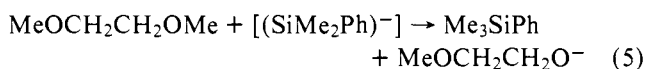
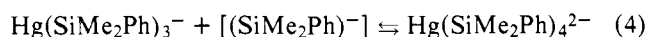
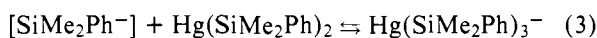
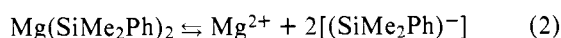
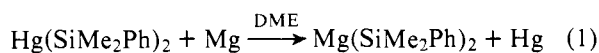


Metal-Silicon Bonded Compounds. 13.
Synthesis, ^1H and ^{13}C NMR Spectra, and Structure of
 $[\text{Mg}_4(\text{OCH}_2\text{CH}_2\text{OCH}_3)_6(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]\text{-}$
 $\{\text{Hg}[\text{Si}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_3\}_2$

Sir:

At this time we report the synthesis, ^1H and ^{13}C NMR spectra, and structure of a novel new compound, bis(1,2-dimethoxyethane)- μ -hexakis(2-methoxyethanolato)tetra-magnesium(II) tris(dimethylphenylsilyl)mercurate(II). The unusual features of this derivative are the formation of the complex cation and the first simple three-coordinate, sp^2 -hybridized mercury atom for which the structure has been proven. This unusual compound is prepared by the direct reaction of $\text{Hg}(\text{SiMe}_2\text{Ph})_2$ with magnesium metal in DME solvent. The reaction proceeds through a number of steps such as those indicated in eq 1–5 which are similar to those reported for the preparation of other silyl metal derivatives.^{1–3}



The progress of the reaction could be followed visually by the gradual change from the bright yellow of the starting mercury compound to red orange (2 days) to deep red; within 2 weeks a brick red compound precipitated. Deep red crystals were obtained from the DME solution as solvent was removed. Anal. Calcd/found: C, 45.80/45.93; H, 6.65/6.90; Mg, 5.01/4.66; Hg, 20.67/20.54; Si, 8.68/8.85; O, 13.19/13.12 (by difference).⁴

Single crystals of this material, obtained as indicated above, were mounted in thin-walled capillaries under an argon atmosphere and data were collected using a Syntex P21 diffractometer with Mo $\text{K}\alpha$ (0.71069 Å) radiation. These crystals were found to be in the monoclinic space group $P2_1/n$, $a = 16.287$ (3) Å, $b = 24.158$ (5) Å, $c = 12.159$ (3) Å, and $\beta = 101.58$ (2)° with two formula units per unit cell. Conventional heavy-atom techniques led to the structure of this compound.⁵ Full-matrix least-squares refinement of 3682 data with $I > 2.5\sigma(I)$ yielded discrepancy factors of $\sum |F_o| - |F_c| / \sum |F_o| = 0.074$ and $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.097$.

The formula unit was found to consist of three discrete ionic groups, the $[\text{Mg}_4(\text{OME})_6(\text{DME})_2]^{+2}$ (DME = $\text{MeOCH}_2\text{CH}_2\text{OMe}$; OME = $(\text{MeOCH}_2\text{CH}_2\text{O})^-$) cation associated with two of the $[\text{Hg}(\text{SiMe}_2\text{Ph})_3]^-$ anions. The cation is shown in Figure 1 and consists of four six-coordinate magnesium atoms tightly bound by two types of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}^-$ bridging units. One of these consists of two pairs of symmetry related three-coordinate oxygen atoms in $\text{Mg}-\text{O}-\text{Mg}$ bridges with an average $\text{Mg}-\text{O}$ distance of 1.985 (2) Å, and the second consists of two four-coordinate oxygen atoms in symmetry related Mg_3O bridges with an average $\text{Mg}-\text{O}$ distance of 2.10 (2) Å. The remaining sites about the magnesium atoms are occupied by coordination with the two oxygen atoms on DME and/or with the methoxy group of the OME moiety. The distortion from octahedral symmetry about the magnesium atoms is clearly shown by the range from 72 to 105° for the $\text{O}-\text{Mg}-\text{O}$ angles. This also is shown by the range in $\text{Mg}-\text{O}$ distances which vary from 1.985 (2) to 2.237 (2) Å. The distances for the coordinated oxygen atoms range between 2.176 (2) and 2.237 (2) Å and are similar to those observed previously for DME coordinated magnesium; however, the range for these

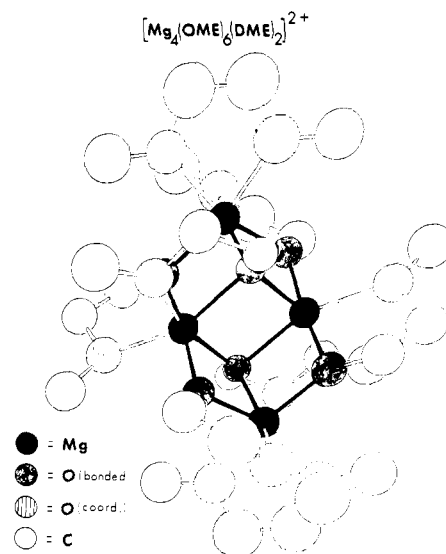


Figure 1. A diagram of the $\text{Mg}_4(\text{OME})_6(\text{DME})_2$ cation.

indicates that the bonds are much weaker than the bridging oxygen bonds and probably differ substantially in strength from one another. Similar oxygen bridging has been observed for $\text{Ti}(\text{OR})_4$,⁶ while the metal atom arrangement has been observed in several additional species including $[\text{EtMg}_2\text{Cl}_3(\text{THF})_3]_2$,⁷ $\{\text{Cd}[\text{SC}(\text{Me})_2\text{CH}_2\text{NH}_2]_2 \cdot \text{CdCl}_2\} \cdot 2\text{H}_2\text{O}$,⁸ and in $\{\text{Zn}[\text{CH}_2\text{NH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{S}]_2 \cdot \text{ZnCl}_2\} \cdot 2\text{H}_2\text{O}$.⁹ The magnesium derivative $[\text{MeMgN}(\text{CH}_3)(\text{CH}_2)\text{-N}(\text{CH}_3)_2]_2$ ¹⁰ crystallizes as a dimer with four-coordinate magnesium atoms rather than giving rise to the more complex structure observed in this system.

Before consideration of the structure of the mercurate ion, we should note that three-coordinate mercury has often been suggested.¹¹ Solid-state structural studies, however, indicate that these structures are not symmetric and usually can be described equally well in terms of distorted two- or five-coordinate systems. Further, in the system which appears to fulfill the structural requirements best, (2,2'-bipyridyl)methylmercury(II) nitrate, the observed value for the $^{199}\text{Hg}-^1\text{H}$ coupling constant is slightly greater than that observed in the starting MeHgNO_3 .¹² This implies that the orbitals used for the formation of the $\text{Hg}-\text{C}$ bond in the complex are not significantly altered from the sp -hybrid orbitals of the starting material and are certainly not sp^2 in nature.

In the present case the anion $[\text{Hg}(\text{SiMe}_3)_3]^-$ shows trigonal, planar symmetry around the mercury atom with average $\text{Si}-\text{Hg}-\text{Si}$ angles of 119.8° and average $\text{Si}-\text{Hg}$ bond distances of 2.516 Å. The bond distance lies between the values obtained for linear and tetrahedral silylmercury derivatives and is consistent with three coordination.^{13,14} This ion represents the first symmetric, three-coordinate mercury ion observed in the solid state and confirms the sp^2 hybridization of the mercury atom previously proposed on the basis of changes in the $^{199}\text{Hg}-^1\text{H}$ coupling constants for the two-, three-, and four-coordinate trimethylsilylmercury derivatives.^{1,2}

Several properties of the materials in solution are indicated by examination of both the ^1H and the ^{13}C NMR spectra shown in Figures 2 and 3. The cation is stable to complete dissociation in pyridine solvent as demonstrated by the ^{13}C spectrum which shows 11 different ^{13}C resonances for the carbon atoms associated with the OME⁻ and DME moieties. These can only arise if the framework of the cation remains intact in solution. The proton spectra of the OME-DME region show temperature-dependent line broadening which indicates that the $\text{O}-\text{Mg}$ coordinate bonds formed by the $-\text{O}-\text{CH}_3$ groups have lifetimes on the order of 0.1–0.001 s. This fact, coupled with the stability of the complex as indicated from

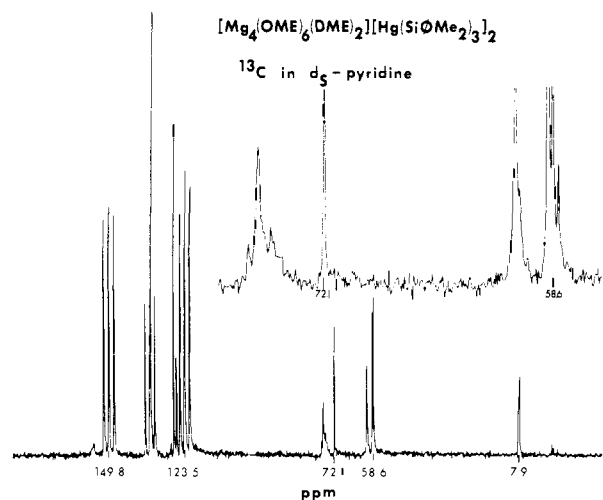


Figure 2. The ^{13}C NMR spectrum of a pyridine- d_5 solution of $[\text{Mg}_4(\text{OME})_6(\text{DME})_2][\text{Hg}(\text{SiPhMe}_2)_3]_2$. The insert shows an expansion of the OME-DME region.

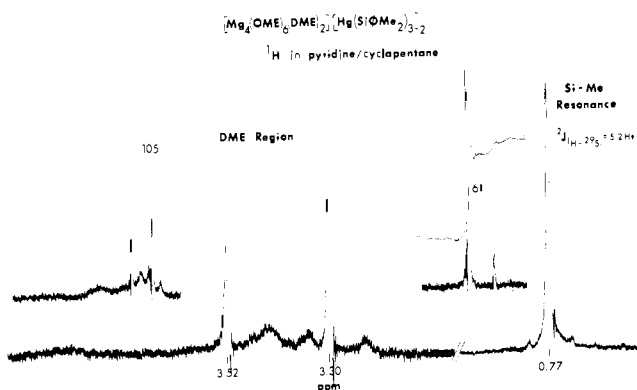


Figure 3. The ^1H NMR spectrum of a 80% pyridine- d_5 -20% cyclopentane solution of $[\text{Mg}_4(\text{OME})_6(\text{DME})_2][\text{Hg}(\text{SiPhMe}_2)_3]_2$ taken at 35°C . The lines at 3.52 and 3.30 ppm correspond to the methylene and methyl groups of DME, respectively. The broad lines are associated with the OME groups. The inserts show the integrated areas of the OME-DME region and the SiMe_2 region.

the ^{13}C NMR spectra, suggests significant differences in the Mg-O bond stabilities, a feature also suggested from differences between bridging and coordinated Mg-O bond distances.

Examination of the ^1H NMR resonance of the methyl group on the anion down to -100°C shows no ^{199}Hg - ^1H coupling which implies that rapid Si-Hg bond breaking and exchange occurs. In the related trimethylsilyl derivatives the ^1H - ^{199}Hg coupling constants have been observed between -40 and -70°C and fall into the range of 18-40 Hz with variation a function of the coordination number of the mercury atom and of the hybridization of the mercury orbitals.^{1,2}

In conclusion we can state that the reaction of Mg metal with $\text{Hg}(\text{SiMe}_2\text{Ph})_2$ gives rise to cleavage of a methyl group from 1,2-dimethoxyethane yielding an unanticipated complex cation with Mg^{2+} . This cation yields a crystalline product with the previously proposed planar, three-coordinate mercurate $\text{Hg}(\text{SiMe}_2\text{Ph})_3^-$. Additional work is now in progress to elucidate the details of these reactions, the stability of the unusual cation, the reactivity of the silylmercurate anions, and the structure of this derivative and a second crystalline modification of this species obtained under slightly different conditions.

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Synthesis, Characterization, and Structure of Diaminoborane

Sir:

Apparently none of the aminoboranes $\text{BH}_x(\text{NH}_2)_{3-x}$ has been previously isolated as a stable molecular species at ordinary temperatures. Aminoborane, BH_2NH_2 , is well known in the form of polymers and oligomers, but is unstable as a monomer under ordinary conditions.¹⁻³ A material having a composition corresponding to triaminoborane, $\text{B}(\text{NH}_2)_3$, can be prepared at low temperatures, but when isolated at ordinary temperatures it loses ammonia to form $\text{B}_2(\text{NH}_3)_3$.^{4,5} The only previous claims for the preparation of diaminoborane, $\text{BH}(\text{NH}_2)_2$, were mere postulates to account for the evolution of excess hydrogen in the reaction of alkali metals with the diammoniate of diborane in liquid ammonia.⁶⁻⁸ However, in these liquid ammonia studies, no attempts were made to isolate or to analyze directly the postulated diaminoborane.

We report here the first preparation and preliminary chemical and structural characterization of $\text{BH}(\text{NH}_2)_2$. Diaminoborane was synthesized by passing a stream of ammonia through molten borane ammine at 125°C in a coiled-tube reaction vessel designed to minimize foam:

