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Synthesis and Characterization of Calcium *N,N*-Dimethylaminodiboranates as Possible Chemical Vapor Deposition Precursors

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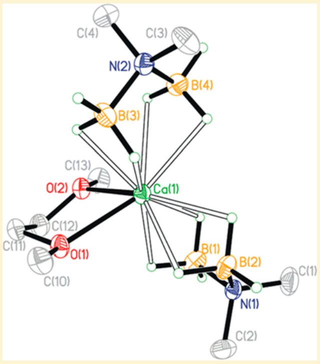
Ⓢ *Supporting Information*



ABSTRACT: The reaction of $CaBr_2$ with 2 equiv of sodium *N,N*-dimethylaminodiboranate, $Na(H_3BNMe_2BH_3)$ in Et_2O at 0 °C followed by crystallization and drying in vacuum yields the unsolvated calcium compound $Ca(H_3BNMe_2BH_3)_2$, **1**. Before the vacuum drying step, the colorless crystals obtained by crystallization consist of the diethyl ether adduct $Ca(H_3BNMe_2BH_3)_2(Et_2O)_2$, **2**. If the reaction of $CaBr_2$ with 2 equiv of $Na(H_3BNMe_2BH_3)$ is carried out in the more strongly coordinating solvent tetrahydrofuran (thf), the solvate $Ca(H_3BNMe_2BH_3)_2(thf)_2$, **3**, is obtained. This compound does not desolvate as easily in vacuum as the diethyl ether compound **2**. Treating the thf adduct **3** with 1,2-dimethoxyethane (dme), bis(2-methoxyethyl) ether (diglyme), or *N,N,N′,N′*-tetramethylethylenediamine (tmeda) in thf affords the new compounds $Ca(H_3BNMe_2BH_3)_2(dme)$, **4**, $Ca(H_3BNMe_2BH_3)_2(diglyme)$, **5**, and $Ca(H_3BNMe_2BH_3)_2(tmeda)$, **6**, respectively, in greater than 60% yields. Treatment of **3** with 2 equiv of the crown ether 12-crown-4 in thf affords the charge-separated salt $[Ca(12\text{-crown-}4)_2][H_3BNMe_2BH_3]_2$, **7**. Crystal structures of all the Lewis base adducts are described. Compounds **2**−**6** all possess chelating κ^2-$BH_3NMe_2BH_3$-κ^2 groups, in which two hydrogen atoms on each boron center are bound to calcium. Compound **7** is the only ionic compound in the series; the Ca atom is completely encapsulated by two 12-crown-4 rings, and the anions are charge-separated counterions within the unit cell. When heated, the dme, diglyme, and tmeda compounds **4**, **5**, and **6** melt without decomposition, and can be sublimed readily under reduced pressure (1 Torr) at 90 °C (**4**) and 120 °C (**5**, **6**). The dme adduct is one of the most volatile calcium compounds known, and is a promising CVD precursor for the growth of calcium-containing thin films.

■ INTRODUCTION

Volatile compounds of the alkaline earth metals are of interest as precursors for the chemical vapor deposition (CVD) of thin films of perovskites, superconductors, and other interesting materials.[1] For the element calcium, a number of coordination complexes are known that can be sublimed without decomposition; among these are the following (sublimation conditions given in parentheses): the cyclopentadienyl complex $Ca(C_5Me_5)_2$ (75 °C, 10^{-4} Torr);[2] the beta-diketiminate complex $Ca\{[Me_2N\text{-}NC(Me)]_2CH\}_2$ (90 °C, 0.05 Torr);[3] the beta-diketonate complexes $Ca\{[OC(CF_3)]_2CH\}_2$ (140 °C, 10^{-3} Torr),[4,5] $Ca\{[OC(C_3F_7)]_2CH\}_2(H_2O)$ (160 °C, 40 Torr),[6] $Ca[OC(CF_3)CHC(Me)O]_2$ (195 °C, 10^{-3} Torr),[4] and $Ca\{[OC(t\text{-}Bu)]_2CH\}_2L_x$;[7−10] and pyrazolylborate complexes such as $Ca[HB(pz)_3]_2$ (160 °C, 10^{-2} Torr).[11−14]

We have recently reported that the chelating borohydride ligand *N,N*-dimethylaminodiboranate, $H_3BNMe_2BH_3^-$, or DMADB, forms a variety of complexes with the alkaline earth metals Mg[15] and Ba.[16] The magnesium compound $Mg(H_3BNMe_2BH_3)_2$ is a monomer in the solid state and in fact is now the most volatile magnesium compound known, with a vapor pressure of 0.8 Torr at room temperature. In contrast, the barium compound $Ba(H_3BNMe_2BH_3)_2$ is polymeric, but mononuclear complexes can be obtained if the metal center is also ligated by certain Lewis bases such as bis(2-methoxyethyl) ether (diglyme). These trends are consistent with the change in ionic radii down the period (Mg^{2+}, 0.86 Å; Ca^{2+}, 1.14 Å; Sr^{2+}, 1.32 Å; Ba^{2+}, 1.49 Å).[17] The larger size of Ba vs Mg makes it more difficult to saturate the coordination sphere and avoid oligomerization or polymerization.

Here, we report the synthesis and characterization of a new class of calcium compounds bearing the *N,N*-dimethylaminodiboranate anion. Some of these compounds are sufficiently volatile to make them potentially useful as precursors for the deposition of calcium containing thin films.

■ RESULTS AND DISCUSSION

Synthesis of $Ca(H_3BNMe_2BH_3)_2$ and Its Adducts with Lewis Bases. The reaction of $CaBr_2$ with 2 equiv of sodium *N,N*-dimethylaminodiboranate, $Na(H_3BNMe_2BH_3)$, in Et_2O at 0 °C gives a white suspension that turns gray as the mixture is warmed to room temperature. Concentration and cooling of the mother liquor to −20 °C affords colorless crystals, which are isolated and dried in vacuum for 15 min at 20 °C. The

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Table 1. Crystallographic Data for the New Calcium Compounds 2−7 at 193 K

	2, L = Et_2O	**3**, L = thf	**4**, L = dme	**5**, L = diglyme	**6**, L = tmeda	**7**, L = 12-crown-4
formula	$C_{12}H_{44}B_4N_2O_2Ca$	$C_{12}H_{40}B_4N_2O_2Ca$	$C_8H_{34}B_4N_2O_2Ca$	$C_{10}H_{38}B_4N_2O_3Ca$	$C_{10}H_{40}B_4N_4Ca$	$C_{20}H_{56}B_4N_2O_8Ca$
FW (g mol^{-1})	331.81	327.78	273.69	317.74	299.77	535.99
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	193	193	193	193	193	193
crystal system	monoclinic	trigonal	triclinic	orthorhombic	monoclinic	monoclinic
space group	$C2$	$P3_221$	$P\bar{1}$	$Pnma$	$P2_1/n$	$P2_1/c$
a (Å)	19.880(2)	11.5087(2)	9.5866(10)	10.2617(15)	10.1637(6)	15.7631(10)
b (Å)	8.5182(10)	11.5087(2)	14.2788(14)	11.2800(16)	14.9076(9)	10.1952(6)
c (Å)	15.1491(16)	28.5959(13)	14.8732(16)	18.027(3)	13.7731(8)	23.2794(15)
α (deg)	90	90	89.536(7)	90	90	90
β (deg)	112.735(7)	90	76.043(7)	90	97.201(4)	104.528(3)
γ (deg)	90	120	77.185(7)	90	90	90
V ($Å^3$)	2366.1(5)	3280.1(2)	1924.4(3)	2086.6(5)	2070.4(2)	3621.6(4)
Z	4	6	4	4	4	4
ρ_{calc} (g cm^{-3})	0.931	0.996	0.945	1.011	0.962	1.115
μ (mm^{-1})	0.268	0.290	0.319	0.305	0.297	0.217
R(int)	0.1465	0.0503	0.1876	0.2875	0.1179	0.1510
abs corr method	face indexed	face indexed	face indexed	face indexed	face indexed	face indexed
max., min transm. factors	0.951/0.915	0.928/0.909	0.970/0.942	0.985/0.948	0.958/0.935	0.9537/0.9287
data/restraints/params	4312/35/247	4850/36/258	7085/148/416	2426/12/134	4583/34/228	8018/94/430
GOF on F^2	0.972	1.025	0.765	0.697	0.988	0.932
R_1 $[I > 2\sigma(I)]^a$	0.0467	0.0291	0.0522	0.0390	0.0474	0.0478
wR_2 (all data)^b	0.1171	0.0797	0.0982	0.0500	0.1180	0.1087
max, min $\Delta\rho_{electron}$ (e·$Å^{-3}$)	0.293/−0.410	0.485/−0.260	0.300/−0.296	0.192/−0.197	0.764/−0.418	0.327/−0.273

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

material isolated in this way is the solvent-free calcium DMADB compound $Ca(H_3BNMe_2BH_3)_2$, **1**. This compound is insoluble in noncoordinating solvents.

$$CaBr_2 + 2Na(H_3BNMe_2BH_3) \rightarrow \underset{\mathbf{1}}{Ca(H_3BNMe_2BH_3)_2} + 2NaBr$$

Before they are dried in vacuum, the colorless crystals obtained from the above reaction consist of the diethyl ether adduct $Ca(H_3BNMe_2BH_3)_2(Et_2O)_2$, **2**. If the reaction of $CaBr_2$ with 2 equiv of $Na(H_3BNMe_2BH_3)$ is carried out in the more strongly coordinating solvent tetrahydrofuran (thf) rather than diethyl ether, the thf solvate $Ca(H_3BNMe_2BH_3)_2(thf)_2$, **3**, is obtained. The thf ligands in this compound are not readily removed when the crystals are exposed to vacuum at room temperature (although desolvation does occur at higher temperatures; see below).

$$CaBr_2 + 2Na(H_3BNMe_2BH_3) + 2L \rightarrow \underset{\substack{\mathbf{2},L=Et_2O\\ \mathbf{3},L=thf}}{Ca(H_3BNMe_2BH_3)_2(L)_2} + 2NaBr$$

The synthesis of calcium DMADB complexes with other coordinated Lewis bases can be achieved by treating the thf adduct **3** with 1 equiv of the desired Lewis base. Thus, treatment of **3** with 1,2-dimethoxyethane (dme), bis(2-methoxyethyl) ether (diglyme), or *N,N,N′,N′*-tetramethylethylenediamine (tmeda) in thf affords the new compounds $Ca(H_3BNMe_2BH_3)_2(dme)$, **4**, $Ca(H_3BNMe_2BH_3)_2(diglyme)$, **5**, and $Ca(H_3BNMe_2BH_3)_2(tmeda)$, **6**, respectively, in greater than 60% yields.

$$Ca(H_3BNMe_2BH_3)_2(thf)_2 + L \rightarrow \underset{\substack{\mathbf{4},L=dme\\ \mathbf{5},L=diglyme\\ \mathbf{6},L=tmeda}}{Ca(H_3BNMe_2BH_3)_2(L)} + 2thf$$

The dme compound **4** can be also obtained by treatment of calcium metal with *N,N*-dimethylamine-borane in refluxing dme. This procedure, which is analogous to one of the preparative routes by which the $Na(H_3BNMe_2BH_3)$ is made,[18] may be advantageous for CVD applications because the presence of halide, even in trace amounts, can be avoided.

$$Ca + 4NMe_2H{\cdot}BH_3 + dme \rightarrow \underset{\mathbf{4}}{Ca(H_3BNMe_2BH_3)_2(dme)} + ...$$

The treatment of **3** with 2 equiv of the crown ether 12-crown-4 in thf and subsequent recrystallization from hot thf yields the charge-separated salt, $[Ca(12\text{-crown-}4)_2][H_3BNMe_2BH_3]_2$, **7**. The 12-crown-4 molecule preferentially coordinates to calcium in a 2:1 ratio: if 1 equiv of 12-crown-4 is added to **3**, the same product, **7**, is obtained but in smaller yield.

$$Ca(H_3BNMe_2BH_3)_2(thf)_2 + 2(12\text{-crown-}4) \rightarrow \underset{\mathbf{7}}{[Ca(12\text{-crown-}4)_2][H_3BNMe_2BH_3]_2} + 2thf$$

Structural Data for the New $Ca(H_3BNMe_2BH_3)_2L_x$ Compounds. Crystal data for all the new calcium DMADB compounds are listed in Table 1, and selected bond distances and angles are given in Tables 2−7. For crystal structures containing more than one molecule in the asymmetric unit, the

Table 2. Selected Bond Distances and Angles for $Ca(BH_3NMe_2BH_3)_2(Et_2O)_2$, 2

	Bond Distance (Å)		
Ca(1)–B(1)	2.837(4)	Ca(1)–O(1)	2.380(2)
Ca(1)–B(2)	2.789(4)	Ca(1)–O(2)	2.403(2)
Ca(1)–B(3)	2.851(4)	Ca(1)–H(11)	2.41
Ca(1)–B(4)	2.780(4)		
	Bond Angle (°)		
O(1)–Ca(1)–O(2)	83.12(8)	B(1)-Ca(1)-B(2)	55.20(10)
O(1)–Ca(1)–B(1)	141.19(9)	B(1)-Ca(1)-B(3)	106.49(13)
O(1)–Ca(1)–B(2)	87.28(9)	B(1)-Ca(1)-B(4)	108.12(13)
O(1)–Ca(1)–B(3)	96.46(10)	B(2)-Ca(1)-B(3)	112.88(12)
O(1)–Ca(1)–B(4)	110.68(11)	B(2)-Ca(1)-B(4)	158.43(14)
O(2)–Ca(1)–B(1)	97.95(10)	B(3)-Ca(1)-B(4)	55.05(12)
O(2)–Ca(1)–B(2)	107.54(10)	B(1)-N(1)-B(2)	111.0(2)
O(2)–Ca(1)–B(3)	139.52(10)	B(3)-N(2)-B(4)	110.9(3)
O(2)–Ca(1)–B(4)	87.07(10)		

Table 3. Selected Bond Distances and Angles for $Ca(BH_3NMe_2BH_3)_2(thf)_2$, 3

	Bond Distance (Å)		
Ca(1)–O(1)	2.361(1)	Ca(1)–B(3)	2.790(2)
Ca(1)–O(2)	2.365(1)	Ca(1)–B(4)	2.844(2)
Ca(1)–B(1)	2.783(2)	Ca–H (avg)	2.41
Ca(1)–B(2)	2.835(2)		
	Bond Angle (deg)		
O(1)–Ca(1)–O(2)	82.27(4)	B(1)–Ca(1)–B(4)	119.01(5)
O(1)–Ca(1)–B(1)	84.89(5)	B(2)–Ca(1)–B(3)	115.07(6)
O(1)–Ca(1)–B(2)	139.51(5)	B(2)–Ca(1)–B(4)	109.47(7)
O(1)–Ca(1)–B(3)	105.27(5)	B(3)–Ca(1)–B(4)	55.08(5)
O(1)–Ca(1)–B(4)	95.88(5)	B(1)–N(1)–B(2)	111.1(1)
O(2)–Ca(1)–B(1)	102.90(5)	B(3)–N(2)–B(4)	111.1(1)
O(2)–Ca(1)–B(2)	97.77(6)	N(1)–B(1)–Ca(1)	97.92(9)
O(2)–Ca(1)–B(3)	84.54(5)	N(1)–B(2)–Ca(1)	95.42(9)
O(2)–Ca(1)–B(4)	137.79(5)	N(2)–B(3)–Ca(1)	97.89(9)
B(1)–Ca(1)–B(2)	55.44(6)	N(2)–B(4)–Ca(1)	95.83(9)
B(1)–Ca(1)–B(3)	168.29(6)		

Table 4. Selected Bond Distances and Angles for $Ca(BH_3NMe_2BH_3)_2(dme)$, 4

	Bond Distance (Å)		
Ca(1)–O(1)	2.393(3)	Ca(2)–O(3)	2.359(3)
Ca(1)–O(2)	2.376(2)	Ca(2)–O(4)	2.402(3)
Ca(1)–B(3)	2.767(5)	Ca(2)–B(5)	2.788(5)
Ca(1)–B(1)	2.771(5)	Ca(2)–B(6)	2.798(6)
Ca(1)–B(2)	2.797(5)	Ca(2)–B(7)	2.805(5)
Ca(1)–B(4)	2.799(5)	Ca(2)–B(8)	2.808(6)
Ca(1)–H (avg)	2.34	Ca(2)–H (avg)	2.38
	Bond Angle (deg)		
O(1)–Ca(1)–O(2)	69.87(9)	O(3)–Ca(2)–O(4)	68.80(9)
O(1)–Ca(1)–B(1)	101.7(1)	O(3)–Ca(2)–B(5)	89.2(1)
O(1)–Ca(1)–B(2)	101.0(1)	O(3)–Ca(2)–B(6)	140.5(1)
O(1)–Ca(1)–B(3)	86.3(1)	O(3)–Ca(2)–B(7)	99.7(1)
O(1)–Ca(1)–B(4)	137.6(1)	O(3)–Ca(2)–B(8)	111.6(1)
O(2)–Ca(1)–B(1)	85.5(1)	O(4)–Ca(2)–B(5)	104.6(1)
O(2)–Ca(1)–B(2)	138.7(1)	O(4)–Ca(2)–B(6)	99.4(1)
O(2)–Ca(1)–B(3)	106.6(1)	O(4)–Ca(2)–B(7)	137.5(1)
O(2)–Ca(1)–B(4)	100.8(1)	O(4)–Ca(2)–B(8)	89.4(1)
B(1)–Ca(1)–B(2)	56.1(1)	B(5)–Ca(2)–B(6)	56.3(2)
B(1)–Ca(1)–B(3)	167.30(16)	B(5)–Ca(2)–B(7)	116.31(16)
B(1)–Ca(1)–B(4)	119.14(15)	B(5)–Ca(2)–B(8)	158.24(16)
B(2)–Ca(1)–B(3)	112.99(16)	B(6)–Ca(2)–B(7)	112.12(17)
B(2)–Ca(1)–B(4)	110.51(16)	B(6)–Ca(2)–B(8)	105.62(16)
B(3)–Ca(1)–B(4)	55.89(14)	B(7)–Ca(2)–B(8)	55.8(2)
B(1)–N(1)–B(2)	112.5(3)	B(5)–N(3)–B(6)	112.6(3)
B(3)–N(2)–B(4)	111.8(3)	B(7)–N(4)–B(8)	112.5(3)

Table 5. Selected Bond Distances and Angles for $Ca(BH_3NMe_2BH_3)_2(diglyme)$, 5[a]

	Bond Distance (Å)		
Ca(1)–O(1)	2.437(2)	Ca(1)–B(4)	2.794(5)
Ca(1)–O(2)	2.393(2)	Ca(1)–H(11)	2.41(2)
Ca(1)–B(1)	2.836(6)	Ca(1)–H(21)	2.48(2)
Ca(1)–B(2)	2.953(5)	Ca(1)–H(31)	2.54(2)
Ca(1)–B(3)	2.976(5)	Ca(1)–H(41)	2.33(2)
	Bond Angle (deg)		
O(1)–Ca(1)–O(2)	67.53(4)	N(1)–B(1)–Ca(1)	100.8(3)
O(1)–Ca(1)–O(1)′	135.03(8)	N(1)–B(2)–Ca(1)	96.8(2)
O(1)–Ca(1)–B(1)	106.39(5)	N(2)–B(3)–Ca(1)	94.1(2)
O(1)–Ca(1)–B(2)	87.98(5)	N(2)–B(4)–Ca(1)	101.7(2)
O(1)–Ca(1)–B(3)	87.57(5)	B(1)–Ca(1)–B(2)	52.8(2)
O(1)–Ca(1)–B(4)	106.28(5)	B(3)–Ca(1)–B(4)	53.5(1)
O(2)–Ca(1)–B(1)	139.9(1)	B(1)–N(1)–B(2)	109.6(3)
O(2)–Ca(1)–B(2)	87.1(1)	B(3)–N(2)–B(4)	110.7(3)
O(2)–Ca(1)–B(3)	81.3(1)		
O(2)–Ca(1)–B(4)	134.8(1)		

[a] Symmetry transformations used to generate equivalent atoms: ′ = x, $-y+1/2$, z.

best behaved molecule (as judged from the displacement parameters) was in all cases given the label of molecule 1. In the discussion below, where only one metric parameter is given, it will be for molecule 1.

Molecules of $Ca(H_3BNMe_2BH_3)_2(Et_2O)_2$, **2**, and $Ca(H_3BNMe_2BH_3)_2(thf)_2$, **3**, occupy general positions within their respective unit cells. The four boron atoms and two oxygen atoms in the Ca coordination sphere describe a distorted octahedron for both **2** (Figure 1) and **3** (Figure 2). Whereas trigonal prisms have six large interligand angles of about 120–145° (the diagonals of the square faces), octahedra have three large interligand angles of about 180° (between mutually *trans* ligands). The coordination geometries about the calcium atoms in both **2** and **3** are best considered to be distorted octahedra because only three angles are greater than 120°, although the angles deviate significantly from 180° owing to the small bite angles of the chelating DMADB ligands.

The O–Ca–O angle between the coordinated ether molecules is 83.08(9)° in **2** and 82.27(4)° in **3**. The average Ca–O distance is 2.39 Å to Et_2O and 2.36 Å to thf. Of the four Ca···B distances in each molecule, two are shorter and two are longer, with the difference being about 0.06 Å. Specifically, each DMADB ligand exhibits in one short Ca···B distance of 2.780(4)–2.790(2) Å and one long Ca···B distance of 2.835(2)–2.851(4) Å. In both **2** and **3**, the shorter Ca···B distances involve boron atoms that are trans to each other. The hydrogen atoms were found in the difference maps, and their locations could be refined subject to light restraints; the average Ca–H distance in both **2** and **3** is 2.40 Å. The total coordination number of the calcium centers in **2** and **3** is 10 (2 oxygen and 8 hydrogen atoms).

Molecules of the dme adduct **4** reside in general positions with two independent molecules in the asymmetric unit. The four boron atoms and two oxygen atoms in the coordination

Table 6. Selected Bond Distances and Angles for $Ca(BH_3NMe_2BH_3)_2(tmeda)$, 6

Bond Distance (Å)			
Ca(1)−N(3)	2.560(2)	Ca(1)−B(3)	2.773(3)
Ca(1)−N(4)	2.585(2)	Ca(1)−B(4)	2.812(2)
Ca(1)−B(1)	2.762(3)	Ca−H (avg)	2.39
Ca(1)−B(2)	2.843(3)		
Bond Angle (deg)			
N(3)−Ca(1)−N(4)	72.70(6)	B(1)−Ca(1)−B(2)	55.76(7)
N(3)−Ca(1)−B(1)	91.63(6)	B(3)−Ca(1)−B(4)	55.84(7)
N(3)−Ca(1)−B(2)	144.32(7)	B(1)−N(1)−B(2)	111.7(2)
N(3)−Ca(1)−B(3)	103.18(7)	B(3)−N(2)−B(4)	111.6(2)
N(3)−Ca(1)−B(4)	99.45(7)	N(1)−B(1)−Ca(1)	97.9(1)
N(4)−Ca(1)−B(1)	106.00(7)	N(1)−B(2)−Ca(1)	94.6(1)
N(4)−Ca(1)−B(2)	100.56(7)	N(2)−B(3)−Ca(1)	97.1(1)
N(4)−Ca(1)−B(3)	90.77(7)	N(2)−B(4)−Ca(1)	95.5(1)
N(4)−Ca(1)−B(4)	143.76(7)		

Table 7. Selected Bond Distances and Angles for $[Ca(12\text{-}crown\text{-}4)_2][BH_3NMe_2BH_3]_2\cdot 2thf$, 7[a]

Bond Distance (Å)			
Ca(1)−O(1)	2.441(1)	Ca(1)−O(7)	2.409(1)
Ca(1)−O(2)	2.382(1)	Ca(1)−O(8)	2.423(1)
Ca(1)−O(3)	2.419(1)	N(1)−B(1)	1.587(3)
Ca(1)−O(4)	2.418(1)	N(1)−B(2)	1.596(3)
Ca(1)−O(5)	2.421(1)	N(1)−C(1)	1.475(3)
Ca(1)−O(6)	2.431(1)	N(1)−C(2)	1.455(3)
Bond Angle (deg)			
O(1)−Ca(1)−O(2)	69.22(5)	C(1)−N(1)−B(2)	108.7(2)
O(2)−Ca(1)−O(3)	68.47(5)	C(2)−N(1)−B(1)	109.8(2)
O(3)−Ca(1)−O(4)	68.40(5)	C(2)−N(1)−B(2)	108.7(2)
O(1)−Ca(1)−O(4)	68.70(5)	C(3A)−N(2A)−C(4A)	107.1(3)
O(5)−Ca(1)−O(6)	68.23(5)	C(3A)−N(2A)−B(3A)	110.3(4)
O(6)−Ca(1)−O(7)	69.64(5)	C(3A)−N(2A)−B(4A)	109.1(3)
O(7)−Ca(1)−O(8)	69.08(4)	C(4A)−N(2A)−B(3A)	107.0(4)
O(5)−Ca(1)−O(8)	68.97(5)	C(4A)−N(2A)−B(4A)	109.2(3)
C(1)−N(1)−C(2)	108.7(2)	B(1)−N(1)−B(2)	112.8(2)
C(1)−N(1)−B(1)	108.1(2)	B(3A)−N(2A)−B(4A)	113.8(3)

[a] Atoms in the major component of the disordered DMADB ion are designated with the letter A.

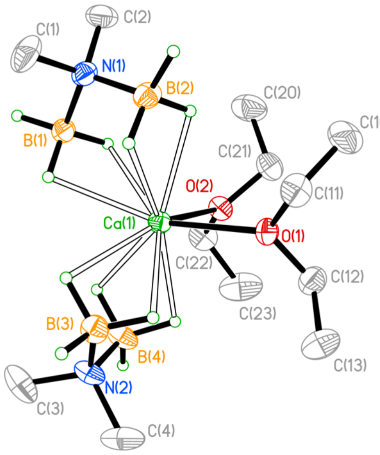

Figure 1. Molecular structure of $Ca(BH_3NMe_2BH_3)_2(Et_2O)_2$, **2**. Ellipsoids are drawn at the 30% probability level. Hydrogens attached to carbon have been removed for clarity.

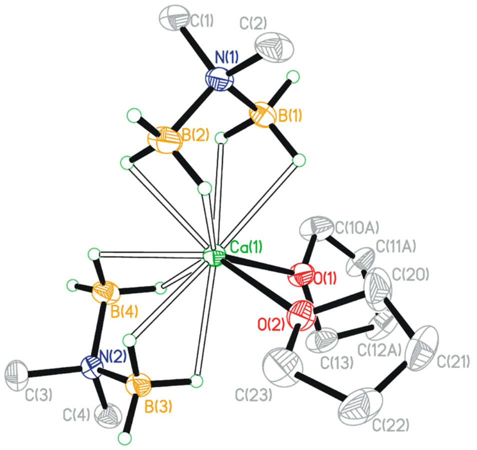

Figure 2. Molecular structure of $Ca(BH_3NMe_2BH_3)_2(thf)_2$, **3**. Ellipsoids are drawn at the 30% probability level. Hydrogens attached to carbon and the atoms in the minor component of the disordered thf ligand have been removed for clarity.

sphere of the calcium atom describe a highly distorted octahedron (Figure 3).

The O−Ca−O angle of the dme ligand of 69.87(9)° is about 13° smaller than those in **2** and **3** because of the chelating nature of the ligand. The Ca−O distance of 2.376(2) Å, however, is essentially identical to those seen for the Et_2O and thf analogues. As seen for **2** and **3**, each independent DMADB ligand has one shorter Ca···B distance of 2.767(5)−2.771(5) Å and one longer Ca···B distance of 2.797(5)−2.799(5) Å, but the difference is only about 0.03 instead of 0.06 Å. The smaller difference suggests that the asymmetry in the binding of the DMADB ligands in these calcium complexes is not a trans effect, but rather increases as the steric crowding in the molecule increases: because of its chelating nature, a single dme ligand is less sterically demanding than two Et_2O or two thf ligands. The average Ca−H distance in **4** is 2.34 Å, and the total coordination number is 10 (2 oxygen and 8 hydrogen atoms).

Molecules of the diglyme compound **5** lie on a mirror plane that bisects the diglyme ligand and that contains the calcium atom and the two DMADB ligands. The four boron atoms and three oxygen atoms in the inner coordination sphere describe a distorted pentagonal bipyramidal geometry about the Ca center

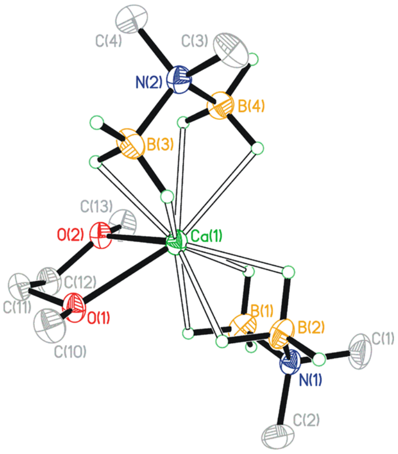

Figure 3. Molecular structure of $Ca(BH_3NMe_2BH_3)_2(dme)$, **4**. Ellipsoids are drawn at the 30% probability level. Hydrogens attached to carbon have been removed for clarity.

(Figure 4), with the outer oxygen atoms of the diglyme ligand occupying the two axial sites. The Ca−O distance to the central oxygen atom is 2.393(2) Å and those to the outer oxygen atoms are slightly longer at 2.437(2) Å. The O−Ca−O angles between the central and the outer oxygen atoms of the diglyme ligand are both 67.53(4)°. The two DMADB ligands, which occupy four of the equatorial sites of the pentagonal bipyramid, are bound asymmetrically so that two of the four Ca···B distances per molecule are short and two are long. Each independent DMADB ligand forms one short Ca···B distance of 2.794(5)−2.836(6) Å and one long Ca···B distance of 2.953(5)−2.976(5) Å. Unlike **2** and **3**, however, the longer (not shorter) distances are seen for boron atoms that are approximately trans to other boron atoms. Here, the difference of about 0.15 Å is much greater than the differences seen in **2**−**4**, and this finding again suggests that the unsymmetrical binding of the DMADB ligands is a result of steric effects, here owing to the greater coordination number of the Ca center in **5**. The average Ca−H distance in **5** is 2.44 Å, and the total coordination number is 11 (3 oxygen and 8 hydrogen atoms).

Molecules of the tmeda compound **6** reside in general positions. The four boron atoms and the two nitrogen atoms of the tmeda ligand describe a highly distorted octahedron about the Ca center (Figure 5). The N−Ca−N angle of the tmeda ligand is 72.70(6)°, and the average Ca−N distance is 2.57 Å. As seen in the compounds above, each DMADB ligand has one short Ca···B distance of 2.762(3)−2.773(3) Å and one long Ca···B distance of 2.812(2)−2.843(3) Å. The about 0.06 Å difference in these distances suggests that tmeda is more sterically demanding than two Et_2O or thf molecules or a single dme ligand, but is less demanding than a single tridentate diglyme molecule; this ordering is consistent with chemical expectations. The average Ca−H distance is 2.39 Å. The total coordination number of **6** is 10 (2 nitrogen and 8 hydrogen atoms).

The two 12-crown-4 ligands in **7** encapsulate the calcium atom, and the eight oxygen atoms describe an approximate square antiprism about the Ca center. The cations and DMADB anions are completely charge separated (Figure 6). The Ca−O distances lie within a small range of 2.382(1) to 2.441(1) Å. The total coordination number of the Ca center in **7** is 8 (8 oxygens atoms).

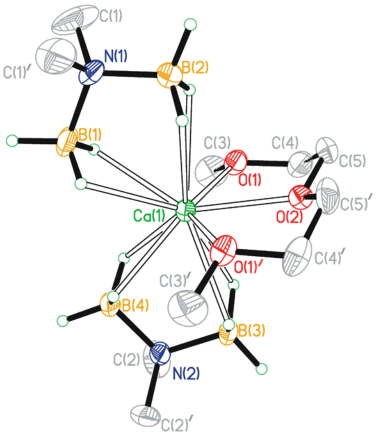

Figure 4. Molecular structure of $Ca(BH_3NMe_2BH_3)_2(diglyme)$, **5**. Ellipsoids are drawn at the 30% probability level. Hydrogens attached to carbon have been removed for clarity. Primed atoms are related to unprimed atoms by the crystallographic mirror plane.

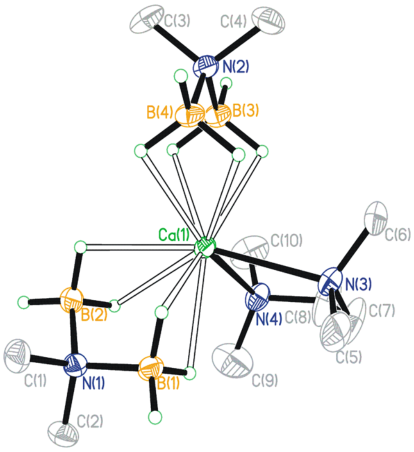

Figure 5. Molecular structure of $Ca(BH_3NMe_2BH_3)_2(tmeda)$, **6**. Ellipsoids are drawn at the 30% probability level. Hydrogens attached to carbon have been removed for clarity.

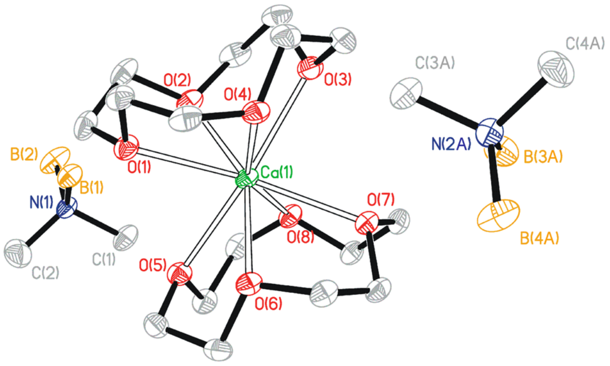

Figure 6. Molecular structure of $[Ca(12\text{-}crown\text{-}4)_2][BH_3NMe_2BH_3]_2\cdot 2thf$, **7**. Ellipsoids are drawn at the 30% probability level. The thf molecules of solvation and the hydrogen atoms have been removed for clarity.

Comparison of Structural Properties with Those of Other Known Calcium Compounds. Compounds **2**−**6** all possess chelating κ^2-$BH_3NMe_2BH_3$-κ^2 groups, in which two of the three hydrogen atoms on each boron are bound to calcium. Compound **7** is the only ionic compound in the series: the Ca atom is completely encapsulated by two 12-crown-4 ligands and the DMADB units are charge-separated counterions within the unit cell. All of the Ca···B distances for **2**−**6** lie within the range 2.762(3)−2.976(5) Å; these distances are consistent with Ca···B bond distances seen for other calcium borohydride ligands that are bound in a κ^2 fashion: $Ca[(\kappa^2\text{-}BH_3PPh_2)_2CH]_2(thf)$ 2.754(3)−2.908(4) Å,[19,20] $Ca[\kappa^2\text{-}BH_3PMe_2C(SiMe_3)_2]_2(thf)_4$ 2.751(2) Å,[21] $Ca_2[(\kappa^2\text{-}BH_3PPh_2)_2C]_2(thf)_2$ 2.725(4)−2.785(4) Å.[20] In contrast, Ca···B distances in which the borohydride ligands are bound in a κ^3 fashion are much shorter, as expected: $Ca(\kappa^3\text{-}BH_3CH_3)_2(dme)_2$ 2.617(3) Å,[22] $Ca(\kappa^3\text{-}BH_4)_2(dme)_2$ 2.65 Å,[23] $[Ca(\kappa^3\text{-}BH_4)(thf)_5][BPh_4]$ 2.610(4) Å,[24] $[(HC(Me_2pz)_3)Ca(\kappa^3\text{-}BH_4)(thf)_2][BPh_4]$ 2.580(2) Å,[24] and $Ca(\kappa^3\text{-}BH_4)(DIPPnacnac)(THF)_2$ 2.600(5) Å.[25] In addition, some Ca···B distances are not known experimentally but have been calculated: $Ca(\kappa^2\text{-}BH_4)_2$ 2.69 Å and $Ca(\kappa^3\text{-}BH_4)_2$ 2.49 Å.[26]

The chelating DMADB ligands in the new calcium compounds exhibit B−Ca−B angles of 53.2−56.0°. Other known B−M−B angles for various metal DMADB compounds are Ba^{2+} 46.9°,[16] Eu^{2+} 50.3°,[27] Th^{4+} 50.8°,[28] U^{3+} 52.9°,[29,30] Ln^{3+} 52.9°,[31] Y^{3+} 53.4°,[31] Sr^{2+} 53.5°,[32] and Mg^{2+} 60.8°.[15] These data show that, as expected on geometrical grounds, the B−M−B angle of the DMADB ligand decreases as the ionic radius of the metal center increases.

The average Ca−O distances of 2.39, 2.36, 2.38, 2.42, and 2.41 Å in **2**, **3**, **4**, **5**, and **7**, respectively, compare well with those of 2.378−2.501 Å in other calcium diethyl ether adducts,[33−37] 2.355−2.502 Å in other calcium thf adducts,[19−21,24,38−40] 2.415−2.507 in other calcium dme adducts,[22,23,39,40] 2.444−2.514 Å in other calcium diglyme complexes,[38,41,42] and 2.380−2.55 Å in other calcium 12-crown-4 adducts.[43−45]

Compound **6** has an average Ca−N distance of 2.57 Å and an average N−Ca−N angle of 72.70°. Known Ca−N bond distance and N−Ca−N angles for calcium tmeda adducts are $Ca(tBu_2pz)_2(tmeda)$ 2.535(3) Å and 70.3(2)°,[46] $[p\text{-}tBu\text{-}calix[4](OC_5H_9)_2(O)_2Ca(tmeda)]$ 2.580(4)−2.600(4) Å and 67.51(11)°,[47] $[Ca(Ph)(\mu\text{-}Ph)(tmeda)]_2$ 2.571(2)−2.610(2) Å and 70.50(6)°,[48] $CaI_2(tmeda)_2$ 2.562(5)−2.570(5) Å and 75.5(2)°,[38] and $Ca(Ph)I(tmeda)_2$ 2.590(5)−2.575(5) Å and 74.0(2)°.[49]

Spectroscopic Properties of the New Calcium DMADB Compounds. The IR spectrum of the desolvated compound $Ca(H_3BNMe_2BH_3)_2$, **1**, exhibits bands between 2500 and 2000 cm^{-1} that are characteristic of B−H stretches: one very strong peak at 2257 cm^{-1} due to bridging B−H···Ca groups and weaker, higher-frequency bands at 2352 (m), 2400 (m), and 2426 (w) cm^{-1} due to terminal B−H groups. For the Lewis base adducts **3**−**6**, the bands are shifted somewhat in frequency and those due to terminal B−H groups are stronger than they are in **1**. The latter result suggests that **1** is polymeric with many B−H···Ca interactions, which are broken upon coordination of Lewis bases to the Ca center. In general, the spectra are consistent with those seen for other known DMADB complexes.[15,27−30,50]

The pattern of bands in the IR spectrum of the 12-crown-4 complex **7** is rather different from that seen in the spectra of **3**−**6**, as might be expected from the presence of noncoordinating DMADB anions in the solid-state structure of **7**. There are two intense but broad peaks at 2209 and 2307 cm^{-1} as well as a shoulder at 2155 cm^{-1} and a medium intensity peak at 2062 cm^{-1}. At present, there are two other structurally characterized compounds that contain charge-separated DMADB anions, and the IR spectra of these compounds in the B−H stretching region are similar to that of **7**.[16,32]

Compound **1** contains a singlet for the NMe_2 protons of the *N,N*-dimethylaminodiboranate (DMADB) ligand, and a 1:1:1:1 quartet at δ 1.35 for the BH_3 groups. The coupling constant to the ^{11}B nucleus ($I = {}^3/_2$) is 92 Hz. The ^{11}B NMR spectrum of the desolvated compound **1** consists of a resonance at δ −8.64 that appears as a 1:3:3:1 quartet due to the same coupling of the ^{11}B nucleus to three protons.

The ^1H NMR spectra of **1** and **7** were acquired in d_6-DMSO because of the low solubilities of these compounds in less polar solvents, whereas spectra of **3**−**6** were acquired in d_6-benzene. In d_8-DMSO, the chemical shifts of the NMe_2 protons in **1** and **7** of δ 2.05 and 2.09, respectively, agree with those measured for other with known DMADB compounds in the same solvent.[16] In contrast, in d_6-benzene the chemical shifts of the NMe_2 resonances of **3**−**6** all lie between δ 2.46 and 2.58, or about 0.4 ppm downfield of the shifts seen in d_6-DMSO. We have evidence (see below) that DMSO is not completely displacing the DMADB groups from the calcium centers, so that this chemical shift difference is a shielding effect due to the aromaticity of the benzene solvent. The NMe_2 chemical shifts seen for **3**−**6** are in agreement with those observed in other DMADB complexes of divalent metal ions in d_6-benzene or d_8-toluene.[15,27]

The ^1H NMR spectra for **3**−**6** in d_6-benzene also contain a 1:1:1:1 quartet between δ 2.08 and 2.14 due to the BH_3 groups of the DMADB ligands. For all four compounds the coupling constant to the ^{11}B nucleus ($I = {}^3/_2$) is between 90 and 92 Hz. The ^1H NMR chemical shifts for the BH_3 groups are also affected by the choice of NMR solvent: **1** and **7** in d_6-DMSO have chemical shifts at δ 1.35 and δ 1.39, respectively, that are about 0.7 ppm upfield of those seen in benzene.

The ^{11}B NMR spectra of all the new compounds consist of a binomial quartet (with the same 90−92 Hz coupling constant) at chemical shifts between δ −8.43 and δ −8.91. Interestingly, the ^{11}B NMR chemical shifts are not significantly influenced by the choice of NMR solvent or the nature of the Ca-DMADB interaction, as is true for the ^1H NMR shifts. In addition, these ^{11}B NMR shifts are different from those seen for DMADB complexes of other alkaline earth and alkali metals. For comparison, the ^{11}B NMR chemical shifts of magnesium DMADB compounds are between δ −12.14 and −12.85,[15] and that of the starting material, NaDMADB, is δ −11.11. The ^{11}B NMR shifts seen for the calcium complexes are, however, similar to those seen for Sr and Ba DMADB complexes, which lie between δ −7.60 and δ −8.95.[16,32] These results suggest that, even in DMSO, the DMADB ligands are still largely coordinated to the calcium centers.

Volatility Studies. The volatilities of the new calcium compounds were investigated to determine the potential utility of these compounds as CVD precursors. When heated, the base free and thf adducts **1** and **3** melt with decomposition at 195 and 117 °C, respectively, and neither sublimes under reduced pressure (1 Torr) at temperatures up to 150 °C. These findings are consistent with the expectation that these unidentate Lewis bases readily dissociate from the Ca centers. In contrast, the dme, diglyme, and tmeda compounds **4**, **5**, and **6** melt at 94, 139, and 133 °C, respectively, and the resulting liquids are thermally stable (i.e., no gas evolution occurs) up to 150 °C. These compounds bearing multidentate Lewis bases sublime readily under reduced pressure (1 Torr) at 90 °C (**4**) and 120 °C (**5**, **6**). The 12-crown-4 compound **7** does not melt up to 240 °C and does not sublime under reduced pressure (1 Torr) up to 150 °C; these properties are consistent with the salt-like nature of this compound in the solid state.

■ CONCLUSIONS

The results presented in this paper reveal that the chelating *N,N*-dimethylaminodiboranate (DMADB) ligand affords volatile calcium complexes when the metal is also ligated by an appropriate Lewis base. The Lewis bases diethyl ether and tetrahydrofuran coordinate to the calcium centers relatively weakly, and these ligands dissociate upon attempted sublimation in vacuum. The crown ether 12-crown-4 binds very strongly, so much so that two crown ether molecules coordinate to each Ca center, and the DMADB groups become charge-separated counterions. Not surprisingly, this latter complex is completely nonvolatile. Notably, however, the complexes $Ca(H_3BNMe_2BH_3)_2(dme)$, $Ca(H_3BNMe_2BH_3)_2(diglyme)$, and $Ca(H_3BNMe_2BH_3)_2(tmeda)$ have volatilities that compare favorably with those of the most volatile calcium compounds known. The dme complex, which is the most volatile of the three, sublimes at 90 °C and 1 Torr.

■ EXPERIMENTAL SECTION

All manipulations were carried out under argon or in vacuum using standard Schlenk and cannula techniques. Pentane, tetrahydrofuran, 1,2-dimethoxyethane (dme), and diethyl ether were distilled from sodium/benzophenone before use. Bis(2-methoxyethyl) ether (diglyme) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) were distilled from sodium. 1,4,7,10-Tetraoxacyclododecane (12-crown-4; Aldrich), $CaBr_2$ (99.5%; Strem), and calcium granules (−6 mesh, 99.5%, Strem) were used as received. Sodium *N*,*N*-dimethylaminodiboranate was synthesized by the literature procedure.[18] Elemental analyses were carried out by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Nicolet Impact 410 infrared spectrometer as Nujol mulls between KBr plates. The NMR data were collected on a General Electric GN300WB instrument at 7.00 T (^{11}B), a Varian Unity 400 instrument at 9.4 T (^{1}H and ^{11}B), or a Varian Unity-500 spectrometer at 11.75 T (^{1}H). Chemical shifts are reported in δ units (positive shifts to high frequency) relative to $SiMe_4$ (^{1}H) or $BF_3{\cdot}Et_2O$ (^{11}B). Melting points were determined in closed capillaries under argon on a Thomas-Hoover Unimelt apparatus.

Bis(*N*,*N*-dimethylaminodiboranato)calcium $Ca(BH_3NMe_2BH_3)_2$, 1, and Bis(*N*,*N*-dimethylaminodiboranato)bis(diethyl ether)calcium $Ca(BH_3NMe_2BH_3)_2(Et_2O)_2$, 2. To anhydrous $CaBr_2$ (2.00 g, 10.00 mmol) was added a solution of sodium *N*,*N*-dimethylaminodiboranate (1.90 g, 20.0 mmol) in diethyl ether (100 mL). The resulting suspension was stirred for 18 h, during which time the color of the mixture changed from white to gray. The suspension was filtered, and the filtrate was concentrated under vacuum to about 20 mL and cooled to −20 °C. After 24 h, the small colorless prisms were collected. The as-isolated crystals consist of the diethyl ether adduct $Ca(BH_3NMe_2BH_3)_2(Et_2O)_2$, **2**, but drying under vacuum at 25 °C for 15 min yields the unsolvated compound **1**. Yield of **1**: 1.21 g (66%). Mp. 195 °C (dec). Anal. Calc for $C_4H_{24}N_2B_4Ca$: C, 26.2; H, 13.2; N, 15.3; B, 23.6; Ca, 21.8. Found: C, 26.3; H, 13.3; N, 15.6; B, 21.8; Ca, 20.8. ^{1}H NMR (d_6-dmso, 20 °C): δ 2.05 (s, NMe_2), 1.35 (1:1:1:1 q, J_{BH} = 91.9 Hz, BH_3). ^{11}B NMR (d_6-dmso, 20 °C): δ −8.64 (q, J_{BH} = 91.6 Hz). IR (cm^{-1}): 2426 w, 2400 m, 2352 m, 2257 vs, 1283 m, 1269 m, 1242 m, 1216 w, 1183 s, 1174 s, 1152 vs, 1043 m, 1032 s, 963 w, 929 w, 908 w, 825 w.

Bis(*N*,*N*-dimethylaminodiboranato)bis(tetrahydrofuran)calcium, $Ca(BH_3NMe_2BH_3)_2(thf)_2$, 3. To anhydrous $CaBr_2$ (327 mg, 1.63 mmol) was added a solution of sodium *N*,*N*-dimethylaminodiboranate (310 mg, 3.27 mmol) in tetrahydrofuran (20 mL). The resulting suspension was stirred for 15 h, during which time the color of the mixture changed from white to gray. The solvent was removed under vacuum, and the resulting solid was extracted with hot heptane (50 mL). The hot extracts were filtered, the solvent was removed under vacuum, and the residue dissolved in tetrahydrofuran (50 mL). The resulting solution was filtered, concentrated to about 10 mL, and cooled to −20 °C to afford colorless blocks. Yield: 0.315 g (59%). Mp. 117−120 °C (dec). Anal. Calc for $C_{12}H_{40}N_2B_4O_2Ca$: C, 44.0; H, 12.3; N, 8.55; B, 13.2; Ca, 12.2. Found: C, 43.6; H, 12.7; N, 8.50; B, 13.4; Ca, 12.4. ^{1}H NMR (C_6D_6, 20 °C): δ 3.55 (m, α-CH_2), 2.48 (s, NMe_2), 2.14 (1:1:1:1 q, J_{BH} = 90.0 Hz, BH_3), 1.17 (m, β-CH_2). ^{11}B NMR (C_6D_6, 20 °C): δ −8.79 (q, J_{BH} = 90.0 Hz). IR (cm^{-1}): 2379 s, 2355 vs, 2303 s, 2235 vs, 1264 m, 1235 m, 1213 m, 1180 vs, 1149 vs, 1027 s, 929 m, 907 m, 877 m, 803 w.

Bis(*N*,*N*-dimethylaminodiboranato)(1,2-dimethoxyethane)calcium, $Ca(BH_3NMe_2BH_3)_2(dme)$, 4. *Method A.* To $Ca(DMADB)_2(thf)_2$ (300 mg, 0.915 mmol) in tetrahydrofuran (50 mL) was added 1,2-dimethoxyethane (1.0 mL, 9.63 mmol). The resulting solution was stirred for 2 h. The solvent was removed under vacuum, and the residue was sublimed at 80 °C under vacuum onto a water-cooled coldfinger. After 24 h, the small colorless prisms were collected. Yield: 250 mg (61%). Mp. 93−95 °C. Anal. Calc for $C_8H_{34}N_2O_2B_4Ca$: C, 35.1; H, 12.5; N, 10.2; B, 15.8; Ca, 14.6. Found: C, 36.2; H, 13.2; N, 9.62; B, 16.4; Ca, 14.8. ^{1}H NMR (C_6D_6, 20 °C): δ 2.89 (s, OMe), 2.73 (s, OCH_2), 2.47 (s, NMe_2), 2.08 (broad 1:1:1:1 q, J_{BH} = 94 Hz, BH_3). ^{11}B NMR (C_6D_6, 20 °C): δ −8.43 (q, J_{BH} = 91.6 Hz). IR (cm^{-1}): 2398 sh, 2307 s, 2231 s, 2080 w, 1265 m, 1233 m, 1213 m, 1179 s, 1151 s, 1104 m, 1058 s, 1019 s, 928 m, 906 w, 862 m, 830 w, 804 m.

Method B. To calcium granules (−6 mesh, 10.0 g, 250 mmol) was added a solution of *N*,*N*-dimethylamine-borane (750 mg, 12.7 mmol) in 1,2-dimethoxyethane (100 mL). The reaction mixture was heated to reflux for 18 h, cooled to room temperature, and then filtered. The solvent was removed under vacuum, and the resulting solid was sublimed at 90 °C under vacuum onto a water-cooled coldfinger. After 18 h, the small colorless prisms were collected. Yield: 345 mg (40%).

Bis(*N*,*N*-dimethylaminodiboranato)[bis(2-methoxyethyl) ether]calcium, $Ca(BH_3NMe_2BH_3)_2(diglyme)$, 5. To a solution of $Ca(DMADB)_2(thf)_2$ (300 mg, 0.915 mmol) in tetrahydrofuran (50 mL) was added bis(2-methoxyethyl) ether (0.15 mL, 1.05 mmol). The mixture was stirred for 12 h, and then the solvent was removed under vacuum. The residue was extracted with hot heptane (50 mL), and the heptane extract was filtered and cooled to −20 °C. After 24 h, the small colorless plates were collected. Yield: 246 mg (85%). Mp. 139 °C. Anal. Calc for $C_{10}H_{38}N_2O_3B_4Ca$: C, 37.8; H, 12.1; N, 8.8; B, 13.6; Ca, 12.6. Found: C, 37.8; H, 12.6; N, 8.8; B, 13.9; Ca, 12.7. ^{1}H NMR (C_6D_6, 20 °C): δ 3.23 (s, OMe), 2.78 (m, OCH_2), 2.58 (s, NMe_2), 2.14 (broad 1:1:1:1 q, J_{BH} = 92 Hz, BH_3), 1.93 (m, OCH_2). ^{11}B NMR (C_6D_6, 20 °C): δ −8.9 (q, J_{BH} = 91.8 Hz). IR (cm^{-1}): 2372 s, 2355 s, 2318 vs, 2300 s, 2261 s, 2222 sh, 2072 w, 1270 m, 1236 m, 1211 m, 1176 s, 1151 s, 1120 m, 1093 s, 1061 s, 1011 s, 928 m, 906 m, 873 m, 836 w, 826 w 808 w.

Bis(*N*,*N*-dimethylaminodiboranato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)calcium, $Ca[BH_3NMe_2BH_3]_2(tmeda)$, 6. To a solution of $Ca(DMADB)_2(thf)_2$ (300 mg, 0.915 mmol) in tetrahydrofuran (50 mL) was added *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.15 mL, 0.98 mmol). The mixture was stirred for 12 h, and then the solvent was removed under vacuum. The residue was extracted with hot heptane (50 mL), and the extracts were filtered and cooled to −20 °C. After 24 h, the small colorless prisms were collected. Yield: 210 mg (77%). Mp. 133 °C. Anal. Calc for $C_{10}H_{40}N_4B_4Ca$: C, 40.1; H, 13.5; N, 18.7; B, 14.4; Ca, 13.3. Found: C, 39.9; H, 13.8; N, 18.7; B, 14.3; Ca, 13.2. ^{1}H NMR (C_6D_6, 20 °C): δ 2.46 (s, NMe_2 of DMADB ligand), 1.93 (s, NMe_2 of tmeda ligand), 1.68 (s, NCH_2). The ^{1}H NMR resonance for the BH_3 groups in **6** is obscured by the resonances due to the tmeda ligand. ^{11}B NMR (C_6D_6, 20 °C): δ −8.88 (q, J_{BH} = 89.5 Hz). IR (cm^{-1}): 2417 sh, 2388 s, 2378 s, 2300 s, 2238 vs, 2076 w, 1285 m, 1268 m, 1232 m, 1210 m, 1178 s, 1148 s, 1122 w, 1070 vw, 1022 s, 949 m, 931 m, 906 w, 804 w, 790 m, 771 w.

Bis(1,4,7,10-tetraoxacyclododecane)calcium *N*,*N*-Dimethylaminodiboranate, $[Ca(12\text{-}crown\text{-}4)_2][BH_3NMe_2BH_3]_2$, 7. To a solution of $Ca(DMADB)_2(thf)_2$ (300 mg, 0.915 mmol) in tetrahydrofuran (50 mL) was added 1,4,7,10-tetraoxacyclododecane (0.30 mL, 1.83 mmol). The solution was stirred for 12 h, and the resulting cloudy solution was heated to 65 °C and filtered while hot. The residue from the hot filtration was extracted with additional hot thf (20 mL). The two filtered extracts were cooled to −20 °C to afford colorless blocks. These colorless blocks contain 2 equiv of thf per formula unit, but drying them under vacuum at 25 °C yields the thf free compound, for which data are given here. Yield: 118 mg (24%). Mp. >240 °C. Anal. Calc for $C_{20}H_{56}N_2O_8B_4Ca$: C, 44.8; H, 10.5; N, 5.2; B, 8.1; Ca, 7.5. Found: C, 44.8; H, 11.0; N, 5.3; B, 7.9; Ca, 7.4. ^{1}H NMR (d_6-dmso, 20 °C): δ 3.54 (s, OCH_2), 2.09 (s, NMe_2), 1.39 (1:1:1:1 q, J_{BH} = 91.0 Hz, BH_3). ^{11}B NMR (d_6-dmso, 20 °C): δ −8.63 (q, J_{BH} = 91.6 Hz). IR (cm^{-1}): 2344 vs, 2271 vs, 2222 vs, 2169 vs, 2062 m, 1300 s, 1286 s,.1243 s, 1178 sh, 1151 s, 1130 m, 1074 vs, 1010 s, 923 s, 854 s, 782 m.

Crystallographic Studies.[51] Single crystals of **2** and **3** were grown from diethyl ether, **4** was grown by sublimation, **5** and **6** were grown from hot heptane, and **7** was grown from thf. All crystals were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and least-squares refinement yielded the cell dimensions given in Table 1. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations (e.s.d.'s) by correction for background, and Lorentz and polarization effects. No corrections for crystal decay were necessary, but a face-indexed absorption correction was applied. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Except where noted all unique data were used in the least-squares refinement.

The structures were solved using direct methods (SHELXTL). Correct positions for all the non-hydrogen atoms were deduced from an E-map and subsequent least-squares refinement and difference Fourier calculations. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and the imaginary components of anomalous dispersion. In the final cycle of least-squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. Hydrogen atoms attached to the boron atoms were located in the difference maps, and their positions were refined with independent isotropic displacement parameters, unless otherwise noted. Chemically equivalent B−H distances were restrained to be equal within an esd of 0.01 Å. Methyl and methylene hydrogens atoms were placed in idealized positions with C−H equal to 0.98 and 0.99 Å, respectively; methyl groups were allowed to rotate about the relevant C−X axes to find the best least-squares positions. The displacement parameters for methylene hydrogens were set equal to 1.2 times U_{eq} for the attached carbon; those for methyl hydrogens were set to 1.5 times U_{eq}. Unless otherwise noted, no correction for isotropic extinction was necessary. Successful convergence was indicated by the maximum shift/error of 0.001 or less for the last cycle. A final analysis of variance between observed and calculated structure factors showed no apparent errors. Final refinement parameters are given in Table 1. Aspects of the refinement unique to each structure are reported in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of experimental details for X-ray diffraction experiments and CIF files for compounds **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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