

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.

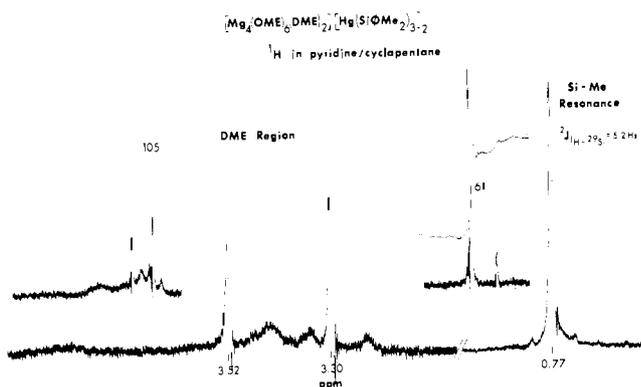


Figure 3. The ^1H NMR spectrum of a 80% pyridine- d_5 -20% cyclopentane solution of $[\text{Mg}_4(\text{OME})_6(\text{DME})_2][\text{Hg}(\text{SiPhMe}_2)_3]_2$ taken at 35°C . The lines at 3.52 and 3.30 ppm correspond to the methylene and methyl groups of DME, respectively. The broad lines are associated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



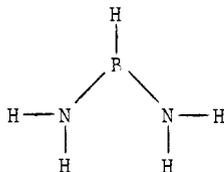
Table I. Rotational Constants for Four Isotopic Species of Diaminoborane

	$^{10}\text{B}(\text{NH}_2)_2$	$^{11}\text{B}(\text{NH}_2)_2$	$^{10}\text{B}(\text{ND}_2)_2$	$^{11}\text{B}(\text{ND}_2)_2$
<i>A</i> , MHz	53752.6 ± 0.42 ^a	52382.9 ± 0.47	33035.1 ± 1.2	32507.6 ± 2.7
<i>B</i> , MHz	9092.31 ± 0.074	9093.23 ± 0.085	7424.7 ± 0.37	7424.8 ± 0.87
<i>C</i> , MHz	7777.42 ± 0.052	7748.59 ± 0.060	6064.4 ± 0.37	6045.9 ± 1.2
κ	-0.942800	-0.939749	-0.89913	-0.89578
Δ , amu Å ²	-0.0047 ± 0.001	-0.0032 ± 0.001		

^a Error limits are one standard deviation.

The product and excess ammonia were collected in a -196 °C trap. The product was then separated from ammonia by fractional condensation in a -104 °C trap. Yields were 10–17%. Anal. Calcd for BN_2H_5 : B, 24.65; N, 63.86; H, 11.49. Found: B, 24.15; N, 60.66; H, 11.60. In the liquid state, diaminoborane decomposes to form a glassy solid with the evolution of ammonia. Hence properties such as the melting point and the vapor pressure of the liquid have not been determined. However, as a vapor the compound can be kept for several days at room temperature with negligible formation of ammonia, and solutions in liquid ammonia appear to be indefinitely stable even at room temperature. No significant mass spectral peaks with $m/e > 44$ (corresponding to $^{11}\text{B}(\text{NH}_2)_2$) were observed for $\text{BH}(\text{NH}_2)_2$ or mixtures of $\text{BH}(\text{NH}_2)_2$ and NH_3 .

The ^{11}B NMR spectrum of $\text{BH}(\text{NH}_2)_2$ in either liquid ammonia or tetrahydrofuran is a 126-Hz doublet, consistent with the structure shown. When either borazine or the glassy



solid from the decomposition of $\text{BH}(\text{NH}_2)_2$ is dissolved in liquid ammonia, the ultimate products are $\text{BH}(\text{NH}_2)_2$ and a small amount of NH_3BH_3 and $\text{B}(\text{NH}_2)_3$. ^{11}B NMR spectra show that several intermediates are involved in these reactions. The chemical shifts in liquid ammonia of $\text{BH}(\text{NH}_2)_2$ and $\text{B}(\text{NH}_2)_3$ are 28.0 and 26.7 ppm downfield of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, respectively.

The infrared spectrum of gaseous diaminoborane has not been completely assigned, but several features are clearly evident. There are four strong N–H stretching bands (two at 3556 cm^{-1} and two at 3464 cm^{-1}) and a strong BH stretch at 2517 cm^{-1} . A preliminary normal coordinate analysis shows the B–N stretching to be highly mixed with the motions of other internal coordinates. Consequently, it is not obvious which of the strong bands at 1605 or 1393 cm^{-1} corresponds to the often cited⁹ asymmetric B–N stretch.

A total of 33 rotational transitions in the 8–42-GHz region have been assigned for four different isotopic species of diaminoborane. The spectra are consistent with a slightly asymmetric top having a permanent dipole parallel to the *B* principal axis. Determination of the line centers is complicated by the splitting due to the nuclear electric quadrupole coupling of the boron and the two nitrogens.

Table I lists the rotational constants based on a least-squares fit of the transition frequencies. Because of a limited supply of the two perdeuterio species, their rotational constants have not yet been as well determined as those of the normal species. The small negative inertial defect Δ strongly suggests a planar C_{2v} structure for diaminoborane. Using the 12 rotational constants, and assuming a planar structure, a least-squares procedure was used to determine the following bond lengths and angles:¹⁰ $r_{\text{BH}} = 1.190 \pm 0.02$, $r_{\text{BN}} = 1.419 \pm 0.002$, $r_{\text{NH cis}} = 1.028 \pm 0.01$, $r_{\text{NH trans}} = 0.983 \pm 0.01$ Å; $\angle\text{NBN} = 121.95$

± 0.1, $\angle\text{BNH (cis)} = 117.5 \pm 2.0$, and $\angle\text{BNH (trans)} = 125.0 \pm 2.0^\circ$. There are large error limits for the two BNH angles because they are highly correlated. The rotational constants of unsymmetrically deuterated species are being determined since they substantially reduce this correlation and the other error limits. The 1.42-Å BN bond length is between the single-bond length of 1.54 Å and double-bond length of 1.36 Å. This indicates substantial π bond character in the NBN framework. The other bond lengths are typical.

From Stark splitting data, the dipole moment is found to be 1.25 ± 0.01 D (OCS taken as 0.71521) and is coaxial with the B–H bond. The sign of the dipole moment has not been determined.

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Stable Dimethyl, Methyl, and Unsubstituted Vinylidene Complexes

Sir:

Vinylidene ($>\text{C}=\text{CH}_2$), the valence tautomer of acetylene, occupies an important position among monohapto carbon ligands in transition metal chemistry.^{1–5} Some chemical transformations which relate these monohapto ligands are shown in Scheme I. This scheme also emphasizes similarities in the electrophilicity of the α position and the nucleophilicity of the β position in the isoelectronic series: terminal metal carbonyl, acetylide, and vinylidene.⁶ The electrophilicity of a vinylidene complex depends markedly^{2,5} on the auxiliary ligands, the metal, and the total charge on the complex.

We recently reported⁵ on the reactivity of the iron acetylides Ia and Ib toward electrophiles. Whereas protonation of Ib