$ClSiH_3$ in the temperature range 330–370 °C. With similar A factors, this result implies that insertion into $ClSiH_3$ had an activation energy at least 5 kcal/mol greater. If the A factor for insertion into Si_2H_6 were ten times higher, the difference in insertion activation energies would still have to be equal or greater than 2.5 kcal/mol. We have also observed that SiH_2 insertion into CH_3PH_2 does not compete with insertion into Si_2H_6[3] under conditions where SiH_3PH_2[3] was of similar stability to Si_3H_8. Thus, again assuming similar activation entropies, the activation energy for SiH_2 insertion into CH_3PH_2 is significantly greater than for SiH_2 insertion into CH_3SiH_3. The fact that the activation energies of SiH_2 insertion into silicon-hydrogen (and phosphorus-hydrogen) bonds can differ by as much as 3–5 kcal/mol strongly suggests that the absolute E values for all of these SiH_2 insertion reactions are significantly greater than the very low values (from 0 to 1.3 kcal/mol) previously suggested.[4,24]

Acknowledgment. The authors are indebted to H. E. O'Neal for most valued discussions.

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Metal–Silicon Bonded Compounds. 9.[1] The Synthesis and Structure of Bis(trimethylsilyl)magnesium 1,2-Dimethoxyethane Adduct

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Abstract: Bis(trimethylsilyl)magnesium (I) was prepared by direct reaction of magnesium metal with bis(trimethylsilyl)mercury in either DME or THF solvent. Both chemical analyses and NMR spectral studies showed that the crystalline product obtained was the ether adduct of I. Limited variable temperature NMR studies indicate a complex reaction path is followed with formation of several silylmercury complexes. The structure of I has been determined from single-crystal x-ray data collected by counter methods. It crystallizes in the orthorhombic space group *Pbcn* with unit cell parameters $a = 16.461$ (2), $b = 9.348$ (1), and $c = 11.950$ (2) Å with four molecules of $Mg(SiMe_3)_2 \cdot DME$ per unit cell. Full-matrix least-squares refinement with fixed contributions for the hydrogen atoms gave discrepancy factors of $R_1 = 0.047$ and $R_2 = 0.054$ for 640 reflections with $I > 2.5\sigma(I)$. The magnesium atom is surrounded by two silicon atoms and two oxygen atoms which form a distorted tetrahedron. The Mg–Si distances are 2.630 (2) Å with an Si–Mg–Si angle of 125.2 (1)°, while the Mg–O distances are 2.124 (4) Å with an O–Mg–O angle of 76.3 (2)° determined by the configuration of the DME chelate ring. The dihedral angle between the Si–Mg–Si and O–Mg–O planes is 89.7°.

A number of silyl-main group metal derivatives have been reported[2] and in the past few years several structures have appeared which show direct silicon-metal bonds.[3-5] These include recent examples which have silicon-mercury bonds[4,5] and electron deficient silicon bridge bonds in silyllithium hexamer.[3] Reports have appeared over the years which indicate formation of silylmagnesium species,[2] but no conclusive work has appeared with regard to the composition or nature of these nor have they been isolated. We now wish to report the synthesis, a few properties, and the solid state crystal and molecular structure of the first example of a compound containing a silicon-to-magnesium bond, bis(trimethylsilyl)magnesium 1,2-dimethoxyethane.

Experimental Section

All studies were carried out using standard Schlenk tube, drybox, or high vacuum techniques. All solvents used were of standard reagent quality and were dried by refluxing over NaK or $LiAlH_4$ and distilled for immediate use or storage on the vacuum system. The magnesium used in the initial experiments was of high purity obtained from Dow Chemical Co.; however, subsequent studies were carried out with equal success using Grignard quality magnesium turnings. The trimethyl-

Table I. Atomic Coordinates for Mg(SiMe$_3$)$_2$·DME[a,b]

Atom	*x*	*y*	*z*	*B*
Si(1)	0.1228 (1)	0.3885 (2)	0.1521 (1)	
Mg(2)	0.0 (0)	0.2590 (2)	0.2500 (0)	
C(3)	0.1572 (5)	0.3208 (10)	0.0114 (6)	
C(4)	0.2212 (4)	0.3981 (7)	0.2313 (6)	
C(5)	0.0984 (4)	0.5816 (7)	0.1265 (8)	
C(6)	0.1070 (4)	0.0882 (7)	0.4201 (5)	
O(7)	0.0403 (2)	0.0803 (3)	0.3448 (3)	
C(8)	0.0384 (4)	−0.0499 (6)	0.2832 (5)	
H(1)	0.1710	0.2222	0.0280	13.47
H(2)	0.2038	0.3684	−0.0215	13.47
H(3)	0.1106	0.3114	−0.0377	13.47
H(4)	0.2660	0.4399	0.1899	10.83
H(5)	0.2322	0.2977	0.2249	10.83
H(6)	0.2109	0.4324	0.3066	10.83
H(7)	0.0513	0.5882	0.0779	11.37
H(8)	0.1420	0.6397	0.0964	11.37
H(9)	0.0799	0.6252	0.1956	11.37
H(10)	0.1583	0.0487	0.3949	9.74
H(11)	0.0856	0.0300	0.4805	9.74
H(12)	0.1054	0.1787	0.4598	9.74
H(13)	0.0216	−0.1116	0.3442	8.21
H(14)	0.0865	−0.0893	0.2480	8.21

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{ISO}
Si(1)	4.64 (7)	5.09 (7)	7.84 (9)	−0.93 (7)	0.42 (8)	−0.34 (8)	5.62 (8)
Mg(2)	4.56 (11)	4.53 (12)	8.27 (15)	0.0 (0)	1.00 (13)	0.0 (0)	5.50 (12)
C(3)	14.53 (56)	19.89 (80)	10.10 (47)	−8.25 (55)	4.78 (44)	−4.56 (51)	12.24 (58)
C(4)	6.59 (38)	11.33 (48)	13.21 (47)	−1.24 (33)	−0.54 (37)	1.21 (44)	9.85 (44)
C(5)	8.34 (43)	6.24 (37)	25.29 (82)	−1.28 (29)	−0.88 (54)	4.61 (45)	10.33 (50)
C(6)	9.24 (42)	9.22 (46)	9.22 (39)	1.39 (34)	−2.61 (37)	−1.57 (35)	8.85 (41)
O(7)	5.99 (20)	5.31 (20)	7.42 (21)	1.21 (14)	−0.17 (18)	−0.57 (18)	6.07 (20)
C(8)	8.04 (39)	5.51 (27)	9.88 (45)	0.80 (25)	−1.39 (31)	−0.89 (32)	7.47 (35)

[a] Standard deviations from the variance-covariance matrix are given in parentheses for the least significant digit(s). [b] The form of the anisotropic temperature factor reported here is $-\frac{1}{4}(B_{11}a^2h^2 + B_{22}b^2k^2 + B_{33}c^2l^2 + 2B_{12}abhk + 2B_{13}achl + 2B_{23}bckl)$.

Table II. Bond Distances and Angles for Mg(SiMe$_3$)$_2$·DME

Distance (Å)		Angles (deg)	
Mg(2)-Si(1)	2.630 (2)	Si(1)-Mg(2)-Si(1′)	125.2 (1)
Mg(2)-O(7)	2.124 (4)	Si(1)-Mg(2)-O(7)	111.0 (1)
O(7)-C(6)	1.422 (6)	Mg(2)-O(7)-C(6)	122.5 (3)
O(7)-C(8)	1.422 (6)	O(7)-Mg(2)-O(7′)	76.3 (2)
C(8)-C(8′)	1.492 (10)	Mg(2)-O(7)-C(8)	113.0 (3)
Si(1)-C(3)	1.884 (7)	O(7)-C(8)-C(8′)	107.1 (4)
Si(1)-C(4)	1.878 (6)	C(6)-O(7)-C(8)	112.9 (4)
Si(1)-C(5)	1.874 (7)	Mg(2)-Si(1)-C(3)	118.2 (2)
		Mg(2)-Si(1)-C(4)	117.4 (2)
		Mg(2)-Si(1)-C(5)	110.5 (2)
		C(3)-Si(1)-C(4)	101.9 (3)
		C(3)-Si(1)-C(5)	104.0 (4)
		C(4)-Si(1)-C(5)	102.8 (3)

chlorosilane was graciously supplied by Dow-Corning Corporation and distilled before use.

Synthesis of Compounds. Bis(trimethylsilyl)mercury was prepared by reaction of 0.5% sodium amalgam with trimethylchlorosilane as previously described.[6]

Bis(trimethylsilyl)magnesium 1,2-dimethoxyethane was prepared as follows: A reaction tube was loaded with Hg(SiMe$_3$)$_2$ (10 g, 28.9 mmol), excess of magnesium turnings (5 g, 205.7 mmol), and 20 ml of 1,2-dimethoxyethane (DME), evacuated and sealed. It was then covered with aluminum foil and placed on a rotating shaker. The initial color of the reaction mixture was yellow-green. The reaction proceeded slowly and could be followed by a progressive color change from the initial yellow-green to orange (2–3 days), red-orange (4–8 days), deep red (9–15 days), and finally (4–5 weeks) to a pale red solution from which clear pink crystalline material was precipitated and separated.

The crystalline material was found to be sparingly soluble in hydrocarbon solvents such as cyclopentane but quite soluble in ethers such as DME, THF, or diethyl ether. The crystalline material was very reactive undergoing immediate decomposition on exposure either to air or moisture and even appears to undergo some decomposition when stored under vacuum in the dark. The analysis[7] for this material calculated for Mg(SiMe$_3$)$_2$·DME is: Mg, 9.33; C, 46.1; H, 10.75. Found: Mg, 9.82; C, 47.38; H, 10.53.

Recrystallization of this material from cyclopentane yielded very pale pink crystals which melted between 74 and 77 °C in a sealed capillary.

A similar reaction sequence was observed when THF was used as the solvent, yielding a brownish white solid on removal of the solvent. On dissolving this material in cyclopentane, the solution turned dark green and at low temperature yielded clear, white crystals which melted at room temperature. On removal of the solvent dark yellow-brown crystals appeared which melted between 43 and 44 °C. Analysis for Mg(SiMe$_3$)$_2$·THF Calcd.: Mg, 10.04; C, 49.58; H, 10.74. Found: Mg, 11.11; C, 51.09; H, 10.79.

NMR Studies. The 60-MHz NMR spectra were obtained on a Varian A-60 equipped with a variable temperature probe and control unit. Line positions were determined using the audio frequency side bands of the solvent or of internal cyclopentane and were then corrected to positions relative to Me$_4$Si by addition of the appropriate factor. Negative values indicate positions upfield from Me$_4$Si. All samples were made in the drybox by addition of the appropriate silicon compounds to NMR tubes fitted with standard taper joints and stopcocks. These samples were then removed from the drybox and attached to the vacuum system and the desired solvents and/or standards added, followed by degassing of the samples which were then sealed off. All samples were stored at −20 °C until the spectra were obtained.

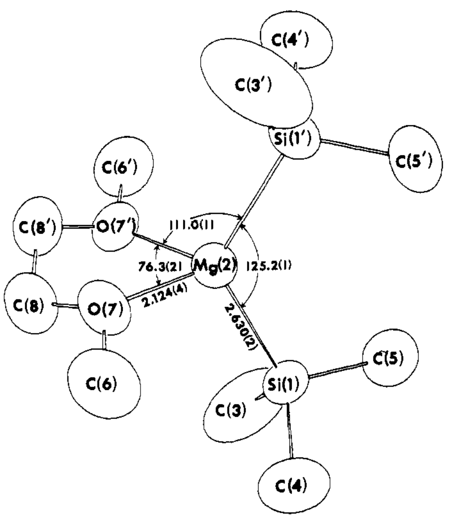


Figure 1. The molecular structure of the bis(trimethylsilyl)magnesium 1,2-dimethoxyethane adduct with significant distances and angles.

X-ray Crystallographic Study. Data Collection. A single crystal of $Mg(SiMe_3)_2 \cdot DME$ with dimensions 0.34 × 0.26 × 0.55 mm was sealed in a capillary under argon and mounted on a Syntex $P2_1$ four-circle diffractometer. The radiation was Mo $K\alpha$ (0.710 69 Å) which had been diffracted from a graphite monochromator in the parallel orientation. Preliminary rotation photographs and counter data revealed the crystal was orthorhombic, *Pbcn* with cell dimensions (determined by accurately centering 15 general reflections) $a = 16.461$ (2), $b = 9.348$ (1), $c = 11.950$ (2) Å, and $\rho = 0.941$ g cm^{-3} calculated for four molecules per unit cell. The high reactivity precluded an experimental density determination. Intensity data were collected by the θ–2θ scan method at a scan rate of 2°/min and with a scan range from $K\alpha_1$ −1.0° to $K\alpha_2$ +1.0°. Standard deviations were assigned to each reflection according to: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.04I)^2]^{1/2}$ where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, and K = ratio of scan time to background time (2.0). Extinction and absorption corrections were not applied.

In the 0–45° 2θ shell there was a slow decrease in the three standards, with a maximum decrease of 9%, which was corrected by application of decay factors. In the 45–50° 2θ shell, the standards dropped by more than 50%; this shell was thus discarded. Of the 1423 independent reflections with $2\theta < 45°$, 642 had $I > 2.5\sigma(I)$ and were used in the solution and refinement of the structure.

Solution and Refinement. The structure was solved by direct methods with the program MULTAN.[8] Phasing was carried out upon 104 E's normalized according to parity groups with magnitudes greater than 1.3. The solution with the highest overall figure of merit was used to calculate an E-map in which six of the eight independent non-hydrogen atoms were found. A subsequent Fourier synthesis established the remaining non-hydrogen positions.[9] Full-matrix anisotropic least-squares refinement on F yielded discrepancy factors of $R_1 = \Sigma||F_o| - |F_c||/|F_o| = 0.155$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.186$. Hydrogen atom positions were assigned 1.0 Å from the carbon atoms in expected geometry and were verified from a different Fourier synthesis.[10] Least-squares refinement of non-hydrogen atomic parameters with fixed contributions from the hydrogen atoms with isotropic thermal parameters set 10% higher than those of the atoms to which they are attached yielded final values of $R_1 = 0.047$, $R_2 = 0.054$, error of fit of 1.671, and a residual electron density in the final difference synthesis of 0.15 e/Å^3.

Atomic coordinates are given in Table I and bond distances and angles in Table II. A listing of calculated and observed structure factors (× 10) is available as supplementary material.[11]

Results and Discussion

Figures 1, 2, and 3 show the molecular labeling with key values, the stereoscopic molecular view of $Mg(SiMe_3)_2 \cdot DME$, and the packing of the molecules, respectively. The structure consists of discrete molecules of crystallographic symmetry 2. The magnesium resides on a twofold axis and is tetrahedrally coordinated to two oxygen atoms and two silicon atoms. The magnesium-silicon distance of 2.63 Å is somewhat longer than the sum of the covalent radii (2.41 Å); this lengthening is comparable to that observed for Mg-C distances ($\Sigma r_i = 2.07$ Å) in a variety of organomagnesium complexes[12] including the somewhat analogous $MgMe_2 \cdot (NC_7H_{13})_2$ complexes[13] in which the observed Mg-C distance is 2.24 Å. The Si-Mg-Si angle of 125° is greater than the tetrahedral value of 109.4°. This results from the steric repulsion of the bulky trimethylsilyl groups and the necessarily small O-Mg-O angle which is re-

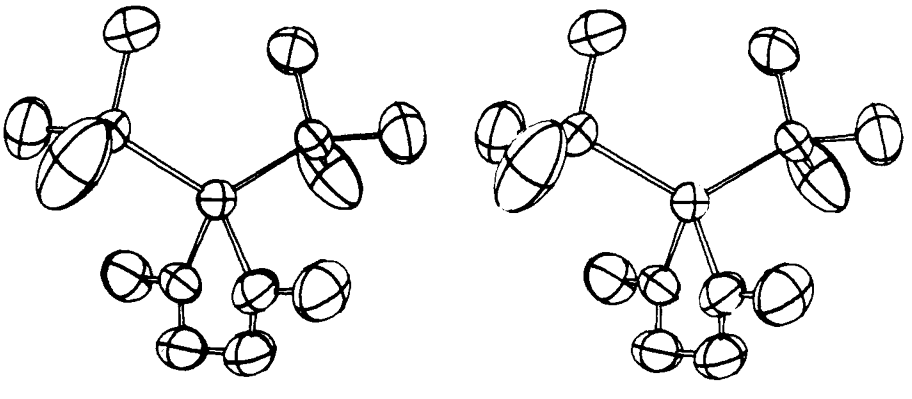


Figure 2. A stereoscopic view of the $Mg(SiMe_3)_2 \cdot DME$ molecule. The atoms are represented by 50% probability thermal ellipsoids with hydrogens deleted for sake of clarity.

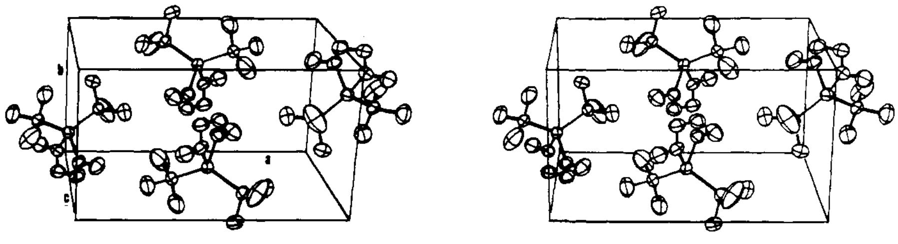


Figure 3. A stereoscopic view of the unit cell of $Mg(SiMe_3)_2 \cdot DME$.

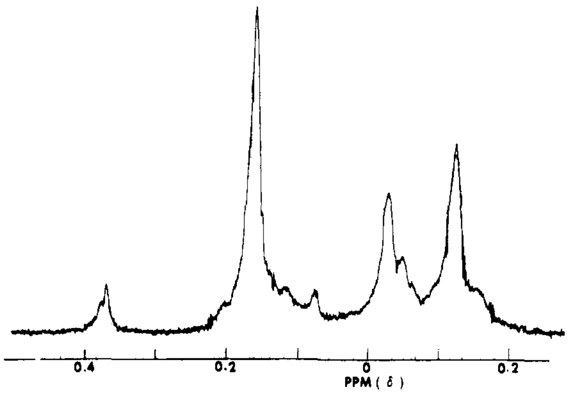


Figure 4. The 60-MHz NMR spectrum of a 1.5/1 mixture of Mg-$(SiMe_3)_2$·DME and $Hg(SiMe_3)_2$ (DME solvent, −50 °C).

quired by the "bite-size" of the DME ligand and the Mg–O distances.[14] The dihedral angle between the planes described by O–Mg–O and the Si–Mg–Si moieties is 89.7°, emphasizing the tendency of the magnesium ion to attain tetrahedral symmetry. The chelate ring adopts a nonplanar skew conformation in order to achieve tetrahedral carbon and oxygen atoms with minimum intramolecular repulsions.

The Si–C distances are essentially equal with an average value of 1.879 Å. This distance is comparable with that of 1.87 (3) reported for $Si(Ph)_4$[15] and of 1.90 (I) reported for the complex $Li_2Hg(SiMe_3)_4$.[16] The C–Si–C angles (102.9° av) are smaller than the tetrahedral value of 109.4°.

The DME moiety appears relatively unstrained. The C–O distances average 1.422 Å and the C–C distance is 1.492, somewhat shorter than expected for sp^3-carbons. The torsion angles of 174.5° for C(6)-C(7)-C(8)-C(8′) and 53.1° for C(7)-C(8)-C(8′)-C(7′) are within 7° of the strain-free values.

The NMR spectrum observed at room temperature for $Mg(SiMe_3)_2$·DME in DME solvent has a single line at δ −0.09 ppm (−5.4 Hz). When the crystalline adduct was dissolved in cyclopentane the upfield methyl resonance shifted to δ −0.03 ppm (2 Hz) and two lines associated with the DME appeared at δ 3.59 and 3.77 ppm. Integration of these signals and the line associated with the $SiMe_3$ group corresponds to formation of the 1:1 adducts as shown by the chemical analysis.

The $Mg(SiMe_3)_2$ derivative obtained in THF solution gives a line associated with the $SiMe_3$ group at δ −0.07 ppm (−4.1 Hz). When the solid material first obtained on removal of the THF under vacuum was dissolved in cyclopentane, the $SiMe_3$ resonance was at δ +0.01 ppm (0.4 Hz). The integrated area of this line vs. the THF multiplet (δ 1.99, 3.92 ppm) indicated formation of the 1:2 complex, $Mg(SiMe_3)_2$·2THF.

This does not correspond to the analysis reported and is indicative of the ease with which the THF molecule may be lost. Thus, on dissolution in cyclopentane followed by its removal under vacuum, it appears that the following loss of solvent occurs:

$$Mg(SiMe_3)_2\cdot 2THF \rightarrow Mg(SiMe_3)_2\cdot THF + THF \quad (1)$$

The new mono THF adduct does not have a sufficient number of groups to satisfy the typical four coordination about the Mg atom without some form of bridge formation. This could either be accomplished via an electron deficient silicon bridge bond as shown in I or via use of the THF molecule to occupy two coordination sites as indicated in II. There is *precedent* for I in the beryllium systems with formation of electron deficient bridged dimers and occupation of the fourth site by a Lewis base.[17]

Table III. Dihedral Angles for $Mg(SiMe_3)_2$·DME

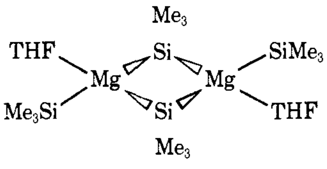
Atoms defining plane 1	Atoms defining plane 2	Angle between plane 1 & 2 (deg)
O(7)-C(8)-C(8′)	C(8)-C(8′)-O(7′)	53.1
C(6)-O(7)-C(8)	O(7)-C(8)-C(8′)	174.5
C(6)-O(7)-Mg(2)	O(7)-Mg(2)-Si(1)	47.7
C(6)-O(7)-Mg(2)	O(7)-Mg(2)-Si(1′)	−96.8
O(7)-Mg(2)-Si(1)	Mg(2)-Si(1)-C(3)	86.4
O(7)-Mg(2)-Si(1)	Mg(2)-Si(1)-C(5)	−153.9
O(7)-Mg(2)-Si(1)	Mg(2)-Si(1)-C(4)	−36.5
C(5)-Si(1)-Mg(2)	Si(1)-Mg(2)-Si(1′)	102.0
C(4)-Si(1)-Mg(2)	Si(1)-Mg(2)-Si(1′)	−135.1
C(3)-Si(1)-Mg(2)	Si(1)-Mg(2)-Si(1′)	155.6
O(7)-Mg(2)-Si(1)	Si(1)-Mg(2)-Si(1′)	138.5
O(7)-O(7′)-Mg(2)	O(7′)-Mg(2)-Si(1)	107.6
C(8)-O(7)-Mg(2)	O(7)-Mg(2)-O(7′)	15.3

[a] These torsion angles are based on a right-handed Klyne-Prelog convention.

Table IV. Equations of Planes,[a] $AX + BY + CZ - D = 0$

Plane	A	B	C	D
Si(1)-Mg(2)-Si(1′)	−0.501	0.0	−0.866	−2.59
O(7)-Mg(2)-O(7′)	0.864	0.0	−0.504	−1.507
O(7)-C(8)-C(8′)	0.476	−0.447	−0.758	−2.472
C(6)-O(7)-C(8)	0.558	0.420	−0.716	−2.266
C(6)-O(7)-Mg(2)	0.623	−0.255	−0.740	−2.828
O(7)-Mg(2)-Si(1)	−0.112	−0.588	−0.801	−3.817
C(3)-Si(1)-Mg(2)	−0.636	0.627	−0.450	0.175
C(4)-Si(1)-Mg(2)	0.285	−0.868	−0.406	−3.314
C(5)-Si(1)-Mg(2)	−0.377	−0.236	−0.896	−3.246

[a] The equations of mean planes are based upon an orthonormal unit set in which X, Y, Z are displacements in angstroms along the directions a, b, and c, respectively.



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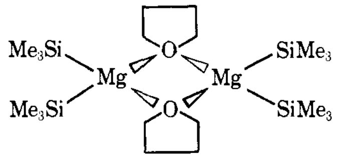

II

Limited variable temperature NMR studies on both the reaction mixture and on mixtures made by addition of $Hg(SiMe_3)_2$ to $Mg(SiMe_3)_2$·DME in DME solution give rise to temperature dependent NMR spectra. At room temperature all mixtures show a single line 1–3 Hz wide with variable position dependent upon composition of the mixture. At approximately −50 °C this line disappears and several new lines are observed indicating that at room temperature all species are exchanging trimethylsilyl groups while at low temperature several species are present which do not undergo exchange on the NMR time scale.

These results are consistent with formation of magnesium silylmercurates similar in character to those reported for the silyllithium-silylmercury system.[18] This conclusion is further supported by examination of the low temperature NMR spectrum shown in Figure 4 in which ^{199}Hg satellites may be seen for the lines at δ −0.13 (−7.5 Hz) and δ 0.03 (1.7 Hz).

The initial interpretation of these results based on a comparison with the corresponding silyllithium–silylmercury systems is that the line at δ −0.03 ppm with $J_{^{199}\mathrm{Hg}-^{1}\mathrm{H}} = 16$ Hz arises from an anion of the form $\mathrm{Hg(SiMe_3)_4}^{2-}$ and that centered at δ 0.13 with $J_{^{199}\mathrm{Hg}-^{1}\mathrm{H}} = 25.6$ Hz is associated with an anion of the form $\mathrm{Hg(SiMe_3)_3}^{-}$. These results are in good agreement with those found for $\mathrm{LiHg(SiMe_3)_3}$, $J_{\mathrm{Hg-H}} = 18$ Hz, and for $\mathrm{Li_2Hg(SiMe_3)_4}$, $J_{\mathrm{Hg-H}} = 26$ Hz. These suggested structures are unconfirmed as yet by other techniques, but the observed ^{199}Hg–^{1}H coupling clearly shows that the species present must contain Hg–Si bonds with relatively long lifetimes which permit the coupling to be observed.

Further work is now in progress to elucidate the structures of these species both in solution and in the solid state and to examine the possibility of formation of electron deficient silyl-bridged magnesium derivatives.

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Supplementary Material Available: Observed and calculated structure amplitudes (×10) (4 pages). Ordering information is given on any current masthead page.

References and Notes

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(10) Ideal positions for the hydrogens were calculated with HFINDR program (Zalkin, 1974) as modified by T. J. Anderson and were in reasonable agreement with positions observed on a three-dimensional Fourier difference synthesis.

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Highly Reduced Organometallic Anions. 1. Syntheses and Properties of Tetracarbonylmetalate(3−) Anions of Manganese and Rhenium

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Abstract: Reductions of $\mathrm{M(CO)_5}^{-}$ and $\mathrm{M_2(CO)_{10}}$ (M = Mn and Re) in hexamethylphosphoramide with sodium metal provide high yields of the "super-reduced" species $\mathrm{M(CO)_4}^{3-}$, which contain manganese and rhenium in their lowest known oxidation states. Infrared and chemical evidence is presented to corroborate proposed formulations for these salts. Their reactions with electrophilic species including $\mathrm{Ph_3ECl}$ (E = Ge, Sn, Pb), $\mathrm{Me_3ECl}$ (E = Ge, Sn), $\mathrm{Ph_3PAuCl}$, and benzyl chloride, provide a unique route to new organometallic derivatives of stoichiometry $\mathrm{(R_3E)_2M(CO)_4}^{-}$, $\mathrm{(Ph_3PAu)_3M(CO)_4}$, and $\mathrm{(C_6H_5CH_2CO)_2Mn(CO)_4}^{-}$. Physical properties of the anionic derivatives are discussed and compared to those of analogous neutral compounds of iron, ruthenium, and osmium.

One of the most exciting recent developments in organometallic chemistry is the recognition that many low-valent organotransition metal fragments mimic to a surprising degree the chemical properties of electronically equivalent groups containing only nonmetallic elements.[1,2] Undoubtedly, the most celebrated work on such mimicry has involved carbene complexes of the type $\mathrm{(OC)_5MC(OR)R'}$ (M = Cr, Mo, and W), which Fischer and co-workers have shown to have reactivity patterns very similar to those of organic esters.[3] In these cases the $\mathrm{M(CO)_5}$ unit is electronically equivalent to the doubly bonded oxygen in an ester. More recently, Lukehart prepared a series of metalloacetylacetonates in which a 15-electron transition metal fragment plays the role of a five-electron carbyne function.[4] Also, our research group has shown that metallodithiocarboxylate anions, which contain a 17-electron transition metal group, resemble organometallic analogues of dithiocarbamates, an extraordinarily versatile and important class of ligands.[5] Most certainly, other novel metalloanalogues of familiar organic and other nonmetallic compounds will be reported in the near future. However, undoubtedly the greatest impact of this new area of organometallic chemistry will be in the selective modification of chemical and physical properties of polymers, catalysts, and reagents by the replacement of familiar nonmetallic functional groups with their transition metal equivalents.

An extremely important, direct, and general method for introducing 17- and 16-electron organometal functionalities into inorganic and organic substrates is by the nucleophilic substitution of carbonyl mono- and dianions for halides, as shown by the following equations: