

Structural and Spectroscopic Studies of Steric and Electronic Substituent Effects in a Series of Magnesium Aminodiborates $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2$

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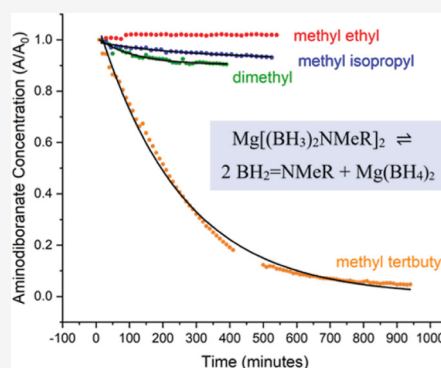
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ABSTRACT: The magnesium *N,N*-dimethylaminodiborate compound $\text{Mg}[(\text{BH}_3)_2\text{NMe}_2]_2$, the most volatile compound of magnesium known, serves as an excellent chemical vapor deposition (CVD) precursor for the growth of thin films such as the dielectric material MgO . To explore how the thermal stability and physical properties of magnesium aminodiborates depend on the steric and electronic properties of the nitrogen-bound substituents, we have made a series of analogues of $\text{Mg}[(\text{BH}_3)_2\text{NMe}_2]_2$, in which one of the two methyl substituents on nitrogen is replaced with an ethyl, *iso*-propyl, or *tert*-butyl group. In the crystal structure of $\text{Mg}[(\text{BH}_3)_2\text{NMe}(t\text{-Bu})]_2$, the magnesium center is coordinated to two chelating $(\text{BH}_3)_2\text{NMe}(t\text{-Bu})$ ligands, each of which binds in a κ^2, κ^2 fashion so that the magnesium center forms eight Mg–H contacts. Unlike $\text{Mg}[(\text{BH}_3)_2\text{NMe}_2]_2$, however, which has a linear $\text{N}\cdots\text{Mg}\cdots\text{N}$ angle and is an isolated molecule in the solid state, the $\text{N}\cdots\text{Mg}\cdots\text{N}$ angle in $\text{Mg}[(\text{BH}_3)_2\text{NMe}(t\text{-Bu})]_2$ is distinctly nonlinear (149.9°) because hydrogen atoms of BH_3 groups of nearby molecules form two additional Mg–H contacts with the magnesium center. When the complexes are heated in toluene solution, the $(\text{BH}_3)_2\text{NMeR}^-$ groups reversibly undergo B–N bond cleavage (with concomitant migration of a hydrogen atom) to release the aminoborane $\text{BH}_2=\text{NMeR}$ and form magnesium borohydride, $\text{Mg}(\text{BH}_4)_2$. For the methyl, ethyl, and *iso*-propyl derivatives, the equilibrium strongly favors $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2$. In contrast, for the *tert*-butyl derivative, the equilibrium strongly favors $\text{BH}_2=\text{NMe}(t\text{-Bu})$ and $\text{Mg}(\text{BH}_4)_2$. The results suggest that more strongly electron-donating groups slightly strengthen the B–N bonds and disfavor B–N bond cleavage, provided that the groups are not too large. In contrast, sterically bulky ligands disfavor B–N bond reformation, thus promoting the dissociative equilibrium that involves B–N bond cleavage. Interestingly, the rates at which the complexes approach equilibrium depend only weakly on the nature of the R group, at least within the series studied. These findings are relevant to the potential use of magnesium aminodiborates as CVD precursors to the superconducting phase MgB_2 .



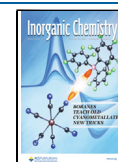
INTRODUCTION

Aminodiborates, $(\text{H}_3\text{B})_2\text{NR}_2^-$, are a class of borohydride anions that contain two BH_3 groups joined by an amido linker. The first aminodiborate salt was reported in 1969, when Keller and coworkers prepared sodium *N,N*-dimethylaminodiborate $\text{Na}(\text{H}_3\text{B})_2\text{NMe}_2$ by treating *N,N*-dimethylaminodiborane, $\text{B}_2\text{H}_5(\text{NMe}_2)$, with NaH in 1,2-dimethoxyethane (dme).¹ In recent years, our group has explored the coordination chemistry of the *N,N*-dimethylaminodiborate anion $(\text{H}_3\text{B})_2\text{NMe}_2^-$, abbreviated DMADB, and have prepared a wide variety of transition metal, alkaline earth, lanthanide, and actinide complexes, many of which are volatile and can be used as precursors for the chemical vapor deposition (CVD) of thin films.^{2–10} As part of these studies, our laboratory has previously reported the synthesis of the DMADB complex $\text{Mg}[(\text{BH}_3)_2\text{NMe}_2]_2$ (**1**), which has the highest vapor pressure at room temperature of any known magnesium compound (0.8 Torr).¹¹ It serves as an excellent CVD precursor to the valuable dielectric material MgO .^{12,13}

The attractive features of metal complexes of the DMADB anion have prompted us to explore the preparation of magnesium complexes of other aminodiborate anions bearing a variety of substituents on nitrogen, which we have previously synthesized as sodium salts.¹⁴ Varying the groups on the nitrogen atom may enable the preparation of new magnesium CVD precursors with greater volatility and improved reaction characteristics compared to $\text{Mg}(\text{DMADB})_2$. Tuning the physical and chemical properties of a CVD precursor by varying substituents has often led to improved CVD processes.^{15–18}

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Here, we report the synthesis of a series of $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2$ complexes, in which one of the two methyl substituents in $\text{Mg}(\text{DMADB})_2$ is replaced with an ethyl, *iso*-propyl, or *tert*-butyl group, with the goal of determining how varying the groups on the nitrogen atom alters the thermal properties and volatilities of the magnesium aminodiborane complexes. We find that, when heated in toluene solution, the compounds undergo reversible cleavage of a B–N bond, concomitant with a hydrogen transfer, to produce the neutral aminoborane $\text{BH}_2=\text{NMeR}$ and an insoluble material, magnesium borohydride $\text{Mg}(\text{BH}_4)_2$. We provide an analysis of the steric and electronic factors that affect both the value of the equilibrium constant and the rate at which it is established. These findings are relevant to the potential use of magnesium aminodiborates as CVD precursors to the superconducting phase MgB_2 .¹⁹

RESULTS AND DISCUSSION

Synthesis and Characterization of Magnesium Aminodiborates. As we have previously reported,¹¹ the solid-state reaction of MgBr_2 and sodium *N,N*-dimethylaminodiborane, $\text{Na}(\text{H}_3\text{B})_2\text{NMe}_2$, at room temperature followed by sublimation affords the volatile compound $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}_2]_2$, **1**, in good yield. We now find that this method can be extended to the preparation of three new magnesium aminodiborates, in which one of the two methyl groups in DMADB is replaced with an ethyl, *iso*-propyl, or *tert*-butyl group: $\text{Mg}[(\text{H}_3\text{B})_2\text{NMeEt}]_2$ (**2**), $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(i\text{-Pr})]_2$ (**3**), and $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$ (**4**). The compounds containing ethyl and *iso*-propyl groups, **2** and **3**, are liquids at room temperature and are best purified by vacuum distillation (60–70 °C, 10 mTorr). The *tert*-butyl compound **4** is a solid and can be purified by sublimation at 60 °C under moderate vacuum. For reasons we do not fully understand, the yield of **3** is low (and sometimes zero).

Spectroscopic Characterization of the New Compounds. The ¹¹B NMR spectra of **1**–**4** each consist of a 1:3:3:1 quartet at δ –11.82, –13.24, –14.08, and –14.80, respectively, with ¹J_{BH} coupling constants of about 90 Hz. For the corresponding sodium salts, electron-donating substituents on the nitrogen atom deshield the ¹¹B NMR shift, whereas sterically bulky substituents shield the ¹¹B NMR shift;¹⁴ these empirical trends also appear to apply to the magnesium compounds. The ¹H NMR spectra are as expected (see the Experimental Section).

The IR spectra of magnesium,¹¹ calcium,⁸ strontium,⁹ and barium² aminodiborane complexes generally contain two strong B–H stretching bands (or groups of bands), one between 2375 and 2500 cm^{–1} due to stretches of terminal B–H bonds and one near 2200 cm^{–1} due to stretches of B–H bonds that bridge to the metal center. Similarly, the IR spectra of **2** and **4** (see the Experimental Section) feature strong bands near 2450 and 2200 cm^{–1} that closely resemble those we saw previously for **1**.

Molecular Structure of $\text{Mg}[(\text{BH}_3)_2\text{NMe}(t\text{-Bu})]_2$. The molecular structure of the methyl/*tert*-butyl compound **4** is presented in Figure 1; crystallographic data and selected bond distances and angles are listed in Tables 1 and 2. Before we discuss the structure of **4**, we briefly summarize the previously determined structure of the dimethyl compound **1**: in this species, the chelating $(\text{BH}_3)_2\text{NMe}_2^-$ ligands are each bound in a κ^2, κ^2 fashion, so that the Mg center is bound to eight hydrogen atoms.¹¹ The N···Mg···N angle is linear (180°), and

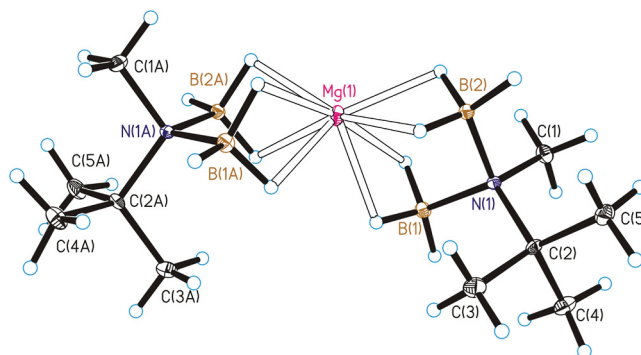


Figure 1. ORTEP representation of $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$, **4**, drawn at the 35% probability level except for hydrogen atoms, which are depicted as arbitrarily sized spheres. This diagram omits the two intermolecular Mg–H bonds, as shown in Figure 2.

the planes of the two B–N–B ligand backbones describe a dihedral angle of 46.7(1)°. This dihedral angle is a consequence of the arrangement of the eight hydrogen atoms attached to Mg, which can be described as a distorted square antiprism (in an ideal square antiprism, this dihedral angle would be exactly 45°). The distorted square antiprismatic geometry is adopted because it best minimizes interligand H···H repulsion among the eight Mg-bound hydrogen atoms.

Like **1**, the magnesium center in the methyl/*tert*-butyl compound **4** is coordinated to two chelating $(\text{BH}_3)_2\text{NMe}(t\text{-Bu})^-$ ligands, each of which binds in a κ^2, κ^2 fashion so that the magnesium center forms eight Mg–H contacts; the Mg–H bond distances range between 2.006(15) and 2.151(16) Å. In contrast, however, the N···Mg···N angle in **4** is distinctly nonlinear [149.93(5)°], and the dihedral angle between the two B–N–B planes is 66.68(10)°. The nonlinearity is the result of the formation of two longer Mg–H contacts (ca. 2.5 Å in length) with hydrogen atoms of BH_3 groups on nearby molecules (Figure 2). Additional distortions of the structure of **4** due to the presence of the sterically bulky *tert*-butyl groups can be seen in the geometry of the ligand itself. In compound **1**, the geometry around the N atom of the ligand is a nearly perfect tetrahedron in which all angles are very close to 109.5°. In contrast, in **4**, the geometry around the N atom of the ligand is distorted from tetrahedral: steric repulsions involving the *tert*-butyl group cause both C1–N1–B angles to be 113°, or several degrees larger than expected.

Thermolysis in Toluene. To determine how the thermal properties of magnesium aminodiborates (and their suitabilities as CVD precursors) change when the substituents on nitrogen are varied, we conducted a series of ¹¹B NMR studies in toluene, in which compounds **1**–**4** were heated to 77 °C. We chose toluene as a solvent because ethers such as THF coordinate to magnesium and will change the reaction chemistry in such a way as to be not relevant to CVD conditions. In addition, THF is prone to ring-opening reactions in the presence of boranes, which would skew the results of the thermolysis experiments.

The observed thermolysis products (Figure 3) are the neutral aminoborane $\text{BH}_2=\text{NR}_2$ and the borohydride $\text{Mg}(\text{BH}_4)_2$, corresponding to the following balanced reaction: $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2 \rightleftharpoons 2 \text{BH}_2=\text{NMeR} + \text{Mg}(\text{BH}_4)_2$. The latter compound is relatively insoluble in toluene and largely precipitates from solution. The formation of these products

Table 1. Crystallographic Data for $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$, **4**

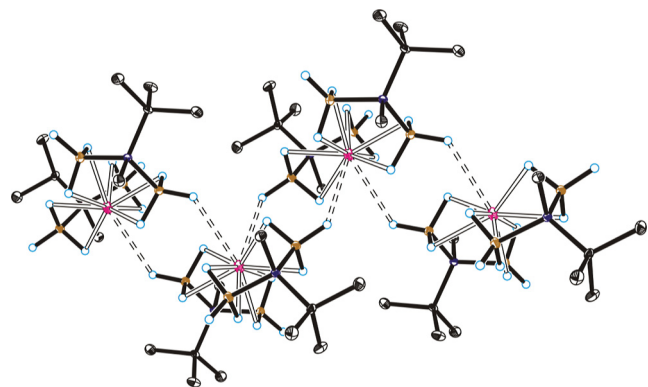
formula	$\text{MgN}_2\text{B}_4\text{C}_{10}\text{H}_{36}$	μ (mm^{-1})	0.090
formula wt	251.96	$F(000)$	568
temp (K)	100	crystal size (mm)	$0.299 \times 0.187 \times 0.036$
λ (deg)	0.71073	θ range (deg)	25.07–2.18
cryst sys	orthorhombic	R_{int}	0.0629
space group	$Pbcn$	abs corr type	multi-scan
a (Å)	19.6270(9)	max, min trans fact	0.6719, 0.7452
b (Å)	10.6290(5)	data/restrs/params	1496/0/150
c (Å)	7.8110(4)	GOF on F^2	1.019
V (Å ³)	1629.49(14)	$R_1[F_o > 4\sigma(F_o)]^a$	0.0358
Z	4	wR_2 (all data) ^b	0.0992
ρ_{calc} (g cm^{-3})	1.027	max, min $\Delta\rho$ (e Å^{-3})	0.27, −0.19

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

Table 2. Selected Bond Distances and Angles for $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$, **4**^a

bond distances (Å)			
Mg(1)–B(1)	2.4059(16)	N(1)–B(1)	1.5888(19)
Mg(1)–B(2)	2.4954(17)	N(1)–B(2)	1.6065(19)
Mg(1)–H(1A)	2.006(15)	B(1)–H(1A)	1.164(15)
Mg(1)–H(1B)	2.068(15)	B(1)–H(1B)	1.126(14)
Mg(1)–H(2F)	2.067(14)	B(2)–H(2F)	1.135(15)
Mg(1)–H(2E)	2.151(16)	B(2)–H(2E)	1.126(17)
Bond Angles (deg)			
B(1)′–Mg(1)–B(1)	141.90(8)	C(1)–N(1)–C(5)	110.33(11)
B(1)–Mg(1)–B(2)	106.84(3)	C(5)–N(1)–B(1)	107.05(11)
B(1)′–Mg(1)–B(2)	54.82(8)	C(5)–N(1)–B(2)	107.03(11)
C(1)–N(1)–B(1)	113.06(10)	B(1)–N(1)–B(2)	105.57(11)
C(1)–N(1)–B(2)	113.39(10)		

^aSymmetry transformations used to generate equivalent atoms: ′ = 1 − x , y , 1/2 − z .

**Figure 2.** ORTEP representation of the intermolecular interactions between magnesium and nearby hydrogen atoms of BH_3 groups in $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$, **4**, drawn at the 35% probability level except for hydrogen atoms, which are depicted as arbitrarily sized spheres.

involves cleavage of one of the N–B bonds, along with transfer of a hydrogen atom from one BH_3 unit to the other.

The aminoborane $\text{BH}_2=\text{NMeR}$ exists in solution as a mixture of the monomer and the cyclic dimer, which appear as triplets in the ^{11}B NMR spectrum at ca. δ 0–5 and 37, respectively (although the two hydrogen atoms in the BH_2 groups are inequivalent when $\text{R} \neq \text{Me}$, the triplet line shape results because the two B–H coupling constants are nearly identical). The monomer/dimer ratio in solution depends on the steric bulk of the R group, with $\text{R} = \text{Me}$ existing mostly as the dimer and $\text{R} = t\text{-Bu}$ mostly as the monomer. For $\text{R} = \text{Pr}$, the monomer and dimer are present in approximately equal

concentrations at equilibrium; because the two groups on nitrogen are different, the dimer exists as a mixture of cis and trans isomers in an approximately 1:2 ratio (two overlapping triplets are seen near δ 5). For $\text{R} = t\text{-Bu}$, only the trans isomer of the dimer is present in solution (one triplet near δ 0); presumably, the cis isomer is disfavored sterically.

Interestingly, the position of the $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2 \rightleftharpoons 2 \text{BH}_2=\text{NMeR} + \text{Mg}(\text{BH}_4)_2$ equilibrium depends strongly on the R groups bound to nitrogen (Figure 4). At equilibrium (which is established within about 10 h at 77 °C), no measurable dissociation is observed for **2**, and only small amounts of $\text{BH}_2=\text{NMeR}$ and $\text{Mg}(\text{BH}_4)_2$ are generated for compounds **1** and **3**, which remain almost completely in the aminodiborane form. In contrast, **4** dissociates almost completely to $\text{BH}_2=\text{NMeR}$ and $\text{Mg}(\text{BH}_4)_2$. For **4**, the total concentration of boron in solution, as measured by adding together the integrals of all the ^{11}B NMR peaks, decreases as heating is continued: at equilibrium, 48% of the initial boron remains in solution, the “missing” boron having precipitated as $\text{Mg}(\text{BH}_4)_2$. This percentage agrees well with our finding that, for $\text{R} = t\text{-Bu}$, the equilibrium $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2 \rightleftharpoons 2 \text{BH}_2=\text{NMeR} + \text{Mg}(\text{BH}_4)_2$ lies almost fully on the right: 50% of the total boron should precipitate from solution as $\text{Mg}(\text{BH}_4)_2$.

To obtain additional information about the rates of N–B bond cleavage and reformation, we fit the aminodiborane concentration versus time curves in Figure 4 to an “approach to equilibrium” rate equation, which was derived as described by Espenson²⁰ with a couple of simplifying assumptions. These thermolysis reactions involve an equilibrium of the form: $\text{A} \rightleftharpoons \text{B} + \text{C}$, where A is the $(\text{BH}_3)_2\text{NMeR}^-$ anion, B is the $\text{BH}_2=$

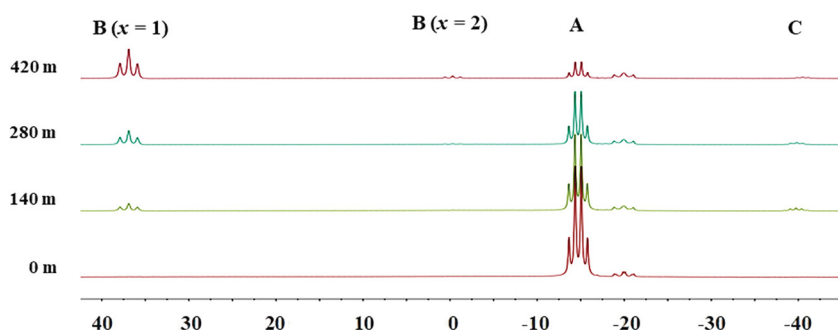


Figure 3. ^{11}B NMR spectra showing the thermolysis of $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$, **4**, at 77°C over the first 420 min. The aminodiboranate (A) converts into the aminoborane (B), which exists in solution as a mixture of monomer and dimer, and borohydride (C). Most of the borohydride precipitates from solution, which accounts for the small intensity of the signal for C. The same products are observed in the thermolysis of **1** and **3**, except that the thermolysis does not proceed to completion but instead proceeds only partway and approaches an equilibrium.

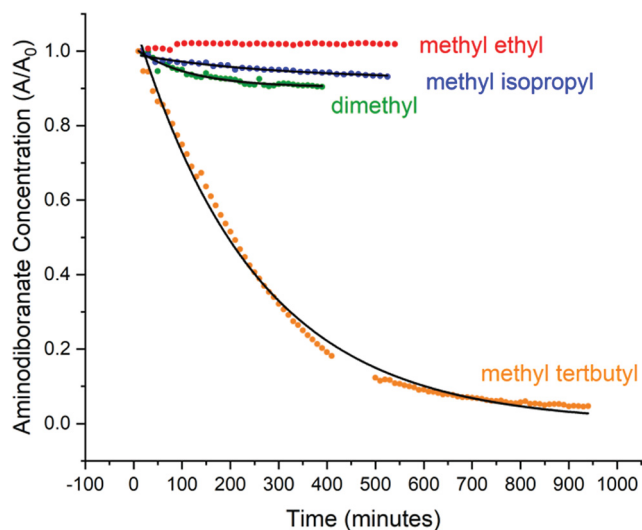


Figure 4. Plot showing change in aminodiboranate concentration vs time for compounds **1**–**4** monitored by ^{11}B NMR spectroscopy. The fits of the data to eq 1 are shown by the solid black curves, except for the methyl–ethyl compound, which showed no detectable approach to equilibrium.

NMeR , and C is the BH_4^- anion. Here, we are expressing the equilibrium in terms of the ligands (rather than the magnesium complexes), so that the balanced reaction is $(\text{BH}_3)_2\text{NMeR}^- \rightleftharpoons \text{BH}_2=\text{NMeR} + \text{BH}_4^-$. This choice, which simplifies the analysis, views the solution as consisting of aminodiboranate ligands and their thermolysis products, with the magnesium ions serving only to balance charge. This view reflects the expectation that the magnesium aminodiboranate complexes undergo intermolecular ligand exchange at rates that are rapid relative to the rate at which the equilibria are established (the thermolysis reactions take many hours to come to equilibrium, and so this assumption seems quite reasonable).

We also assume that the monomeric and dimeric forms of $\text{BH}_2=\text{NMeR}$ are exchanging with one another rapidly compared with the rate at which the thermolysis reactions are taking place, so that the concentration of $\text{BH}_2=\text{NMeR}$, $[\text{B}]$, can be considered as equal to the sum of the monomer concentration and twice the dimer concentration. This assumption seems to be reasonable for two reasons. The rate of dimerization of $\text{BH}_2=\text{NMe}_2$ is $1.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at room temperature;²¹ although the temperature dependence of this rate was not measured, a reasonable extrapolation suggests that

at 77°C , the dimerization rate will be faster than the rates of thermolysis observed for the compounds in this study. In addition, although the monomer $\text{BH}_2=\text{NMeR}$ is likely the initial product of the thermolysis reaction, the dimer is the dominant species in solution even at early times (i.e., within the first 40 min of the thermolysis of **1**).

We make two additional assumptions to simplify the kinetic analysis. Because $\text{Mg}(\text{BH}_4)_2$ has little to no solubility in toluene even at 77°C (see above), its concentration in solution at equilibrium is at its solubility limit and thus is a constant. Therefore, we can assume that the equilibrium constant that governs the thermolysis can be expressed as $K_{\text{eq}} = [\text{B}]/[\text{A}]$, in which the concentration of the borohydride anion, $[\text{C}]$, is subsumed into the equilibrium constant K_{eq} . Finally, we assume that the concentration of the aminoborane, $[\text{B}]$, is zero at time t equals 0 (i.e., before heating), as we have confirmed spectroscopically.

Under these assumptions, the concentration of the aminodiboranate anion, $[\text{A}]$, has the following time dependence (eq 1)

$$[\text{A}]_t = [\text{A}]_0 [k_1 e^{-(k_1+k_{-1})t} + k_{-1}] / (k_1 + k_{-1}) \quad (1)$$

where k_1 and k_{-1} are the forward and backward rate constants for the equilibrium $(\text{BH}_3)_2\text{NMeR}^- \rightleftharpoons \text{BH}_2=\text{NMeR} + \text{BH}_4^-$. This expression fits the observed concentration dependences reasonably well (Figure 4). Details of the curve fits and the derivation of eq 1 can be found in the Supporting Information (Figures S11–S13).

The forward and reverse rate constants obtained from the curve fits are listed in Table 3. Interestingly, the forward rate constants k_1 are similar (equal to within 1 order of magnitude), whereas the reverse rate constants k_{-1} differ by more than 2 orders of magnitude. These results demonstrate that the steric bulk of the N -substituents only weakly affects the rate at which

Table 3. Forward and Reverse Rate Constants for the Thermolyses of **1**–**4** in Toluene at 77°C

compound	k_1 (min^{-1}) at 77°C	k_{-1} (min^{-1}) at 77°C	mole fraction of $\text{Mg}(\text{BH}_4)_2$ at equilibrium at 77°C
dimethyl (1)	10×10^{-4}	80×10^{-4}	0.10
methyl/ethyl (2)			0
methyl/ <i>iso</i> -propyl (3)	2×10^{-4}	30×10^{-4}	0.08
methyl/ <i>tert</i> -butyl (4)	40×10^{-4}	$<0.1 \times 10^{-4}$	1.00

the B–N bonds are cleaved (and H atom transfer occurs) but strongly affects the rate of recombination of the aminoborane and borohydride products to regenerate the aminodiboranate starting material. In this way, sterically bulky groups on nitrogen, as observed in **4**, strongly favor the dissociation reaction and breaking the B–N bond.

Although **1** dissociates measurably to $\text{Mg}(\text{BH}_4)_2$ and $(\text{BH}_2=\text{NMR})_x$, the methyl/ethyl compound **2** does not despite the ethyl group being more sterically bulky than the methyl group. We propose that this behavior is an electronic effect: the more strongly donating ethyl group strengthens the B–N bond and therefore disfavors dissociation but is not bulky enough for steric effects to overcome this electronic strengthening. The methyl/*iso*-propyl compound **3** does dissociate (to an extent similar to **1**), suggesting that the increased steric bulk of the *iso*-propyl group favors dissociation despite its slightly stronger donor strength. We can conclude that, in these thermolysis reactions, there is a competition between electronic and steric effects with the latter playing a small role until the groups become very large, as in the methyl/*tert*-butyl compound **4**.

Finally, we address the question whether the low solubility of $\text{Mg}(\text{BH}_4)_2$ in toluene is driving the reactions we see by Le Chatelier's principle, and whether there is actual evidence that the thermolysis reactions are reversible. If the reactions were being driven forward by the low solubility of $\text{Mg}(\text{BH}_4)_2$, we would expect all four of the compounds we studied to thermolyze completely to $\text{BH}_2=\text{NMeR}$ and $\text{Mg}(\text{BH}_4)_2$ but they do not (only compound **4** does). Furthermore, the ability to obtain good fits of the time-dependent concentration curves to an approach-to-equilibrium kinetic expression is strong evidence of the reversibility of these thermolysis reactions under the conditions studied.

CONCLUSIONS

We have synthesized a series of new magnesium aminodiboranates of the form $\text{Mg}[(\text{BH}_3)_2\text{NMeR}]_2$, in which one of the two methyl substituents in $\text{Mg}(\text{DMADB})_2$ is replaced with an ethyl (**2**), *iso*-propyl (**3**), or *tert*-butyl (**4**) substituent. Compounds **2** and **3** are liquids at room temperature and can be distilled under vacuum at moderate temperatures and pressures, which is advantageous for use as CVD precursors. The structure of compound **4**, as determined crystallographically, shows that the geometry about the N atom is significantly distorted from tetrahedral, probably due to packing effects which promote weak intermolecular interactions.

Thermolysis studies of this series of magnesium aminodiboranates show that in solution, an equilibrium is established that involves cleavage of a B–N bond (and hydride transfer) to generate the aminoborane $\text{BH}_2=\text{NMeR}$ and borohydride. The equilibrium constant for this process depends strongly on the R groups bound to nitrogen in the aminodiboranate ligand. Calculated rate constants determined by fitting the thermolysis data with an “approach to equilibrium” rate equation show the steric bulk of the substituents on nitrogen only slightly affects the barrier for B–N bond cleavage and hydride transfer (k_1) but sterically bulky substituents strongly increase the barrier for reformation of the B–N bond (k_{-1}). When steric factors are small, stronger electron donors lead to stronger B–N bonds and less extensive B–N bond cleavage at equilibrium (we assume here that the energetics associated with the hydrogen-transfer step do not depend significantly on the

nature of the substituents attached to nitrogen). We conclude that magnesium aminodiboranates with sterically bulky substituents on nitrogen (especially *tert*-butyl groups) may be useful for the low-temperature growth of MgB_2 films because they significantly increase the extent to which B–N bond cleavage occurs upon heating.

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. MgBr_2 was used as received from Aldrich. Sodium aminodiboranate salts were synthesized following previously reported procedures.^{14,22} Magnesium dimethylaminodiboranate, **1**, was synthesized by the previously reported procedure.¹¹ Microanalyses were performed by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Nicolet Impact 410 instrument as Nujol mulls between KBr plates. The ^1H and ^{11}B NMR spectra were collected on a Varian Unity Inova 400 MHz spectrometer. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to tetramethylsilane (^1H NMR) or $\text{BF}_3\cdot\text{Et}_2\text{O}$ (^{11}B NMR).

Bis(*N*-methyl-*N*-ethylaminodiboranato)magnesium, $\text{Mg}[(\text{H}_3\text{B})_2\text{NMeEt}]_2$ (2**).** A mixture of $\text{Na}[(\text{H}_3\text{B})_2\text{NMeEt}]$ (1.24 g, 11 mmol) and MgBr_2 (1.03 g, 5.5 mmol) was ground briefly in a mortar and then added to a Schlenk flask containing ca. 30 stainless-steel ball bearings (4.5 mm diameter). The solid mixture was gently agitated for 45 min during which time it became sticky. The reaction mixture was extracted with toluene (2×35 mL), the extract was filtered, and the toluene was removed from the filtrate under vacuum to give a viscous brown oil. The brown oil was distilled under vacuum at 60 °C and 10 mTorr giving a clear, colorless liquid. Yield: 0.328 g (30.5%). Anal. Calcd. For $\text{MgN}_2\text{B}_4\text{C}_6\text{H}_{28}$: C, 36.8; H, 14.4; N, 14.3. Found: C, 36.0; H, 14.0; N, 14.5. ^1H NMR (toluene- d_8): δ 0.84 (t, $^2J_{\text{HH}} = 7.3$ Hz, 3H, CMe), δ 1.80 (1:1:1:1 q, $^1J_{\text{BH}} = 90$ Hz, 6H, BH_3), δ 1.95 (s, 3H, NMe), δ 2.30 (q, $^2J_{\text{HH}} = 7.3$ Hz, 2H, N–CH $_2$). ^{11}B NMR (toluene- d_8): δ –13.24 (q, $^1J_{\text{BH}} = 90$ Hz). IR (cm $^{-1}$): 2443 s, 2356 w, 2293 w, 2254 w, 2198 s, 2159 w, 2081 w, 1385 w, 1321 w, 1313 m, 1207 w, 1174 s, 1147 s, 1097 w, 1051 w, 1028 m, 939 w, 906 w, 816 w, 795 w, 523 w.

Bis(*N*-methyl-*N*-(*iso*-propyl)aminodiboranato)magnesium, $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(i\text{-Pr})]_2$ (3**).** A mixture of $\text{Na}[(\text{H}_3\text{B})_2\text{NMe}(i\text{-Pr})]$ (0.60 g, 5 mmol) and MgBr_2 (0.49 g, 2.6 mmol) was ground briefly in a mortar and pestle and then added to a Schlenk flask charged with ca. 30 stainless-steel ball bearings (4.5 mm diameter). The mixture was gently agitated for 30 min, during which time the solids became sticky. The mixture was extracted with toluene (30 mL), the extracts were filtered, and the toluene was removed from the filtrate under vacuum to afford a viscous brown oil. Distillation of the brown oil under vacuum at 70 °C and 10 mTorr gave a clear, colorless oil. Yield: ca. 10%. ^1H NMR (toluene- d_8): δ 0.95 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, CMe_2), 1.80 (1:1:1:1 q, $^1J_{\text{BH}} = 90$ Hz, 6H, BH_3), 1.98 (s, 3H, NMe), 2.58 (septet, $^3J_{\text{HH}} = 6.6$ Hz, 1H, CH). ^{11}B NMR (toluene- d_8): δ –14.08 (q, $^1J_{\text{BH}} = 90$ Hz). The yield for this reaction was both low and inconsistent, with the reaction sometimes yielding no isolable product. As a result, microanalytical data were not obtained, but the identity of the compound was fully established from its NMR spectra.

Bis(*N*-methyl-*N*-(*tert*-butyl)aminodiboranato)magnesium, $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]_2$ (4**).** A mixture of $\text{Na}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})]$ (1.25 g, 9 mmol) was ground briefly in a mortar and pestle with MgBr_2 (0.79 g, 4.2 mmol) and then added to a Schlenk flask with ca. 30 stainless-steel ball bearings (4.5 mm diameter). The solid mixture was gently agitated for 30 min during which time it became sticky. The reaction was extracted with toluene (3×30 mL), and the toluene was removed from the filtrate under vacuum giving a white solid. Sublimation at 70 °C and 5 mTorr gave the product as colorless crystals. Yield: 0.460 g (40%). Anal. Calcd. For $\text{MgN}_2\text{B}_4\text{C}_{10}\text{H}_{36}$: C, 47.7; H, 14.4; N, 11.12. Found: C, 47.3; H, 14.88; N, 11.05. ^1H NMR (toluene- d_8): δ 1.12 (s, 9H, CMe), δ 1.90 (1:1:1:1 q, $^1J_{\text{BH}} = 89$ Hz, 6H, BH_3), δ 2.14 (s, 3H, NMe). ^{11}B NMR (toluene- d_8): δ –14.80 (q,

$J_{\text{BH}} = 89 \text{ Hz}$). IR (cm^{-1}): 2454 m, 2412 s, 2295 m, 2225 s, 1346 w, 1237 w, 1200 w, 1176 w, 1163 w, 1142 m, 1096 w, 1024 w, 948 w, 842 w, 805 w, 758 w, 723 w.

Thermolysis Studies. Samples were sealed in NMR tubes under vacuum in toluene- d_8 and heated in an NMR probe to 77 °C; the temperature was autocalibrated by spectrometer software using neat ethylene glycol. Concentrations were measured by integration of the ^{11}B NMR resonances in 10 or 15 min intervals for a total of 400–940 min.

Crystallographic Studies. Single crystals of $\text{Mg}[(\text{H}_3\text{B})_2\text{NMe}(t\text{-Bu})_2]_2$, **4**, grown by sublimation, were mounted on Nylon loops with Krytox oil (DuPont) and immediately cooled to 100 K in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and least squares refinement using 4253 reflections yielded the cell dimensions given in Table 1.

Data were collected with an area detector by using the measurement parameters listed in Table 1. The systematic absences $0kl$ ($k \neq 2n$), $h0l$ ($l \neq 2n$), and $hk0$ ($h + k \neq 2n$) were consistent with the space group $Pbcn$, and this choice was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. No corrections for crystal decay were necessary, but a face-indexed absorption correction was applied, the minimum and maximum transmission factors being 0.6719 and 0.7452. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All 1496 unique data were used in the least squares refinement.

The structure was solved by direct methods (SHELXTL). Correct positions for all the non-hydrogen atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0503P)^2 + 0.7296P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and 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 were located in the difference maps, and their positions were refined with independent isotropic displacement parameters. No correction for isotropic extinction was necessary. Successful convergence was indicated by the maximum shift/error of 0.000 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map ($0.27 \text{ e}\text{\AA}^{-3}$) was located $0.74 \text{ \AA}$ from N1. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c03963>.

NMR spectra, NMR spectra of the thermolysis reactions, derivation of approach to equilibrium rate equation, thermolysis curves and line fittings, and IR spectra (PDF)

Accession Codes

CCDC 2218359 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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