen coordinates,

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(13) Rösch, L.; Altnau, G.; Hahn, E.; Havemann, H. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1981**, *36B*, 1234.

(14) Rösch, L. *Angew. Chem.* **1977**, *89*, 497; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 480.

(15) Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *26*, 274. MULTAN—direct methods program.

(16) Local versions of the following programs were used: (1) SYNCOR, Schmonsees, W., data reductions; (2) FORDAP, Zalkin, A., Fourier synthesis; (3) ORFLS and ORFFE, Busing, W.; Martin, K.; Levy, H., full-matrix least-squares and function and error programs; (4) ORTEP, Johnson, C. K., molecular model plotting; (5) HFINDR, Zalkin, A., as modified by Anderson, T. J., calculation of hydrogen position for ideal geometry. (6) scattering factors were taken from: Ibers, J. A.; Hamilton, W. C. "International Tables of X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. Bond Lengths (Å) and Angles (deg) for $(Al(SiMe_3)_3)_2 \cdot TMEDA$

Al–Si(1)	2.470 (3)	Si(1)–Al–Si(2)	111.5 (1)	N–Al–Si(1)	107.3 (2)
Al–Si(2)	2.473 (3)	Si(1)–Al–Si(3)	110.3 (1)	N–Al–Si(2)	106.9 (2)
Al–Si(3)	2.473 (3)	Si(2)–Al–Si(3)	111.9 (1)	N–Al–Si(3)	108.6 (2)
Al–N	2.069 (5)				
N–C(1)	1.465 (8)	C(1)–N–C(2)	107.9 (6)	C(1)–N–Al	109.7 (4)
N–C(2)	1.467 (9)	C(1)–N–C(3)	111.3 (5)	C(2)–N–Al	109.4 (4)
N–C(3)	1.482 (6)	C(2)–N–C(3)	111.2 (5)	C(3)–N–Al	107.2 (3)
C(3)–C(3′)	1.519 (10)	N–C(3)–C(3′)	116.1 (6)		
			Si(1)		
Si–C(1)	1.848 (10)	C(1)–Si–C(2)	100.1 (7)	C(1)–Si–Al	108.7 (3)
Si–C(2)	1.850 (10)	C(1)–Si–C(3)	107.0 (7)	C(2)–Si–Al	115.5 (4)
Si–C(3)	1.803 (10)	C(2)–Si–C(3)	105.6 (7)	C(3)–Si–Al	118.2 (3)
			Si(2)		
Si–C(1)	1.859 (9)	C(1)–Si–C(2)	105.4 (5)	C(1)–Si–Al	107.3 (3)
Si–C(2)	1.853 (8)	C(1)–Si–C(3)	103.9 (6)	C(2)–Si–Al	116.6 (2)
Si–C(3)	1.833 (10)	C(2)–Si–C(3)	105.7 (6)	C(3)–Si–Al	116.5 (3)
			Si(3)		
Si–C(1)	1.890 (8)	C(1)–Si–C(2)	104.8 (4)	C(1)–Si–Al	105.7 (3)
Si–C(2)	1.872 (9)	C(1)–Si–C(3)	105.9 (5)	C(2)–Si–Al	116.8 (3)
Si–C(3)	1.851 (9)	C(2)–Si–C(3)	106.9 (5)	C(3)–Si–Al	115.6 (3)

Dihedral Angles

Al–N–C(3)–C(3′)	178.6 (5)	Si(2)–Al–N–C(3)	−56.2 (4)
Si(1)–Al–N–C(3)	63.5 (4)	Si(3)–Al–N–C(3)	−177.2 (3)

assuming r(C–H) = 0.95 Å and ideal geometry, and isotropic temperature factors (1.1 × carbon value) were introduced as fixed parameters. With the hydrogen parameters recalculated before every cycle, full-matrix anisotropic least-squares refinement on 154 variables yielded discrepancy factors $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.05 and $R_{wF} = [\sum w(|F_o| - |F_c|)^2]$ = 0.063 and error of fit 1.715. The maximum residual electron density was 0.28 e/Å^3 located at coordinates (0.206, 0.694, 0.170). The nearest atoms are Si(1) at 1.217 Å, Al at 1.260 Å, and C(1.1) at 2.497 Å.

Atomic coordinates and bond lengths are given in Tables II and III. Tables of anisotropic temperature factors, calculated hydrogen coordinates, mean planes, and the observed structure factors are available as supplementary material.[17]

The structure of II also was solved by direct methods[15] phasing on 170 E's normalized according to parity groups. The E map obtained from the solution of highest overall figure of merit gave the positions of Mg, Si(1), Si(2), N(1), and N(2). The carbon atoms were located in subsequent difference Fourier maps. After isotropic least squares refinement of all the heavy atoms, calculated H atom positions based on r(C–H) = 0.95 Å and temperature factors $B_H = 1.1B_c$, were introduced as fixed parameters; then, full-matrix anisotropic least-squares refinement was carried out on the 154 non-hydrogen atom parameters to yield discrepancy factors R_F = 0.065, R_{wF} = 0.089, and error of fit of 2.69. The maximum residual electron density was 0.327 e/Å^3 located at coordinates (0.905, 0.870, 0.647). The nearest atoms are Si(2) (1.95 Å), C(12) (1.80 Å), and C(22) (1.88 Å).

The atomic coordinates and bond lengths are given in Tables IV and V. Tables of the anisotropic temperature factors, calculated hydrogen parameters, and observed structure factors are available as supplementary material.[17]

Results and Discussion

The $[Al(SiMe_3)_3]_2 \cdot TMEDA$ molecules is depicted in Figure 1 and is made up of two $(Me_3Si)_3Al \cdot N(Me)_2CH_2$ units related by a center of symmetry located at the mid point of the C(3)–C(3′) bond. This symmetry requires that the TMEDA skeleton and the two Al atoms lie in a plane. The deviations from the mean plane (Table S-III) reveal that C(1.3)Si(3)–Si(3′)C(1.3′) atoms are also nearly coplanar with only a small rotation about the Al–N and Al–Si bonds leading to the displacement of these atoms from the plane. The crystal packing diagram is available.[17]

Table IV. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $Mg(SiMe_3)_2 \cdot TMEDA$

atom	x/a	y/b	z/c	B_{eq}, Å^2
Mg	0.2542 (2)	−0.3711 (2)	1.0048 (2)	4.7 (1)
Si(1)	0.2772 (2)	−0.5308 (3)	1.1377 (2)	6.7 (1)
Si(2)	0.2108 (3)	−0.5119 (3)	0.8630 (2)	7.2 (1)
N(1)	0.3766 (7)	−0.2166 (9)	1.0308 (6)	7.4 (2)
N(2)	0.1655 (7)	−0.1760 (9)	0.9959 (5)	7.3 (2)
C(4)	0.3291 (14)	−0.0822 (18)	1.0099 (10)	12.2 (5)
C(5)	0.2385 (14)	−0.0625 (14)	1.0310 (10)	10.7 (5)
C(1)N(1)	0.4341 (9)	−0.2350 (18)	0.9757 (9)	12.7 (4)
C(2)N(1)	0.4426 (9)	−0.2168 (16)	0.1170 (7)	11.9 (4)
C(1)N(2)	0.1016 (10)	−0.1416 (13)	0.9114 (7)	10.9 (3)
C(2)N(2)	0.1039 (10)	−0.1873 (17)	1.0475 (8)	12.0 (4)
C(1.1)	0.3734 (11)	−0.6774 (12)	1.1515 (7)	12.2 (3)
C(2.1)	0.3094 (12)	−0.4585 (13)	1.2464 (6)	11.7 (2)
C(3.1)	0.1661 (11)	−0.6442 (16)	1.1213 (8)	14.6 (5)
C(1.2)	0.2193 (22)	−0.6979 (15)	0.8789 (8)	14.1 (5)
C(2.2)	0.1005 (17)	−0.4828 (28)	0.7793 (12)	19.1 (8)
C(3.2)	0.2913 (20)	−0.4937 (20)	0.8000 (11)	19.3 (6)

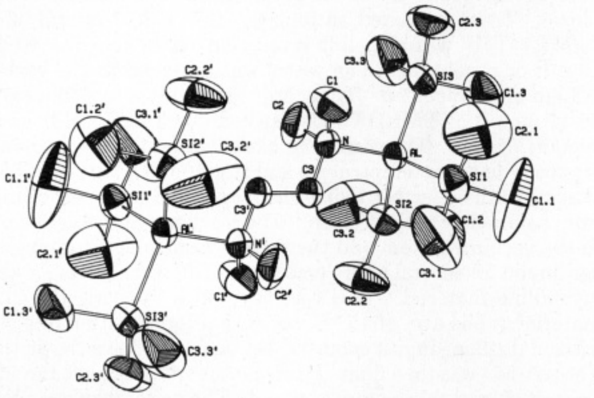

Figure 1. An ORTEP diagram of the $[(Me_2Si)_3Al)]_2 \cdot TMEDA$ molecule with the atoms labeled. The 50% thermal ellipsoids were used; the hydrogen atoms have been omitted for clarity.

In Table VI a comparison of observed bond distance and the sums of the covalent radii for selected silicon– and carbon–metal bonded systems is presented. From these data, it can be seen that the silicon–metal distances are all greater than the sums of their covalent radii while those for the carbon–metal bonds are essentially equivalent to

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[17] See paragraph at the end of the paper regarding supplementary material.

Table V. Bond Lengths (Å) and Angles (deg) for $Mg(SiMe_3)_2 \cdot TMEDA$

Mg-Si(1)	2.631 (4)	Si-Mg-Si	115.3 (1)	Si(1)-Mg-N(1)	110.6 (3)
Mg-Si(2)	2.624 (4)			Si(1)-Mg-N(2)	114.8 (3)
Mg-N(1)	2.191 (8)	N(1)-Mg-N(2)	82.8 (4)	Si(2)-Mg-N(1)	115.1 (3)
Mg-N(2)	2.193 (8)				
		Si(1)			
Si(1)-C(1)	1.90 (1)	C(1)-Si-Mg	112.1 (4)	C(1)-Si-C(2)	103.0 (6)
Si(1)-C(2)	1.87 (1)	C(2)-Si-Mg	124.2 (4)	C(1)-Si-C(3)	99.1 (7)
Si(1)-C(3)	1.85 (1)	C(3)-Si-Mg	110.8 (4)	C(2)-Si-C(3)	104.5 (7)
		Si(2)			
Si(2)-C(1)	1.75 (1)	C(1)-Si-Mg	117.7 (4)	C(1)-Si-C(2)	106 (1)
Si(2)-C(2)	1.74 (2)	C(2)-Si-Mg	122.0 (6)	C(1)-Si-C(3)	99 (1)
Si(2)-C(3)	1.85 (2)	C(3)-Si-Mg	119.9 (6)	C(2)-Si-C(3)	95 (1)
		N(1)			
N(1)-C(4)	1.41 (2)	C(4)-N(1)-Mg	104.5 (8)		
N(1)-C(1)	1.47 (1)	C(1)-N(1)-C(2)	110 (1)	C(1)-N(1)-C(4)	106 (1)
N(1)-C(2)	1.44 (1)	C(1)-N(1)-Mg	112.9 (8)	C(2)-N(1)-C(4)	110 (1)
		C(2)-N(1)-Mg	113.3 (7)		
		N(2)			
N(2)-C(5)	1.46 (2)	C(5)-N(2)-Mg	104.9 (7)		
N(2)-C(1)	1.44 (1)	C(1)-N(2)-C(2)	108 (1)	C(1)-N(2)-C(5)	111 (1)
N(2)-C(2)	1.46 (1)	C(1)-N(2)-Mg	113.6 (7)	C(2)-N(2)-C(5)	108 (1)
		C(2)-N(2)-Mg	111.1 (8)		
C(4)-C(5)	1.48 (2)	C(5)-C(4)-N(1)	116 (1)	C(4)-C(5)-N(2)	112 (1)
		Dihedral Angles			
Mg-N(2)-C(5)-C(4)	−36 (2)	Mg-N(1)-C(4)-C(5)	−38 (2)	N(1)-C(4)-C(5)-N(2)	54 (2)

Table VI. A Comparison of Metal-Silicon and Metal-Carbon Bond Lengths (Å) with the Sums of Their Covalent Radii (Å)

compd	M-Si dist	Σr
$Al(SiMe_3)_3 \cdot OEt_2$[a]	2.47	2.43
$[Al(SiMe_3)_3]_2 \cdot TMEDA$	2.472	
$AlMe_3 \cdot NMe_3$[b]	1.987	2.03
$Mg(SiMe_3)_2 \cdot DME$[c]	2.63	2.55
$Mg(SiMe_3)_2 \cdot TMEDA$	2.627	
$MgMe_2 \cdot TMEDA$[d]	2.166	2.15
$Hg(SiMe_3)_2$[e]	2.500	2.48
$Hg(SiPh_3)_2$[f]	2.490	
$HgMe_2$[g]	2.083	2.07

[a] Reference 9. [b] Reference 18. [c] Reference 8. [d] Reference 22. [e] Reference 2. [f] Reference 3. [g] Koshiwabara, K.; Konaka, Sh.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* 1973, *46*, 407.

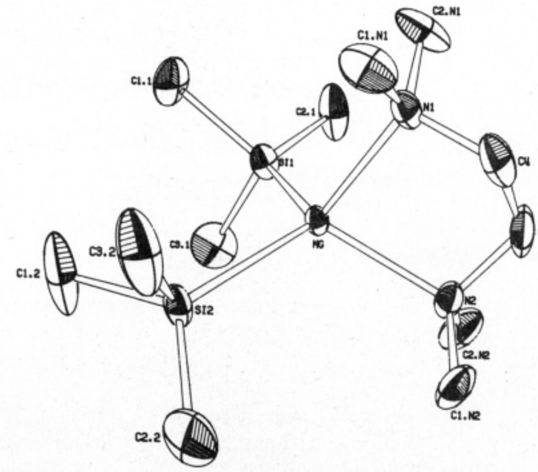

Figure 2. An ORTEP diagram of the $(Me_3Si)_2Mg \cdot TMEDA$ molecule with the atoms labeled. The 50% thermal ellipsoids were used. The hydrogen atoms were omitted for clarity.

them or, in the case of C–Al bonds, shorter than the $\sum r$ with a value of 1.987 Å in $AlMe_3 \cdot NMe_3$[18] which is representative of a wide variety (with the exception of those involved in multicentered bonding) of C–Al bond distance.[19,20] These deviations in bond length, although small, suggest that there is no significant bond polarity effect on the metal–silicon bond length but that this may play a small role in the carbon analogues.

A comparison of the Al–N bond length in I (2.069 Å) with other Al–N bond lengths shows it to be comparable to that observed in $AlH_3 \cdot NMe_3$ (2.063 Å)[20] but to lie between that observed in $AlMe_3 \cdot NMe_3$ (2.099 Å)[21] and in $AlCl_3 \cdot NMe_3$ (1.96 Å).[21] Assuming that the differences in base strength between NMe_3 and a single nitrogen in the TMEDA moiety are small, this variation in bond length may be interpreted as indicating a trend in the acidities of those aluminum compounds as follows: $AlMe_3 > Al(SiMe_3)_3 \approx AlH_3 > AlCl_3$. The indication that $Al(SiMe_3)_3$ is more acidic than $AlMe_3$ is of interest and should be studied by thermochemical means to varify this suggestion.

The Si–Al–Si angles are slightly greater than the N–Al–Si angles probably due to steric effects since bond polarity arguments appear to be ruled out by the bond length data. C–Si–C angles vary, but no clear trend can be discerned and an average value about 105° must be accepted. The average C–Si–Al angle is correspondingly greater than tetrahedral, but these angles clearly indicate a tilting of the $SiMe_3$ groups toward the Al–N axis. Similar behavior was observed in $Mg(SiMe_3)_2 \cdot DME$ where the $SiMe_3$ groups are tilted toward Si–Mg–Si bisector.

The structure of $Mg(SiMe_3)_2 \cdot TMEDA$ is given in Figure 2. The four molecules in the cell are arranged in pairs about centers of symmetry at (0, 0, 0) and (0, $^1/_2$, $^1/_2$). They are packed head-to-tail along the *b* axis, with the MgN_2C_2 rings arranged approximately parallel to each

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[18] Anderson, G. E.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 1947.

[19] Almenningen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928.

[20] An extensive tabulation and discussion of metal–carbon bond lengths is given by: Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235.

[21] Almenningen, A.; Haaland, A.; Haugen, T.; Novak, D. P. *Acta Chem. Scand.* **1973**, *27*, 1821.

other along the $(a + c)/2$ direction. A diagram of the unit cell is available.[17]

The structure is consistent with that of $Mg(SiMe_3)_2\cdot$DME in which the Si–C distance is 2.630 (2) Å and Si–Mg–Si angle is 125.2 (1)°. The smaller Si–Mg–Si angle in the present result (115°) may be explained by VSEPR theory on the basis that the weaker base, TMEDA, will form less polar Mg–N bonds than the Mg–O bonds in the DME adduct. Alternatively the methyl groups on TMEDA may cause interference with those on the trimethylsilyl group forcing the smaller angle separation between these units.

Further, the N–Mg bond distances and angles are similar to those observed for organomagnesium compounds. Comparison with the three complexes $MgMe_2\cdot$TMEDA,[22] $MgPh_2\cdot$TMEDA,[23] and η^5-$C_5H_5MgBr\cdot(Et_2N(CH_2)_2NEt_2)$,[24] which have average N–Mg distances of 2.24, 2.20, and 2.26 Å and N–Mg–N angles of 81.5, 82.5, and 82.5, respectively, are clearly within the range of those observed in the present system.

As in the $Mg(SiMe_3)_2\cdot$DME adduct and in $[Al(SiMe_3)_3]_2\cdot$TMEDA, the Me_3Si groups may be tilted inward toward the Si–Mg–Si bisector; however, the effect is offset by twisting about the Si–Mg bonds and is obscured by poorly determined Si–C bond lengths and C–Si–C angles.

The inconsistency in Si–C bond lengths is partly due to thermal averaging effects on the carbon atom positions. Attempts to correct Si–C bond lengths (Å) based on the "riding model" are as follows: Si_1–C_{11}, 1.96 (1); Si_1–C_{21}, 1.94 (1); Si_1–C_{31}, 1.92 (2); Si_2–C_{12}, 1.99 (2); Si_2–C_{22}, 2.03 (2); Si_2–C_{32}, 1.99 (20). The corrections are somewhat large, but they have the effect of bringing the bond lengths on Si(1) and Si(2) into closer agreement.

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Registry No. I, 84929-13-5; II, 84929-14-6; $Al(SiMe_3)_3\cdot$THF, 62962-49-6; $Mg(SiMe_3)_2\cdot$DME, 62483-43-6.

Supplementary Material Available: Tables containing deviations from the mean plane, anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors, and a packing diagram for I and tables containing anisotropic thermal parameters, observed and calculated structure factors, and a packing diagram also for II (22 pages). Ordering information is given on any current masthead page.

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(22) Greiser, T.; Kopf, J.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1980**, *191*, 1.

(23) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3381.

(24) Johnson, C.; Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *40*, C11.

The Search for Dimethylzirconocene. Crystal Structures of Dimethylzirconocene, Dimethylhafnocene, Chloromethylzirconocene, and (μ-Oxo)bis(methylzirconocene)

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The crystal structures of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CH_3)$, and $[(\eta^5\text{-}C_5H_5)_2Zr(CH_3)]_2O$ have been determined from X-ray data measured by counter methods. Dimethylzirconocene crystallizes in the monoclinic space group $P2_1/n$ with unit-cell parameters a = 6.953 (3) Å, b = 11.902 (5) Å, c = 13.839 (5) Å, β = 91.95 (3)°, and Z = 4 for D_{calcd} = 1.45 g cm^{-3}. Full-matrix least-squares refinement has led to a final R factor of 0.029 based on 1672 independent observed reflections. Dimethylhafnocene is isostructural with a = 6.965 (4) Å, b = 11.854 (5) Å, c = 13.786 (6) Å, β = 92.02 (3)°, and D_{calcd} = 1.98 g cm^{-3}. Refinement on 1662 reflections produced R = 0.041. Chloromethylzirconocene exhibits crystallographically disordered chloro and methyl ligands and is isostructural with the dimethyl derivatives. The cell constants are a = 6.810 (8) Å, b = 11.821 (9) Å, c = 13.818 (9) Å, β = 92.30 (4)°, and D_{calcd} = 1.62 g cm^{-3}. A final R value of 0.043 resulted from the refinement on the basis of 1709 observed reflections. (μ-Oxo)bis(methylzirconocene) crystallizes in the trigonal space group $P3_221$ with a = 8.017 (3) Å, c = 28.376 (6) Å, and D_{calcd} = 1.54 g cm^{-3}. Refinement on 1358 reflections led to R = 0.026. The most important results concern the metal–carbon σ bond lengths in the $(\eta^5\text{-}C_5H_5)_2M(CH_3)_2$ compounds. For M = Zr the two independent determinations are 2.273 (5) and 2.280 (5) Å, while for M = Hf the distances are 2.233 (12) and 2.240 (12) Å. The average for the latter, 2.24 Å, is much shorter than the 2.35 Å value previously reported for $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$. In addition, the longer Zr–C(σ) is the reverse of that found for $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$, M = Zr and Hf. The answer to these apparent discrepancies is found in a consideration of the role of the disordered chloromethylzirconocene structure.

Introduction

For several years our group has been interested in compounds of zirconium and hafnium that contain metal–carbon σ bonds. In the course of sorting out electronic and steric factors that affect the M–C(σ) bond length, we have had the occasion to carry out X-ray structural determinations on a wide range of compounds: $Cp_2M(CO)_2$ (M = Zr,[1] Hf,[2] Cp = $(\eta^5\text{-}C_5H_5)$), $Cp_2M[C_4(C_6H_5)_4]$ (M = Ti,[3] Zr,[4] Hf[3]), $Cp_2M[CH(C_6H_5)_2]_2$ (M = Zr, Hf),[5] $Cp_3Zr(\eta^1\text{-}C_5H_5)$,[6] $Cp_2Hf(\eta^1\text{-}C_5H_5)_2$,[7] $Cp_2Zr(C_6H_5)[CH\{Si(CH_3)_3\}_2]$,[8]

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(1) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812.

(2) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5079.

(3) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.