4942 *Inorg. Chem.* **2010**, *49*, 4942–4948
DOI: 10.1021/ic1000667

Inorganic Chemistry
Article

Highly Volatile Magnesium Complexes with the Aminodiboranate Anion, a New Chelating Borohydride. Synthesis and Characterization of $Mg(H_3BNMe_2BH_3)_2$ and Related Compounds

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Received January 11, 2010

Remarkably volatile magnesium complexes have been prepared with the modified borohydride ligand *N*,*N*-dimethylaminodiboranate, $H_3BNMe_2BH_3^-$. The homoleptic complex $Mg(H_3BNMe_2BH_3)_2$, its monoadducts with tetrahydrofuran and 1,2-dimethoxyethane, and the mixed ligand complex $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$ have been prepared. The homoleptic complex $Mg(H_3BNMe_2BH_3)_2$ has a vapor pressure of 800 mTorr at 25 °C, which makes it the most volatile magnesium complex known. Crystal structures and NMR data are reported for all complexes. The compounds are potentially useful as chemical vapor deposition precursors to MgB_2 and MgO, and as hydrogen storage materials.

Introduction

The discovery in 2001 of superconductivity in magnesium diboride (MgB_2) below 39 K[1] has initiated extensive research into this material. In addition to possessing the highest superconducting transition temperature of all intermetallic superconductors, MgB_2 can be doped to give phases with critical fields as high as 36 T,[2−4] which make this material a potential replacement for the niobium-based phases currently used in superconducting circuits. Thin films of MgB_2 are of particular interest for the fabrication of Josephson junctions, but a major obstacle is that this phase decomposes with loss of magnesium above 425 °C.[5] Overcoming this problem requires either growing the film below 400 °C or using very high Mg partial pressures. MgB_2 films have been prepared by coevaporation of Mg and B at ∼300 °C,[6] by boron deposition and subsequent ex situ annealing under a high Mg pressure in a sealed tube at 900 °C,[7] and by reaction of B_2H_6 at 750 °C with Mg vapor that is generated near the substrate.[8] These methods, however, have not yet proven suitable for the in situ growth of crystalline MgB_2 required for the large scale fabrication of multilayer tunneling junctions.

It is known that high-quality thin films of several metal diboride phases can be grown by chemical vapor deposition (CVD) from transition metal hydroborates such as $Ti(BH_4)_3(dme)$,[9] $Zr(BH_4)_4$,[10] $Hf(BH_4)_4$,[11] and $Cr(B_3H_8)_2$.[12,13] We have recently reported the synthesis and characterization of the new magnesium compound $Mg(B_3H_8)_2$ and derivatives thereof, and our initial studies of their use as CVD precursors to MgB_2 thin films.[14] Significantly, $Mg(B_3H_8)_2$ and its etherates are the only reasonably volatile magnesium hydroborate complexes known; other Mg compounds reported to

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date that contain tetrahydroborate (BH_4^-),[15–28] octahydrotriborate ($B_3H_8^-$),[16,29,30] or nonahydrohexaborate ($B_6H_9^-$)[31] groups are poorly volatile at best.

In addition to their potential use as CVD precursors to metal diborides, metal complexes of borohydride ligands can also be used to deposit films of metal oxides, simply by conducting the depositions in the presence of water vapor.[32] Finally, borohydride complexes of magnesium are being discussed as possible hydrogen storage materials.[28]

We now report the synthesis of a new class of remarkably volatile magnesium complexes of the *N*,*N*-dimethylaminodiboranate ligand $H_3BNMe_2BH_3^-$. Specifically, we describe the preparation and characterization of $Mg(H_3BNMe_2BH_3)_2$, its adducts with ethers, and the mixed ligand complex $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$. The homoleptic complex $Mg(H_3BNMe_2BH_3)_2$ has a vapor pressure of 800 mTorr at 25 °C, which makes it the most volatile magnesium complex known.

Results and Discussion

Synthesis and Characterization of $Mg(H_3BNMe_2BH_3)_2$. The solid state reaction of $MgBr_2$ and sodium *N*,*N*-dimethylaminodiboranate, $Na(H_3BNMe_2BH_3)$, at room temperature followed by sublimation at temperatures as low as 20 °C under a static vacuum affords a colorless crystalline product, $Mg(H_3BNMe_2BH_3)_2$, **1**, in good yield. This synthetic method, which involves grinding or milling of the solid starting materials, avoids the use of solvents such as ethers that can coordinate to the magnesium center. This air- and moisture-sensitive magnesium complex sublimes even at room temperature and has an unusually high vapor pressure of 800 mTorr at 25 °C. It is thermally stable up to 120 °C.

$$MgBr_2 + 2Na(H_3BNMe_2BH_3) \rightarrow Mg(H_3BNMe_2BH_3)_2 + 2NaBr \quad (1)$$

The infrared spectrum of **1** features a strong band at 2449 cm^{-1} due to terminal B−H stretches, and a strong, broad band centered at 2195 cm^{-1} due to bridging B−H stretches. These B−H stretching bands are similar to those observed in the IR spectra of other complexes of the aminodiboranate ligand.[33]

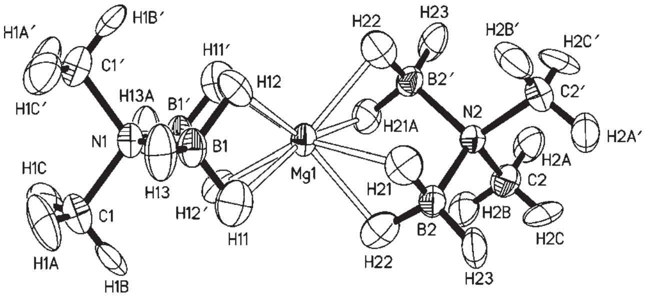

Figure 1. Molecular structure of $Mg(H_3BNMe_2BH_3)_2$, **1**. Ellipsoids are drawn at the 30% probability level. The X-ray data set was of sufficiently high quality that the hydrogen atoms could be refined anisotropically without constraints.

The ^1H NMR spectrum of **1** at 20 °C shows two signals, a singlet at δ 2.04 for the NMe_2 groups and a broad 1:1:1:1 quartet at δ 1.91 for the BH_3 groups (^{11}B has $I = {}^3/_2$). The J_{BH} coupling constant of 90 Hz is nearly identical to the 91 and 92 Hz values observed for the tetrahydrofuran (thf) and 15-crown-5 solvates of $Na(H_3BNMe_2BH_3)$,[34] respectively, and slightly larger than the 74−83 Hz range found in magnesium tetrahydroborates[18,21] At −80 °C, the quartet becomes a broad unresolved signal because of the more rapid spin−lattice relaxation of the ^{11}B and ^{10}B nuclei at a lower temperature, as seen in many transition metal tetrahydroborates.[35,36] Exchange of terminal B−H hydrogen atoms with those that bridge to the metal center (see structure below) is evidently fast on the NMR time scale even at −80 °C.

Crystal Structure of $Mg(H_3BNMe_2BH_3)_2$. The molecular structure of **1** is presented in Figure 1; crystallographic data and selected bond distances and angles are listed in Tables 1 and 2. The molecule lies on a 2-fold axis that passes through the Mg and N atoms. The magnesium center is coordinated to two chelating $H_3BNMe_2BH_3^-$ ligands, which are similar but crystallographically inequivalent. The planes of the two ligands (as defined by the B−N−B backbones) are related by a dihedral angle of 46.7(1)°. If each BH_3 unit is considered to occupy one coordination site, the overall geometry about the magnesium center is nearly exactly halfway between square planar (dihedral angle of 0°) and tetrahedral (dihedral angle of 90°). A similar dihedral angle of 46.5(2)° has been found for the high-spin d^5 manganese analogue $Mn(H_3BNMe_2BH_3)_2$.[33]

Two hydrogen atoms from each BH_3 group bridge to the magnesium center to form a total of eight Mg−H contacts; the Mg−H bond lengths are essentially identical and average 2.02(3) Å. The average B−H distance of 1.14(3) Å within the Mg−H−B bridges is slightly longer than the average terminal B−H distance of 1.05(2) Å, as expected. The dihedral angle between the two Mg(μ-H)$_2$ planes at each end of an aminodiboranate ligand is 93.8°, whereas the average B−Mg−B angle within an aminodiboranate ligand is 66.0(6)°. The Mg···B distances are

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Table 1. Crystallographic Data for $Mg(H_3BNMe_2BH_3)_2$ (**1**), $Mg(H_3BNMe_2BH_3)_2(thf)$ (**2**), $Mg(H_3BNMe_2BH_3)_2(dme)$ (**3**), and $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$ (**4**)

	1	**2**	**3**	**4**
formula	$C_4H_{24}B_4N_2Mg$	$C_8H_{32}B_4N_2OMg$	$C_8H_{34}B_4N_2O_2Mg$	$C_{16}H_{35}B_2NOMg$
formula weight	167.80	239.91	257.92	303.38
T, °C	−80	−80	−80	−80
space group	$I\bar{4}2d$	Cc	$C2/c$	$P2_1/n$
a, Å	11.3649(19)	10.0103(8)	22.5822(17)	11.309(3)
b, Å	11.3649(19)	17.5686(15)	13.6560(10)	14.569(3)
c, Å	19.183(7)	10.5611(8)	14.700(2)	12.255(3)
β, deg	90	111.412(5)	125.324(3)	90.397(4)
V, Å^3	2477.6(10)	1729.2(2)	3698.6(7)	2019.1(8)
Z	8	4	8	4
ρ_{calcd}, g cm^{-3}	0.900	0.922	0.926	0.998
λ, Å	0.71073	0.71073	0.71073	0.71073
μ_{calcd}, cm^{-1}	0.94	0.87	0.88	0.86
transmissn coeff	0.963−0.979	0.982−0.994	0.970−0.989	0.985−0.997
unique reflns	1542	2576	3840	3827
parameters	161	197	268	222
$R_1{}^a$	0.0297	0.0455	0.0349	0.0679
$wR_2{}^b$	0.0688	0.1196	0.0883	0.1393

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $F_o{}^2 > 2\,\sigma(F_o{}^2)$. ^{b} $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$ for all reflections.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Mg(H_3BNMe_2BH_3)_2$ (**1**)^a

Bond Lengths (Å)			
Mg(1)−H(11)	1.990(15)	B(1)−H(11)	1.126(15)
Mg(1)−H(12)	2.021(11)	B(1)−H(12)	1.151(13)
Mg(1)−H(21)	2.058(16)	B(1)−H(13)	1.033(16)
Mg(1)−H(22)	1.998(15)	B(2)−H(21)	1.110(16)
Mg(1)−B(1)	2.3690(14)	B(2)−H(22)	1.166(18)
Mg(1)−B(2)	2.3859(13)	B(2)−H(23)	1.072(12)
Bond Angles (deg)			
H(11)−Mg(1)−H(12)	54.1(6)	H(21)−Mg(1)−H(22)	53.6(6)
H(11)−Mg(1)−H(21)	86.2(6)	B(1)−Mg(1)−B(1)′	66.55(6)
H(11)−Mg(1)−H(22)	91.8(7)	B(1)−Mg(1)−B(2)	119.96(5)
H(12)−Mg(1)−H(21)	92.6(5)	B(1)−Mg(1)−B(2)′	155.05(6)
H(12)−Mg(1)−H(22)	135.6(6)	B(2)−Mg(1)−B(2)′	65.53(6)

^{a} Symmetry transformations used to generate equivalent atoms: ′ = $x, -y + 1/2, -z + 1/4$.

almost equal at 2.369(1) and 2.386(1) Å, and the B−N distances are identical within experimental error at 1.585(1) and 1.581(1) Å. The geometry about the nitrogen atoms is nearly a perfect tetrahedron: the B−N−B, B−N−C, and C−N−C angles of 108.5(1)−110.2(1)° are all within about 1° of the ideal value 109.5°.

Remarkably, the quality of the X-ray data set was sufficiently high that the hydrogen atoms could be refined anisotropically without constraints. The dispositions of the hydrogen atoms explain why the planes of the two ligand backbones are related by the unusual dihedral angle of 46.5°. Each aminodiboranate ligand forms four Mg−H bonds arranged at the corners of a nearly square rectangle, so that the Mg atom has a coordination number of eight and a coordination geometry best described as a distorted square antiprism. The d^0 nature of the Mg center means that steric factors (and not electronic factors) will dictate the coordination geometry, and the square antiprism is one of several geometries that minimizes steric repulsions among the ligands for eight coordinate complexes. Because the two square faces of a square antiprism are rotated with respect to one another by 45°, this same angle must be formed by the two aminodiboranate backbones.

The Mg−H and Mg···B distances in $Mg(H_3BNMe_2BH_3)_2$ are best compared with those of magnesium complexes containing bidentate $BH_4{}^-$ ligands, which are electronically and structurally similar. The Mg−H distance of 2.02(3) Å in **1** falls in the 1.97−2.09 Å range observed in magnesium complexes containing bidentate BH_4 groups.[17−21,23] In contrast, the Mg···B distances of 2.369(1) and 2.386(1) Å in **1** are shorter than those of 2.40−2.54 Å seen for magnesium complexes of bidentate BH_4 ligands.[17−19,21] This shorter Mg···B distance of **1** is a consequence of the chelating nature of the aminodiboranate ligand, which causes the $Mg(\mu\text{-}H)_2B$ units to be non-planar, that is, folded about the H···H axis. In contrast, in Mg-BH_4 complexes the $Mg(\mu\text{-}H)_2B$ units are planar, thus maximizing the Mg···B distance.

Volatility of $Mg(H_3BNMe_2BH_3)_2$. The 800 mTorr vapor pressure of **1** at 25 °C is remarkably high for a magnesium compound, which in part reflects its low molecular weight. It can be sublimed in vacuum at reasonable rates even at room temperature. This volatility makes **1** an attractive CVD precursor for magnesium-containing phases, as we will describe elsewhere. In comparison, all other magnesium compounds have lower volatilities. The widely used CVD source dicyclopentadienylmagnesium (Cp_2Mg) has a vapor pressure of ∼45 mTorr at 25 °C.[37] The magnesium amidinate complexes bis(*N,N′*-di-*tert*-butylacetamidinato)magnesium and bis(*N,N′*-diisopropylacetamidinato)magnesium sublime readily only when heated under vacuum to 70 °C; although they have been reported to be more volatile than Cp_2Mg on the basis of their sublimation temperatures in the same evaporation apparatus, the vapor pressures have not been reported.[38] Magnesium 2,2,6,6-tetramethyl-3,5-heptanedionate (thd), which is a dimer, $Mg_2(thd)_4$,[39] has been

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used as a CVD or atomic layer deposition (ALD) precursor for MgO thin films.[39−42] This compound evaporates at reasonable rates only above 250 °C, as determined by thermogravimetric analyses under a helium flow.[39,43] Monomeric Mg(thd)$_2$L$_x$ complexes can be made with a variety of Lewis bases, but their volatilities are only slightly higher than that of Mg$_2$(thd)$_4$.[44,45] Magnesium complexes of the fluorinated β-diketonate ligand, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (hfa), especially those carrying ancillary diamine ligands, are more volatile than Mg$_2$(thd)$_4$ and its related complexes; however, even the most volatile of the hfa complexes, Mg(hfa)$_2$(Et$_2$NCH$_2$CH$_2$NEt$_2$), evaporates readily only at ~100 °C under 5 Torr of nitrogen.[46] Finally, the heteroleptic β-diketiminato magnesium complex (cyclopentadienyl)(*N,N′*-di-*tert*-butyl-2,4-pentanediketiminato)magnesium is nearly as volatile as Cp$_2$Mg, and the binary β-diketiminato magnesium complexes bis(*N,N′*-di-*tert*-butyl-2,4-pentanediketiminato)magnesium and bis(*N,N′*-diisopropyl-2,4-pentanediketiminato) magnesium sublime at 104 and 160 °C, respectively, at 0.05 Torr.[47]

Synthesis and Characterization of Mg(H$_3$BNMe$_2$BH$_3$)$_2$(thf) and Mg(H$_3$BNMe$_2$BH$_3$)$_2$(dme). Treatment of MgBr$_2$ with Na(H$_3$BNMe$_2$BH$_3$) in thf, followed by sublimation at 70 °C, affords white crystals of the thf adduct Mg(H$_3$BNMe$_2$BH$_3$)$_2$(thf), **2**. Carrying out this reaction in 1,2-dimethoxyethane affords the related compound Mg(H$_3$BNMe$_2$BH$_3$)$_2$(dme), **3**.

$$\mathrm{MgBr_2 + 2Na(H_3BNMe_2BH_3) + L}$$
$$\rightarrow \mathrm{Mg(H_3BNMe_2BH_3)_2(L) + 2NaBr}$$
$$\mathrm{L = thf}\quad(\mathbf{2})$$
$$\mathrm{L = dme}\quad(\mathbf{3})$$

The infrared spectrum of **2** contains three strong bands in the B−H stretch region: a strong terminal B−H stretch at 2391 cm^{-1}, and two strong bridging B−H stretches at 2300 and 2241 cm^{-1}. Very similar bands are seen for **3**. Relative to the features seen for unsolvated **1**, the terminal B−H stretch appears at a lower frequency (and thus largely overlaps with the bridging B−H stretches), whereas the bridging B−H stretches appear at higher frequencies. These differences suggest that the Mg-aminodiboranate interaction is weaker in the ether adducts, a conclusion that is consistent with the longer Mg−H and Mg···B bonds seen in their crystal structures (see below). The ^{1}H NMR spectrum of **2** at 20 °C shows a broad quartet at δ 1.99 for the BH$_3$ groups, and a similar feature at δ 2.11 is seen for **3**.

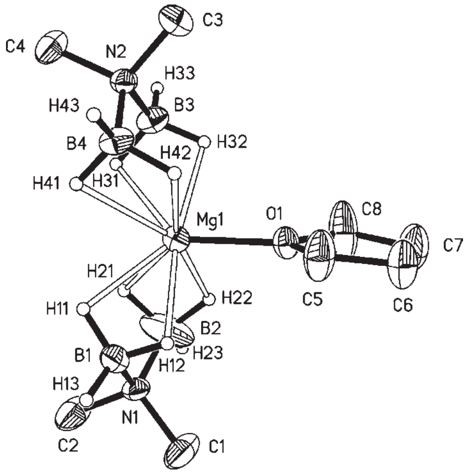

Figure 2. Molecular structure of Mg(H$_3$BNMe$_2$BH$_3$)$_2$(thf), **2**. Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres. Methyl and methylene hydrogen atoms have been deleted for clarity.

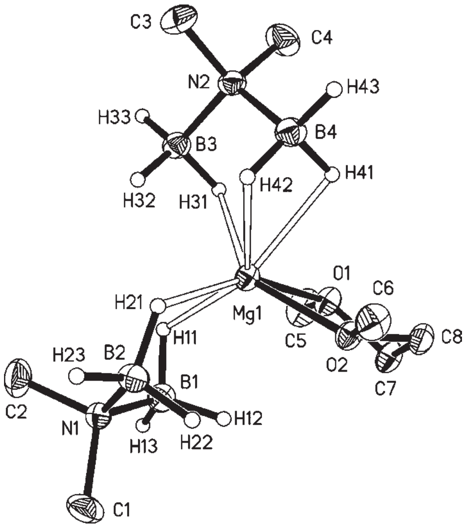

Figure 3. Molecular structure of Mg(H$_3$BNMe$_2$BH$_3$)$_2$(dme), **3**. Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres. Methyl and methylene hydrogen atoms have been deleted for clarity.

Crystal Structures of Mg(H$_3$BNMe$_2$BH$_3$)$_2$(thf) and Mg(H$_3$BNMe$_2$BH$_3$)$_2$(dme). The molecular structures of **2** and **3** are presented in Figures 2 and 3; crystallographic data and selected bond distances and angles are listed in Tables 1, 3, and 4. For the thf adduct **2**, the magnesium center adopts a distorted square pyramidal geometry in which four BH$_3$ groups from two chelating aminodiboranate ligands occupy basal positions and the thf molecule occupies the apical site. Each BH$_3$ group of the aminodiboranate ligand coordinates to the magnesium center in a bidentate mode like that seen in **1**, but the Mg−H distances of 2.13(10) Å are longer by about 0.1 Å than those in **1**. Similarly, the Mg···B distances of 2.484(4)−2.553(5) Å are 0.1−0.15 Å longer than those in **1**. These longer Mg−H and Mg···B distances, which suggest a weaker Mg-aminodiboranate interaction, reflect the higher degree of steric crowding in **2** induced by the presence of the

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Mg(H_3BNMe_2BH_3)_2(thf)$ (**2**)

Bond Lengths (Å)			
Mg(1)−H(11)	2.14(3)	B(1)−H(11)	1.09(3)
Mg(1)−H(12)	2.10(3)	B(1)−H(12)	1.11(3)
Mg(1)−H(21)	2.29(6)	B(1)−H(13)	1.12(3)
Mg(1)−H(22)	1.98(4)	B(2)−H(21)	1.14(3)
Mg(1)−H(31)	2.20(3)	B(2)−H(22)	1.08(3)
Mg(1)−H(32)	2.11(3)	B(2)−H(23)	1.15(3)
Mg(1)−H(41)	2.28(3)	B(3)−H(31)	1.12(2)
Mg(1)−H(42)	1.94(3)	B(3)−H(32)	1.06(3)
Mg(1)−B(1)	2.487(4)	B(3)−H(33)	1.06(3)
Mg(1)−B(2)	2.553(5)	B(4)−H(41)	1.13(2)
Mg(1)−B(3)	2.484(4)	B(4)−H(42)	1.16(3)
Mg(1)−B(4)	2.503(4)	B(4)−H(43)	1.07(3)
Mg(1)−O(1)	2.063(2)		
Bond Angles (deg)			
H(11)−Mg(1)−H(12)	49.7(11)	H(22)−Mg(1)−H(32)	97.0(13)
H(11)−Mg(1)−H(21)	58.5(16)	H(22)−Mg(1)−H(41)	147.5(10)
H(11)−Mg(1)−H(22)	89.6(12)	H(22)−Mg(1)−H(42)	162.2(12)
H(11)−Mg(1)−H(31)	92.3(11)	H(31)−Mg(1)−H(32)	48.1(10)
H(11)−Mg(1)−H(32)	140.4(10)	H(31)−Mg(1)−H(41)	64.3(11)
H(11)−Mg(1)−H(41)	65.3(11)	H(31)−Mg(1)−H(42)	92.7(12)
H(11)−Mg(1)−H(42)	103.8(12)	H(32)−Mg(1)−H(41)	90.9(11)
H(12)−Mg(1)−H(21)	86.0(15)	H(32)−Mg(1)−H(42)	80.2(13)
H(12)−Mg(1)−H(22)	81.0(14)	H(41)−Mg(1)−H(42)	50.3(11)
H(12)−Mg(1)−H(31)	141.9(10)	B(1)−Mg(1)−B(2)	59.91(16)
H(12)−Mg(1)−H(32)	169.9(11)	B(1)−Mg(1)−B(4)	106.80(13)
H(12)−Mg(1)−H(41)	96.1(11)	B(3)−Mg(1)−B(1)	141.87(15)
H(12)−Mg(1)−H(42)	98.6(13)	B(3)−Mg(1)−B(2)	111.21(19)
H(21)−Mg(1)−H(22)	46.0(13)	B(3)−Mg(1)−B(4)	61.62(12)
H(21)−Mg(1)−H(31)	68.2(13)	B(4)−Mg(1)−B(2)	151.0(2)
H(21)−Mg(1)−H(32)	99.8(16)	O(1)−Mg(1)−B(1)	110.65(12)
H(21)−Mg(1)−H(41)	101.6(13)	O(1)−Mg(1)−B(2)	103.2(2)
H(21)−Mg(1)−H(42)	151.7(13)	O(1)−Mg(1)−B(3)	107.48(13)
H(22)−Mg(1)−H(31)	98.4(13)	O(1)−Mg(1)−B(4)	105.79(12)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Mg(H_3BNMe_2BH_3)_2(dme)$ (**3**)

Bond Lengths (Å)			
Mg(1)−H(11)	1.984(13)	B(1)−H(11)	1.164(13)
Mg(1)−H(21)	2.010(13)	B(1)−H(12)	1.130(13)
Mg(1)−H(31)	2.119(13)	B(1)−H(13)	1.091(15)
Mg(1)−H(32)	2.395(13)	B(2)−H(21)	1.187(13)
Mg(1)−H(41)	2.157(14)	B(2)−H(22)	1.137(13)
Mg(1)−H(42)	2.199(13)	B(2)−H(23)	1.147(14)
Mg(1)−B(1)	2.6077(18)	B(3)−H(31)	1.162(14)
Mg(1)−B(2)	2.8680(19)	B(3)−H(32)	1.127(13)
Mg(1)−B(3)	2.6333(18)	B(3)−H(33)	1.112(14)
Mg(1)−B(4)	2.5621(18)	B(4)−H(41)	1.154(12)
Mg(1)−O(1)	2.1118(10)	B(4)−H(42)	1.177(14)
Mg(1)−O(2)	2.0865(9)	B(4)−H(43)	1.114(14)
Bond Angles (deg)			
H(11)−Mg(1)−H(21)	78.0(5)	B(1)−Mg(1)−B(2)	56.11(5)
H(11)−Mg(1)−H(31)	77.7(5)	B(1)−Mg(1)−B(3)	107.59(6)
H(11)−Mg(1)−H(32)	75.0(5)	B(3)−Mg(1)−B(2)	111.14(6)
H(11)−Mg(1)−H(41)	148.9(5)	B(4)−Mg(1)−B(1)	161.98(6)
H(11)−Mg(1)−H(42)	134.2(5)	B(4)−Mg(1)−B(2)	114.43(6)
H(21)−Mg(1)−H(31)	117.6(5)	B(4)−Mg(1)−B(3)	59.36(5)
H(21)−Mg(1)−H(32)	70.2(5)	O(1)−Mg(1)−B(1)	88.65(5)
H(21)−Mg(1)−H(41)	120.9(5)	O(1)−Mg(1)−B(2)	136.33(5)
H(21)−Mg(1)−H(42)	69.9(6)	O(1)−Mg(1)−B(3)	103.16(5)
H(31)−Mg(1)−H(32)	48.2(5)	O(1)−Mg(1)−B(4)	105.91(5)
H(31)−Mg(1)−H(41)	71.6(5)	O(2)−Mg(1)−B(1)	103.57(5)
H(31)−Mg(1)−H(42)	89.1(5)	O(2)−Mg(1)−B(2)	86.22(5)
H(32)−Mg(1)−H(41)	88.0(5)	O(2)−Mg(1)−B(3)	148.83(5)
H(32)−Mg(1)−H(42)	64.1(5)	O(2)−Mg(1)−B(4)	90.19(5)
H(41)−Mg(1)−H(42)	51.4(5)	O(2)−Mg(1)−O(1)	77.38(4)

additional thf ligand. In **2**, the B−H distances to the bridging hydrogen atoms of 1.11(2) Å and those to the terminal hydrogen atoms of 1.10(2) Å are essentially identical. The average B−Mg−B angle of 60.7° is some 6° smaller than that in **1** owing to the longer Mg···B distances in **2**.

The magnesium center in the dme adduct **3** adopts a distorted octahedral geometry in which two aminodiboranate groups and one dme group act as chelating ligands. Unlike **1** and **2**, in which eight hydrogen atoms form close contacts with the Mg atom, in **3** only five hydrogen atoms (H11, H21, H31, H41, and H42) form short Mg−H−B bridges, which range from 1.98(1) to 2.20(1) Å. The next shortest Mg−H contacts of 2.43(1) and 2.39(1) Å are formed to H12 and H32, respectively; all the other Mg−H distances are greater than 3 Å. The Mg···B distances of 2.608(2)−2.868(2) Å are also considerably longer than those in **2** by ~0.2 Å. The large Mg−H and Mg···B distances are consistent with the higher degree of steric congestion caused by the bidentate dme ligand. Boron atom B(2) is clearly bound in a κ^1H fashion to the Mg center; the other three boron atoms bind an a fashion that is either κ^2H or distorted κ^2H. The long M···B distances in **3** cause the B−Mg−B angles of 56.11(5) and 59.36(5)° within each aminodiboranate ligand to be smaller than those in **1** and **2.**

Synthesis and Characterization of $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$. Treatment of the magnesium pentamethylcyclopentadienyl complex $[(C_5Me_5)MgCl(thf)]_2$ with 1 equiv of $Na(H_3BNMe_2BH_3)$ in diethyl ether affords the aminodiboranate complex $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$, **4**, which can be obtained as white crystals by sublimation at 60 °C and 0.05 Torr.

$$^{1}/_{2}[(C_5Me_5)MgCl(thf)]_2 + Na(H_3BNMe_2BH_3) \rightarrow (C_5Me_5)Mg(H_3BNMe_2BH_3)(thf) + NaCl \quad (4)$$

The B−H stretching modes in the IR spectrum of **4** closely resemble those seen for **2** and **3**: there is a strong terminal B−H stretching band at 2393 cm^{-1} and three strong bridging B−H stretching bands at 2297, 2241, and 2185 cm^{-1}. The ^1H NMR spectrum of **4** at 20 °C contains a broad singlet at δ 2.21 for the BH_3 groups, a singlet at δ 2.14 for the C_5Me_5 ring, a singlet at δ 1.94 for the NMe_2 groups, and characteristic resonances for the thf protons. Interestingly, on the basis of the solid state structure (see below) there should be two NMe_2 environments: one methyl group should be proximal to the C_5Me_5 group and the other should be distal. Evidently, an exchange process renders these two groups equivalent; there is also only one signal for the NMe_2 group in the ^{13}C NMR spectrum.

Crystal Structure of $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$. The molecular structure of **4** is shown in Figure 4; crystallographic data and selected bond distances and angles are listed in Tables 1 and 5. The magnesium center is coordinated to one η^5-C_5Me_5 ligand, one chelating $H_3BNMe_2BH_3^-$ ligand, and one thf molecule. All the BH_3 groups are bound to the magnesium center by means of two bridging hydrogen atoms. Three of the Mg−H distances are equal, averaging 2.22(8) Å, and one may be slightly longer at 2.30(4) Å. The Mg···B distances are

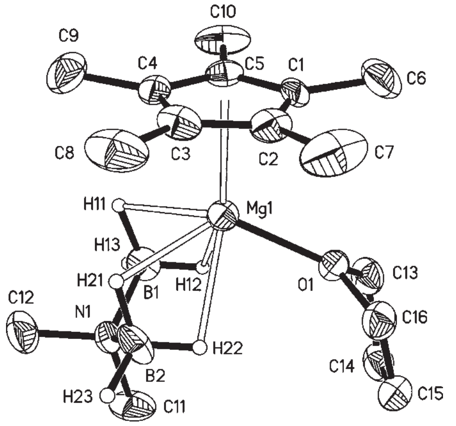

Figure 4. Molecular structure of $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$, **4**. Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres. Methyl and methylene hydrogen atoms have been deleted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$ (**4**)

	Bond Lengths (Å)		
Mg(1)−H(11)	2.30(4)	Mg(1)−C(4)	2.393(5)
Mg(1)−H(12)	2.18(4)	Mg(1)−C(5)	2.360(5)
Mg(1)−H(21)	2.17(4)	Mg(1)−O(1)	2.055(3)
Mg(1)−H(22)	2.21(4)	B(1)−H(11)	1.22(4)
Mg(1)−B(1)	2.534(7)	B(1)−H(12)	1.05(3)
Mg(1)−B(2)	2.554(8)	B(1)−H(13)	1.15(3)
Mg(1)−C(1)	2.374(5)	B(2)−H(21)	1.18(4)
Mg(1)−C(2)	2.386(5)	B(2)−H(22)	1.05(4)
Mg(1)−C(3)	2.414(6)	B(2)−H(23)	1.07(4)
	Bond Angles (deg)		
H(11)−Mg(1)−H(12)	49.8(13)	H(21)−Mg(1)−H(22)	48.1(14)
H(11)−Mg(1)−H(21)	69.6(14)	B(1)−Mg(1)−B(2)	60.6(2)
H(11)−Mg(1)−H(22)	91.8(14)	O(1)−Mg(1)−B(1)	103.9(2)
H(12)−Mg(1)−H(21)	90.1(15)	O(1)−Mg(1)−B(2)	101.0(2)
H(12)−Mg(1)−H(22)	72.4(13)		

nearly identical at 2.534(7) and 2.554(8) Å. Although of marginal significance statistically, the refined B−H distances to the hydrogens that are proximal to the C_5Me_5 ring (1.22(4) and 1.18(4) Å) are slightly longer than those to hydrogens that are distal (1.15(3) and 1.15(4) Å). The terminal B−H distances are 1.15(3) and 1.07(4) Å. The Mg−C distances fall in a narrow range 2.360(5)−2.414(6) Å; the average Mg−C distance of 2.38(1) Å is similar to that of 2.38(2) Å seen in $[(C_5Me_5)MgCl(thf)]_2$[48] but shorter than that of 2.44(3) Å seen in CpMg(η^2-t-BuC(NMes)$_2$)(thf), where Mes = 2,4,6- $C_6H_2Me_3$.[49]

Concluding Remarks

We have demonstrated that the *N*,*N*-dimethylaminodiboranate ligand affords highly volatile magnesium complexes that sublime at temperatures as low as 20 °C in vacuum, and in fact the homoleptic complex **1** has the highest volatility of all known magnesium complexes. This high volatility arises from the large steric angle formed by four Mg−H−B interactions per ligand, which leads to the formation of low-molecular-weight monomeric complexes. In addition, the volatility is probably enhanced by the negative charges on the B−H hydrogen atoms, which generate intermolecular electrostatic repulsion forces that partially counterbalance the attractive London forces. We have also demonstrated that aminodiboranate ligands can be combined with other ligands such as ethers and cyclopentadienyl rings to form heteroleptic complexes. This finding suggests that the molecular properties of aminodiboranate complexes, such as thermal decomposition pathways and volatilities, should be controllable synthetically. Studies of the CVD of magnesium-containing thin films from these precursors are underway.

Experimental Section

All experiments were carried out under vacuum or under argon by using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium/benzophenone immediately before use. The starting materials $Na(H_3BNMe_2BH_3)$[34] and $(C_5Me_5)MgCl(thf)$[50] were prepared by literature procedures. $MgBr_2$ was used as received from Aldrich. Microanalyses were performed by the University of Illinois Microanalytical Laboratory, by using combustion and ICP-MS analyses (the latter for magnesium and boron). The IR spectra were recorded on a Nicolet Impact 410 instrument as Nujol mulls between KBr plates. The ^1H and ^{13}C NMR data were collected on a Varian Gemini 500 instrument at 499.699 and 125.663 MHz, respectively. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to tetramethylsilane (^1H NMR) or $BF_3\cdot Et_2O$ (^{11}B NMR). Field ionization (FI) mass spectra were recorded on a Micromass 70-VSE mass spectrometer. The shapes of all peak envelops correspond with those calculated from the natural abundance isotopic distributions. Melting points and decomposition temperatures were determined in closed capillaries under argon on a Thomas-Hoover Unimelt apparatus. Vapor pressures were measured by placing samples in a closed vessel equipped with a MKS 627B absolute capacitance manometer. The pressure increase as a function of time was plotted, and the vapor pressure determined from the y-axis intercept obtained by extrapolating the linear portion of the curve at longer times back to $t = 0$.

Bis(*N*,*N*-dimethylaminodiboranato)magnesium, $Mg(H_3BNMe_2BH_3)_2$, 1. Solid $MgBr_2$ (1.94 g, 10.5 mmol) and $Na(H_3BNMe_2BH_3)$ (2.0 g, 21.0 mmol) were ground together briefly in a mortar and pestle. The dry solid mixture was transferred to a 100 mL round-bottom Schlenk flask, and 30−40 steel balls (4.5-mm diameter) were added. The flask was gently agitated for 30 min. Sublimation at 70 °C under static vacuum afforded white crystals (under a dynamic vacuum, substantial amount of the product can be lost). Yield: 1.13 g (64%). Vapor pressure at 25 °C: 0.8 ± 0.1 Torr. Mp: 70 °C. Anal. Calcd for $C_4H_{24}N_2B_4Mg$: C, 28.6; H, 14.4; N, 16.6; B, 25.8; Mg, 14.5. Found: C, 28.6; H, 15.1; N, 16.6, B, 25.7; Mg, 14.1. ^1H NMR (C_7D_8, 20 °C): δ 2.04 (s, 12H, NMe$_2$), 1.91 (q, J_{BH} = 90.0 Hz, 12H, BH$_3$). $^{13}C\{^1H\}$ NMR (C_7D_8, 20 °C): δ 50.98 (s, NMe$_2$). $^{11}B\{^1H\}$ NMR (C_7D_8, 20 °C): δ −12.85 (s). MS(FI) [fragment ion, relative abundance]: m/z 167 $[(Mg(H_3BNMe_2BH_3)_2\text{-}H)^+$, 100], 263 $[(Mg_2(H_3BNMe_2BH_3)_3\text{-}H)^+$, 45]. IR (cm^{-1}): 2449 s, 2355 w, 2294 w, 2195 s, 2149 m, 2078 w, 1312 s, 1239 m, 1219 m, 1178 s, 1142 s, 1022 s, 927 m, 904 m, 810 m, 521 s, 421 s.

Bis(*N*,*N*-dimethylaminodiboranato)(tetrahydrofuran)magnesium, $Mg(H_3BNMe_2BH_3)_2(thf)$, 2. To a suspension of $MgBr_2$ (0.51 g, 2.8 mmol) in thf (20 mL) at room temperature was added a solution of $Na(H_3BNMe_2BH_3)$ (0.53 g, 5.6 mmol) in thf (30 mL). After the reaction mixture had been stirred for

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8 h at room temperature, the solvent was removed in vacuum. Sublimation at 70 °C and at 0.05 Torr afforded white crystals. Yield: 0.31 g (47%). Anal. Calcd for $C_8H_{32}N_2B_4OMg$: C, 40.1; H, 13.4; N, 11.7; B, 18.0; Mg, 10.1. Found: C, 39.5; H, 13.3; N, 11.3; B, 16.0; Mg,.10.5. ^{1}H NMR (C_7D_8, 20 °C): δ 3.57 (m, 4H, OCH_2), 2.33 (s, 12H, NMe_2), 1.99 (q, J_{BH} = 84.5 Hz, 12H, BH_3), 1.28 (m, 4H, $OCH_2\mathit{CH_2}$). $^{13}C\{^1H\}$ NMR (C_7D_8, 20 °C): δ 69.2 (s, OCH_2), 52.4 (s, NCH_3), 25.5 (s, $OCH_2\mathit{CH_2}$). $^{11}B\{^1H\}$ NMR (C_7D_8, 20 °C): δ −12.51 (s). IR (cm^{-1}): 2391 s, 2300 s, 2241 s, 2975 w, 1298 m, 1237 m, 1216 m, 1177 s, 1148 s, 1023 s, 929 m, 873 s, 816 m, 693 w.

Bis(*N*,*N*-dimethylaminodiboranato)(1,2-dimethoxyethane)magnesium, $Mg(H_3BNMe_2BH_3)_2(dme)$, 3. To a suspension of $MgBr_2$ (0.51 g, 2.8 mmol) in 1,2-dimethoxyethane (20 mL) at room temperature was added a solution of $Na(H_3BNMe_2BH_3)$ (0.53 g, 5.6 mmol) in 1,2-dimethoxyethane (30 mL). After the reaction mixture had been stirred for 8 h at room temperature, the solvent was removed in vacuum. Sublimation at 70 °C and at 0.05 Torr afforded white crystals. Yield: 0.27 g (37%). Anal. Calcd for $C_8H_{34}N_2B_4O_2Mg$: C, 37.3; H, 13.3; N, 10.9; B, 16.8; Mg, 9.42. Found: C, 36.4; H, 13.2; N, 10.4; B, 17.1; Mg, 9.92. ^{1}H NMR (C_6D_6, 20 °C): δ 3.00 (s, 6H, OMe), 2.81 (s, 4H, OCH_2), 2.48 (s, 12H, NMe_2), 2.11 (q, J_{BH} = 88.5 Hz, 12H, BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 69.6 (s, OCH_2), 59.6 (s, OCH_3), 52.6 (s, NMe_2). $^{11}B\{^1H\}$ NMR (C_6D_6, 20 °C): δ −12.14 (s). IR (cm^{-1}): 2411 w, 2357 s, 2290 s, 2230 s, 2066 w, 1299 w, 1276 w, 1236 w, 1212 w, 1176 s, 1148 s, 1094 m, 1054 s, 1018 s, 925 w, 871 m, 811 w.

(Pentamethylcyclopentadienyl)(*N*,*N*-dimethylaminodiboranato)(thf)magnesium(II), $(C_5Me_5)Mg(H_3BNMe_2BH_3)(thf)$, 4. To a suspension of $(C_5Me_5)MgCl\cdot thf$ (0.99 g, 3.7 mmol) in Et_2O (25 mL) at −78 °C was added a solution of $Na(H_3BNMe_2BH_3)$ (0.38 g, 4.0 mmol) in Et_2O (20 mL). The reaction mixture was stirred for 10 min, allowed to warm to room temperature, and stirred for 5 h to give a colorless solution and a white precipitate. The solution was filtered, and the filtrate was taken to dryness in vacuum. Sublimation at 60 °C and at 0.05 Torr in vacuum yielded white crystals. Yield: 0.68 g (63%). Anal. Calcd for $C_{16}H_{35}NB_4OMg$: C, 63.3; H, 11.6; N, 4.62; B, 7.13; Mg, 8.01. Found: C, 62.1; H, 11.7; N, 5.11; B, 9.20; Mg, 8.24. ^{1}H NMR (C_6D_6, 20 °C): δ 3.42 (m, 4H, OCH_2), 2.21 (br, 6H, BH_3), 2.14 (s, 15H, C_5Me_5), 1.94 (s, NMe_2), 1.17 (m, 4H, $OCH_2\mathit{CH_2}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 110.40 (s, $\mathit{C_5}Me_5$), 69.55 (s, OCH_2), 52.45 (s, NMe_2), 25.32 (s, $OCH_2\mathit{CH_2}$), 11.16 (s, $C_5\mathit{Me_5}$). $^{11}B\{^1H\}$ NMR (C_6D_6, 20 °C): δ −12.92 (s). IR (cm^{-1}): 2434 sh, 2393 s, 2297 s, 2241 s, 2185 s, 2077 m, 1342 w, 1311 w, 1294 w, 1277 w, 1238 w, 1213 w, 1176 s, 1146 s, 1024 s, 926 m, 910 m, 874 s, 806 m, 681 w.

X-ray Structure Determinations.(51) Single crystals of all four compounds, grown by sublimation, were mounted on glass fibers with Krytox oil (DuPont), and immediately cooled to −80 °C in a cold nitrogen gas stream on the diffractometer. Data for **1**−**4** were collected with an area detector by using the measurement parameters listed in Table 1. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, and Lorentz and polarization effects. Systematically absent reflections were deleted and symmetry-equivalent reflections were averaged to yield the sets of unique data. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. All structures were solved using direct methods (SHELXTL). The correct positions for all non-hydrogen atoms of **1**−**4** were deduced from E-maps. Final refinement parameters for **1**−**4** are given in Table 1. A final analysis of variance between observed and calculated structure factors showed no apparent errors. Full details of the refinements of **1**−**4** are reported in the Supporting Information.

Acknowledgment. We thank the National Science Foundation for support of this research under grant numbers CHE07-50422 and DMR-0420768. We also thank Scott R. Wilson and Teresa Prussak-Wieckowska for collecting the X-ray crystallographic data.

Supporting Information Available: Details of the X-ray crystallographic refinements and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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