

Sodium Aminodiborates $\text{Na}(\text{H}_3\text{BNR}_2\text{BH}_3)$: Structural and Spectroscopic Studies of Steric and Electronic Substituent Effects

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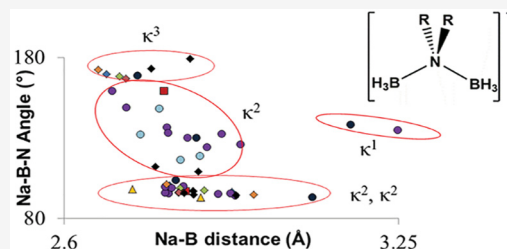


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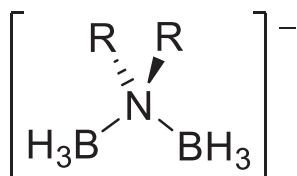
Supporting Information

ABSTRACT: We describe the syntheses of a series of sodium aminodiborate salts, $\text{Na}(\text{H}_3\text{B}-\text{NR}_2-\text{BH}_3)$, with different substituents on nitrogen, including sodium salts of the unsubstituted aminodiborate, $\text{H}_3\text{B}-\text{NH}_2-\text{BH}_3^-$, and of the N-substituted anions $\text{H}_3\text{B}-\text{NRR}'-\text{BH}_3^-$, where $\text{NRR}' = \text{NHMe}$, NHet , $\text{NH}(\text{SiMe}_3)$, NET_2 , $\text{N}(i\text{-Pr})_2$, $\text{N}(\text{SiMe}_3)_2$, $\text{NMe}(i\text{-Pr})$, $\text{NMe}(t\text{-Bu})$, $\text{NMe}(\text{SiMe}_3)$, and the pyrrolidine and piperidine derivatives NC_4H_8 , NC_5H_{10} , and $\text{NC}_5\text{H}_8\text{-cis-2,6-Me}_2$. The compounds have been characterized by ^1H and ^{11}B NMR spectroscopy and IR spectroscopy; crystallographic studies have been carried out for the unsolvated *N,N*-dimethylaminodiborate salt $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ and several sodium aminodiborate salts in which the sodium ions are solvated with ethers (dioxane, diglyme, tetrahydrofuran, and 12-crown-4) or amines (*N,N,N',N'*-tetramethylethylenediamine). One of the structures contains a rare example of an ether ligand in which one oxygen atom bridges between two metal ions. General structural and spectroscopic trends as a function of the substituents on nitrogen are discussed.



INTRODUCTION

Aminodiborates, $\text{H}_3\text{B}-\text{NR}_2-\text{BH}_3^-$, 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 $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ by treating dimethylaminoborane, $(\text{NMe}_2)_2\text{B}_2\text{H}_5$, with NaH in 1,2-dimethoxyethane (dme).¹ In 1999, Nöth and Thomas developed an alternative synthesis of $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ that entails heating solutions of dimethylamine–borane, $\text{HNMe}_2\cdot\text{BH}_3$, over Na metal.² Nöth and Thomas's method is advantageous in that $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ can be prepared on large scales (> 25 g) in one step from commercially available starting materials.

In recent years, our group has explored the coordination chemistry of the *N,N*-dimethylaminodiborate anion $\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3^-$, abbreviated DMADB. In particular, we have shown that DMADB can be used to prepare 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.^{3–11}

The attractive features of metal complexes of the DMADB anion have prompted us to explore the preparation of sodium salts of other aminodiborate anions. Varying the groups on the nitrogen atom may enable the preparation of new CVD precursors with greater volatility and improved reaction characteristics compared to the DMADB analogs. Here, we report that Nöth and Thomas's method can be extended to prepare sodium salts of a variety of aminodiborate anions with hydrogen or alkyl substituents attached to nitrogen, provided that the alkyl group(s) is sterically relatively small (such as ethyl). In contrast, we find that aminodiborate salts with bulky alkyl or silyl groups (such as *iso*-propyl or trimethylsilyl) are best prepared by Keller's method. We also report single-crystal X-ray diffraction studies of several sodium aminodiborate salts and their adducts with various ethers and tertiary amines.

RESULTS AND DISCUSSION

$\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ and Its Lewis Base Adducts. As mentioned in the Introduction, the salt $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ (1) can be made by both Keller's method¹ and by Nöth and Thomas's method.² We have found that crystals of solvent-free

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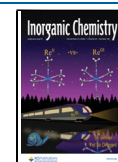


Table 1. Selected Distances (Å) for NaDMADB and Its Adducts

	1 ^b	1a	1b	1c	1d
Na...B	2.693(2)	2.851(2)	2.8648(17)	2.794(2)	
	2.7995(19)		2.7327(16)	2.829(2)	
	2.802(2)			2.837(2)	
	2.9068(19)				
Na-L ^a		2.3638(14)	2.4943(10)	2.4767(14)	2.454(3)
			2.3715(9)	2.4937(14)	2.457(3)
			2.5394(9)		2.464(3)
			2.6546(9)		2.475(3)
					2.496(3)
					2.496(3)
					2.497(3)
					2.556(3)
Na-H	2.278(15)	2.484(16)	2.517(13)	2.433(15)	
	2.320(15)		2.514(15)	2.524(15)	
	2.502(16)		2.309(13)	2.592(15)	
	2.387(15)		2.352(14)	2.472(16)	
	2.541(16)			2.467(14)	
	2.260(15)				
	2.511(16)				
	2.143(15)				
Na...Na	4.1417(12)		4.0501(10)	3.9234(11)	
	4.1648(11)				
ref	this work	this work	this work	this work	this work

^aL = O for 1a, 1b, and, 1d; L = N for 1c. ^bDistances for NaI only.

Table 2. Selected Distances (Å) for Sodium Aminodiboranate Salts and Their Adducts

	3a	4a	6a	7a	8a	9	12
Na...B	2.8503(13)	2.822(4)	2.926(2)	2.666(3)	2.872(4)	2.7490(10)	2.7426(10)
	2.9341(14)	2.823(3)	2.805(3)	2.799(3)	2.707(4)	2.7852(9)	2.8174(110)
	2.8603(13)	2.720(3)	2.862(2)	2.968(3)	2.825(4)	2.8258(10)	2.8573(10)
	2.7694(14)					2.8645(10)	3.0821(11)
	2.8509(13)						3.1569(11)
	2.8335(14)						
	2.7766(14)						
	2.8449(13)						
Na-O	2.3346(9)	2.362(2)	2.380(1)	2.3816(17)	2.341(2)		
	2.3354(8)	2.3333(18)	2.367(1)	2.4179(17)	2.307(2)		
Na-H	2.505(11)	2.436(19)	2.44(2)	2.49(2)	2.38(4)	2.334(12)	2.373(12)
	2.603(12)	2.46(2)	2.62(2)	2.623(19)	2.41(3)	2.302(12)	2.407(12)
	2.472(11)	2.53(2)	2.37(2)	2.401(19)	2.44(3)		2.403(12)
	2.502(12)	2.40(2)	2.46(2)		2.56(3)		
	2.338(11)						
	2.354(11)						
	2.595(12)						
	2.410(11)						
	2.524(12)						
Na...Na	3.8365(8)	3.7916(18)	3.7700(19)	3.8912(18)	3.844(2)	3.8056(6)	3.8540(7)
	3.8072(8)						
ref	12	12	this work	12	this work	this work	this work

$\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ can be obtained by crystallization from Et_2O . X-ray crystallographic data are given in Table S1, and selected bond distances and angles are given in Tables 1 and 2.

Unsolvated **1** crystallizes as a complex ionic polymer with 16 formula units per cell (4 per asymmetric unit) (Figure 1). Each

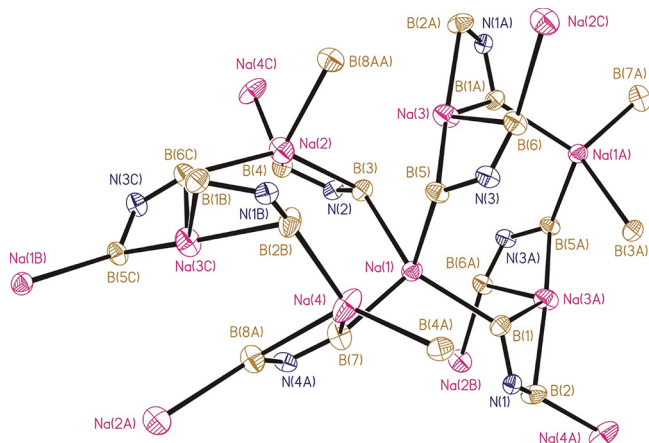
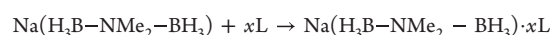


Figure 1. ORTEP representation of a portion of the structure of polymeric $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$, **1**. Ellipsoids are drawn at the 35% probability level. Hydrogen and carbon atoms have been omitted for clarity.

Na ion has a unique coordination environment and every boron atom forms contacts with two sodium atoms. For two of the aminodiboranate anions in the asymmetric unit, the two boron atoms make contact with four different sodium ions (we will call these anions “bridging”); for the other two anions, the two boron atoms make contact with the same sodium ion (we will call these aminodiboranate anions “chelating”) and also form separate contacts to two other sodium ions.

The sodium ions all form contacts with four BH_3 groups, but in different ways. Sodium ion Na1 is coordinated to one BH_3 group of four different bridging anions, sodium ions Na2 and Na4 are coordinated to one chelating aminodiboranate anion and one BH_3 group of two different bridging anions, and sodium ion Na3 is chelated by two anions. Of the 16 unique $\text{Na}\cdots\text{B}$ contacts, 14 of them range from 2.693(2) to 2.933(2) Å (the wide range will be discussed in more detail below), and the locations of the hydrogen atoms suggest that these $\text{Na}\cdots\text{B}$ interactions are bridged by two hydrogen atoms (Table S2). In contrast, the $\text{Na}(3)\cdots\text{B}(3)$ and $\text{Na}(4)\cdots\text{B}(8\text{A})$ contacts have longer distances of 3.249(2) and 3.058(7) Å, and the locations of the hydrogen atoms suggest that these interactions are bridged by one hydrogen atom. The majority of the $\text{Na}-\text{H}$ distances range between 2.32 and 2.53 Å with one $\text{Na}-\text{H}$ distance that is much shorter than the others at about 2.14 Å. We will show below that the $\text{Na}\cdots\text{B}$ distances and $\text{Na}-\text{B}-\text{N}$ angles, along with the locations of the hydrogen atoms, can be used to classify the nature of the $\text{Na}\cdots\text{H}_3\text{B}$ interactions present in the solid state.

Lewis base adducts of $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$, **1**, with tetrahydrofuran, dioxane, and benzo-15-crown-5 have been prepared previously, and the crystal structures of the latter two have been described.^{1,2,13} We have prepared some related adducts of **1** with both ethers (dioxane, diglyme, 12-crown-4) and amines (*N,N,N',N'*-tetramethylethylenediamine, tmeda):



$\text{L} = \text{dioxane}$ ($x = 1$; **1a**),

diglyme ($x = 1$; **1b**),

tmeda ($x = 1$; **1c**),

12-crown-4 ($x = 2$; **1d**)

Whereas Keller reported a compound of stoichiometry $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)(\text{diox})_{0.5}$,¹ we isolated a 1:1 adduct of **1** with dioxane. It is likely that the amount of dioxane present in the crystallized material depends on the reaction stoichiometry and conditions (see below).

The structure of the dioxane adduct $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)(\text{dioxane})$, **1a**, consists of $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ units that are linked by bridging $\text{Na}\cdots\text{BH}_3$ interactions into chains (Figure 2); the dioxane molecules bridge between two sodium

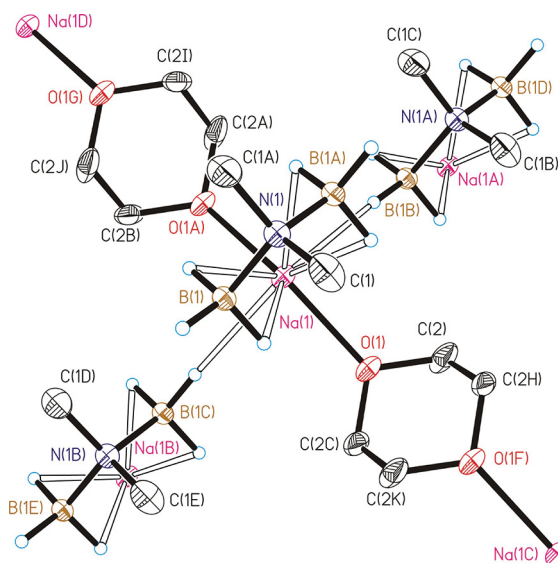


Figure 2. ORTEP representation of $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)(\text{diox})$, **1a**. Ellipsoids are drawn at the 35% probability level. Hydrogen atoms attached to carbon have been omitted for clarity.

ions in different chains to form a layered network. Each Na ion is bound to one chelating aminodiboranate anion, to two hydrogen atoms from DMADB groups that chelate to neighboring Na cations, and to two dioxane molecules. The six hydrogen and two oxygen atoms about each Na atom describe a distorted antiprism with one square face and one rectangular face. The $\text{Na}\cdots\text{B}$ distances are 2.851(2) Å, the $\text{Na}-\text{O}$ distances are 2.364(1) Å, and the $\text{Na}-\text{H}$ distances are 2.48(2) Å (Table S3).

The diglyme adduct $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)(\text{diglyme})$, **1b**, crystallizes as a dimer in which the non-bonded $\text{Na}\cdots\text{Na}$ distance is 4.050(1) Å (Figure 3). Each Na ion is coordinated to one chelating DMADB anion. For each diglyme ligand, two adjacent oxygen atoms, O(1) and O(2), chelate to one of the two sodium ions in the dimer, whereas the third oxygen atom, O(3), bridges between the two sodium atoms. This compound thus contains a rare example of an ether oxygen atom that bridges between two metal centers.¹⁴ If each of the B atoms in the DMADB anion is regarded as occupying one coordination site, then each sodium atom in the dimer adopts a distorted octahedral geometry. The mean $\text{Na}-\text{O}$ distance of 2.52 Å is somewhat longer than that observed for the dioxane adduct **1a**. The $\text{Na}\cdots\text{B}$ distances of 2.73 and 2.86 Å, and the $\text{Na}-\text{H}$

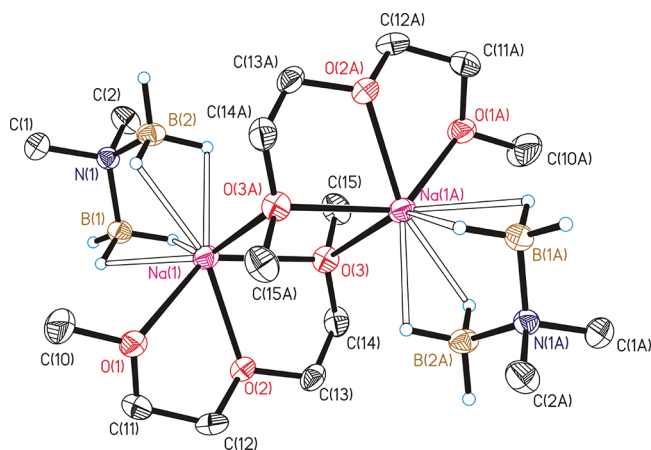


Figure 3. ORTEP representation of $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)$ - (diglyme), **1b**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms attached to carbon have been omitted for clarity.

distances of 2.31 to 2.52 Å, are similar to those in the dioxane adduct (Table S4).

The tmeda adduct $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)(\text{tmeda})$, **1c**, also crystallizes as a dimer ($\text{Na}\cdots\text{Na}$ distance of 3.923(1) Å). Each sodium ion is bound to one chelating tmeda ligand and to one chelating DMADB anion. Each sodium atom also interacts with two hydrogen atoms from a DMADB anion that chelates to the adjacent Na center. Thus, one BH_3 group from each DMADB anion bridges between the two sodium atoms (Figure 4). The environment about the Na centers can be described as

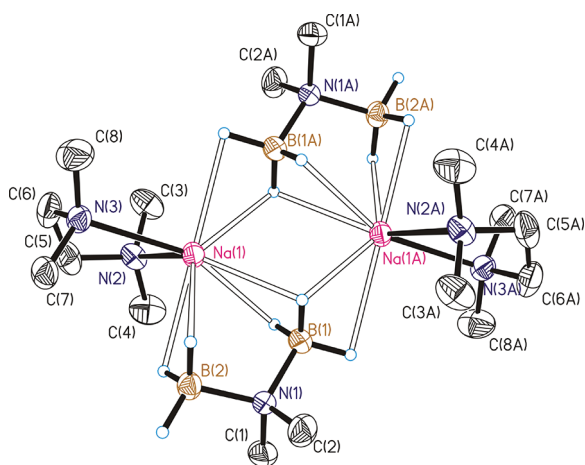


Figure 4. ORTEP representation of $\text{Na}(\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3)(\text{tmeda})$, **1c**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms attached to carbon have been omitted for clarity.

a distorted capped tetrahedron in which the tetrahedron is described by atoms N(1), N(2), B(1), and B(2), with B(1A) occupying the capping site. The $\text{Na}\cdots\text{B}$ distances of 2.79 to 2.83 Å are similar to those observed for compounds **1**, **1a**, and **1b**. The $\text{Na}-\text{H}$ distances, which range from 2.43 to 2.59 Å, are also similar to those in the other salts (Table S5).

The 12-crown-4 adduct $[\text{Na}(\text{12-crown-4})_2][\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3]$, **1d**, is an ionic salt in which the Na cation is bound only to two 12-crown-4 molecules, whose oxygen atoms describe a square antiprismatic coordination geometry (Figure 5). The DMADB group forms a charge-separated counterion in the

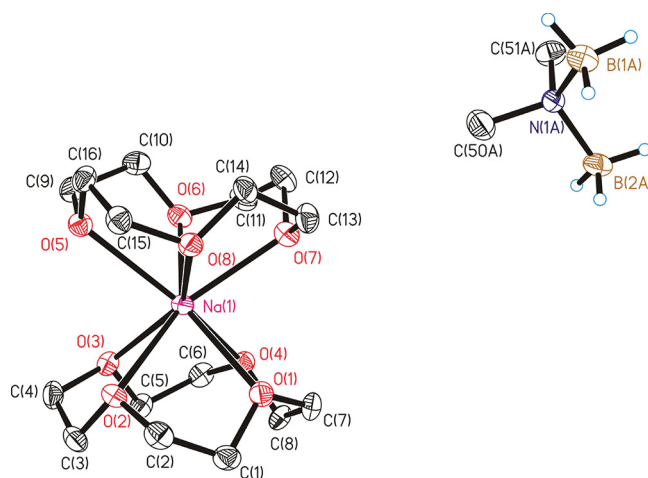
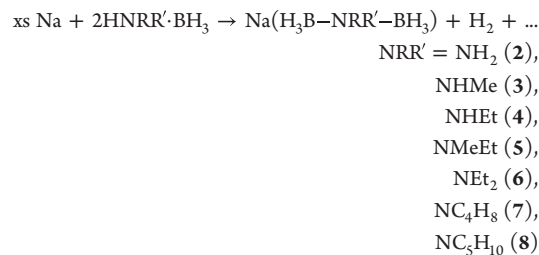


Figure 5. ORTEP representation of $[\text{Na}(\text{12-crown-4})_2][\text{H}_3\text{B}-\text{NMe}_2-\text{BH}_3]$, **1d**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

solid state. The $\text{Na}-\text{O}$ distances, which range from 2.45 to 2.56 Å, are similar to those observed in **1a** and **1b** (Table S6).

Synthesis and Characterization of New Amino-diborane Salts by the Method of Nöth and Thomas.

The method of Nöth and Thomas,² involving the sodium reduction of an amine-borane adduct, can be extended to prepare other aminodiborane salts bearing a variety of substituents on nitrogen. We have previously reported that this method works to prepare the unsubstituted aminodiborane salt $\text{Na}(\text{H}_3\text{B}-\text{BNH}_2-\text{BH}_3)$, **2**, as well as $\text{Na}(\text{H}_3\text{B}-\text{NHMe}-\text{BH}_3)$ (**3**), $\text{Na}(\text{H}_3\text{B}-\text{NHEt}-\text{BH}_3)$ (**4**), $\text{Na}(\text{H}_3\text{B}-\text{NMeEt}-\text{BH}_3)$ (**5**), $\text{Na}[\text{H}_3\text{B}-\text{N}(\text{C}_4\text{H}_8)-\text{BH}_3]$ (**7**), and $\text{Na}[\text{H}_3\text{B}-\text{N}(\text{C}_5\text{H}_{10})-\text{BH}_3]$ (**8**), where $\text{N}(\text{C}_4\text{H}_8)$ = pyrrolido and $\text{N}(\text{C}_5\text{H}_{10})$ = piperido.¹² Here, we extend this series to include the *N,N*-diethyl substituted salt $\text{Na}(\text{H}_3\text{B}-\text{NEt}_2-\text{BH}_3)$ (**6**). Sodium borohydride is often formed as a minor side product of the Nöth and Thomas method, as reported previously for the *N,N*-dimethyl derivative **1**, but unlike the aminodiborane salts, it is relatively insoluble in diethyl ether and it is left behind when the reaction products are extracted into this solvent.²



We have previously reported that treatment of sodium aminodiborane salts with 1,4-dioxane followed by extraction and subsequent crystallization from Et_2O affords the adducts $\text{Na}(\text{H}_3\text{B}-\text{NRR}'-\text{BH}_3)(\text{diox})_x$, **3a**, **4a**, and **7a**, where x is either 0.5 or 1.¹² Similarly, treatment of the sodium aminodiborane salts **6** and **8** with 1,4-dioxane followed by crystallization from Et_2O affords the adducts $\text{Na}(\text{H}_3\text{B}-\text{NEt}_2-\text{BH}_3)(\text{diox})$ (**6a**) and $\text{Na}(\text{H}_3\text{B}-\text{NC}_5\text{H}_{10}-\text{BH}_3)(\text{diox})$ (**8a**).

Unlike **1a**, in which the sodium ions are well separated (the nearest $\text{Na}\cdots\text{Na}$ distance being 6.21 Å), in **6a** and **8a** the sodium atoms are arranged in pairs separated by ca. 3.8 to 3.9 Å (Figures 6 and 7), as seen for the *N*-methylaminodiborane

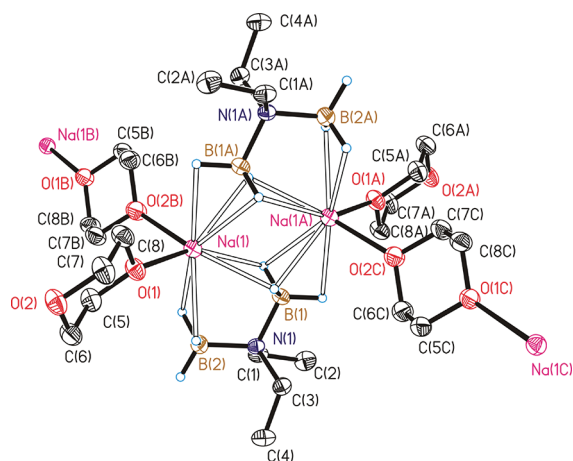


Figure 6. ORTEP representation of $\text{Na}(\text{H}_3\text{B}-\text{NEt}_2-\text{BH}_3)(\text{diox})$, **6a**. Ellipsoids are drawn at the 35% probability level. Hydrogen atoms attached to carbon have been omitted for clarity.

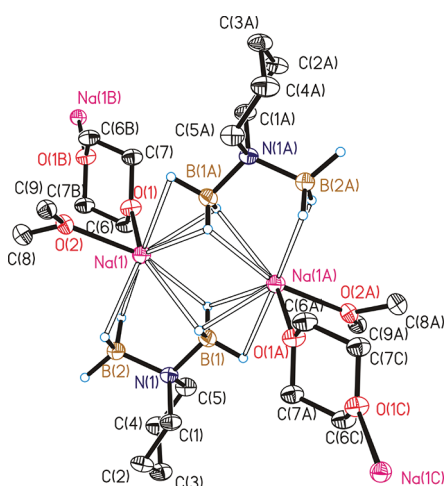


Figure 7. ORTEP representation of $\text{Na}(\text{H}_3\text{B}-\text{NC}_5\text{H}_{10}-\text{BH}_3)(\text{diox})$, **8a**. Ellipsoids are drawn at the 35% probability level. Hydrogen atoms attached to carbon have been omitted for clarity.

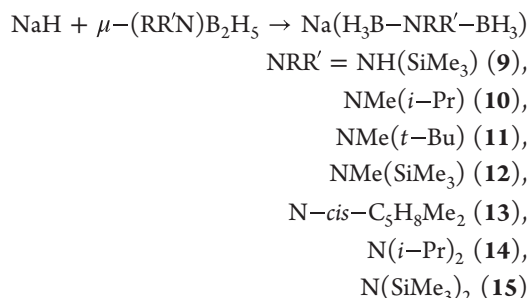
complex **3a**. The sodium atoms are each bound to one chelating $\text{H}_3\text{B}-\text{NRR}'-\text{BH}_3$ anion, to three hydrogen atoms from the $\text{H}_3\text{B}-\text{NRR}'-\text{BH}_3$ anion that bridges to the adjacent sodium ion in the pair, and to two dioxane ligands; one of the latter “replaces” the interpair bridging hydrogen interaction seen in **3a**. The boron and oxygen atoms describe a trigonal bipyramidal arrangement (again as in **3a**), but with the oxygen atoms occupying one axial and one equatorial site. The dioxane molecules, which bridge between Na atoms in different dinuclear units, knit the atoms into a polymeric network.

In **4a–8a**, the $\text{Na}\cdots\text{B}$ distances range between 2.666 and 2.968 Å, the $\text{Na}-\text{O}$ distances range between 2.307 and 2.382 Å, and the $\text{Na}-\text{H}$ distances range between 2.33 and 2.63 Å (Tables S6 and S7).

Synthesis and Characterization of New Amino-diboranate Salts by Keller’s Method. In efforts to make sterically bulky aminodiboranates by Nöth and Thomas’s method, we carried out the reaction of *N*-(*tert*-butyl)amine-borane, (*t*-Bu) $\text{NH}_2\cdot\text{BH}_3$, and *N,N*-di(*iso*-propyl)amine-borane, (*i*-Pr) $_2\text{NH}\cdot\text{BH}_3$, with sodium in refluxing THF. After 3 days, the ^{11}B NMR spectra indicated that, at best, only traces of the desired aminodiboranate product were present. Nöth and

Thomas’s method appears not to work well for sterically bulky amines.

Fortunately, we have found that Keller’s method is useful for the synthesis of sterically bulky aminodiboranates that cannot be prepared by the method of Nöth and Thomas. This reaction proceeds through the treatment of the aminodiborane $\mu-(\text{NRR}')_2\text{B}_2\text{H}_5$ with NaH to form the corresponding amino-diboranate:



The new compounds **9–15**, which are best purified by crystallization from diethyl ether, are soluble in THF but their solubility in diethyl ether varies. Compounds **11** and **13** are only moderately soluble in Et_2O , whereas **9**, **10**, **12**, **14**, and **15** are more soluble.

Both the *N*-trimethylsilyl substituted compounds **9** and **12** are polymeric in the solid state. For **9**, the cations and anions are linked into two-dimensional sheets by means of $\text{Na}\cdots\text{H}-\text{B}$ bridges through the BH_3 centers (Figure 8). The closest

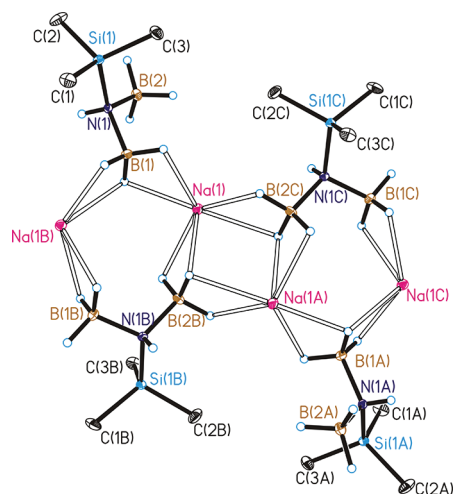


Figure 8. ORTEP representation of $\text{Na}[\text{H}_3\text{B}-\text{NH}(\text{SiMe}_3)-\text{BH}_3]$, **9**. Ellipsoids are drawn at the 35% probability level. Hydrogen atoms bound to carbon have been omitted for clarity.

neighbors to the sodium ion are six hydrogen atoms best described as forming a distorted trigonal antiprismatic arrangement, with the boron atoms forming a distorted tetrahedron about the sodium ion ($\tau_4 = 0.80$, where values of 0 and 1 indicate ideal square-planar and tetrahedral geometries, respectively).¹⁵ Within each BH_3 unit, two of the hydrogen atoms are bound to different sodium ions while the third hydrogen binds to both of these sodium ions. The $\text{Na}\cdots\text{B}$ distances fall between 2.75 and 2.86 Å, whereas the $\text{Na}-\text{H}$ distances are between 2.21 and 2.54 Å.

In $\text{Na}[\text{H}_3\text{B}-\text{NMe}(\text{SiMe}_3)-\text{BH}_3]$, **12**, the local environment of the sodium cations (Figure 9) consists of five boron atoms

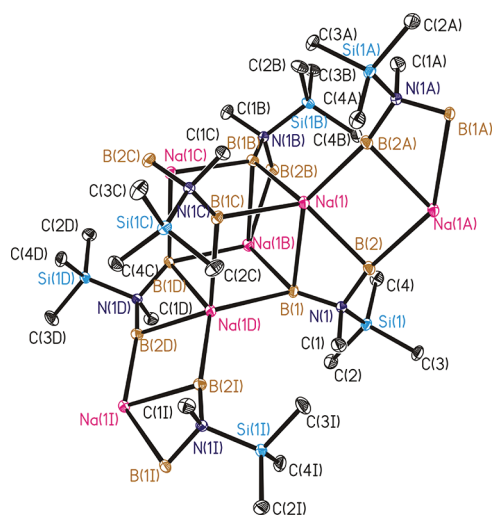


Figure 9. ORTEP representation of $\text{Na}[\text{H}_3\text{B}-\text{NMe}(\text{SiMe}_3)-\text{BH}_3]$, **12**. Ellipsoids are drawn at the 35% probability level. Hydrogen atoms have been omitted for clarity.

arranged in a distorted square pyramid ($\tau_5 = 0.32$, where values of 0 and 1 indicate ideal square-pyramidal and trigonal bipyramidal geometries, respectively).¹⁶ The seven closest hydrogen atoms describe a distorted pentagonal bipyramidal geometry, but two other hydrogen atoms are close enough to form contacts with each sodium cation, forming a bicapped pentagonal bipyramidal coordination polyhedron. The sodium ions are linked together by BH_3 units into cubelike arrangements in which the vertices consist of alternating sodium and boron atoms. Each boron atom in the cube links to a sodium ion of an adjacent cube by means of the other BH_3 unit on the aminodiboranate anion. The $\text{Na}-\text{H}$ contact lengths range between 2.37 and 2.72 Å. The $\text{Na}\cdots\text{B}$ distances that make up the edges of the cube are 2.857, 3.082, and 3.157 Å, whereas the $\text{Na}\cdots\text{B}$ distances, which link the cubes together, are 2.743 and 2.817 Å.

Comparison of Structural Properties. The crystal structures of the sodium aminodiboranate compounds above show that the majority of the $\text{Na}-\text{H}$ contacts present in the aminodiboranate salts fall between 2.3 and 2.6 Å, although a few lie between approximately 2.7 and 2.8 Å. For comparison, the ionic radius of a hydride ion as found in NaH is 1.47 Å, and

the ionic radius of a sodium cation with coordination number of 8 is 1.18 Å;^{17,18} the sum of these radii is 2.65 Å. It is reasonable to consider $\text{Na}-\text{H}$ distances of 3 Å or greater as being chemically not significant.

In part, because the crystallographically determined hydrogen atom positions are subject to some uncertainty, for the rest of this discussion, we will count the number of chemically significant $\text{Na}-\text{H}$ interactions, but construct a classification of the kinds of $\text{Na}\cdots\text{BH}_3$ interactions in terms of the $\text{Na}\cdots\text{B}$ distances and $\text{Na}-\text{B}-\text{N}$ angles, which are much more precisely determined. A plot of the $\text{Na}\cdots\text{B}$ distance vs the $\text{Na}-\text{B}-\text{N}$ angle is shown in Figure 10.

The nearest-neighbor $\text{Na}\cdots\text{B}$ distances vary quite widely: the shortest are about 2.66 Å, many are near 2.80–2.90 Å, and others are even longer. These distances suggest that several different kinds of $\text{Na}\cdots\text{BH}_3$ interactions are present in the solid state (Figure 11), which differ in the arrangement of the hydrogen atoms relative to the positions of the sodium and boron atoms.

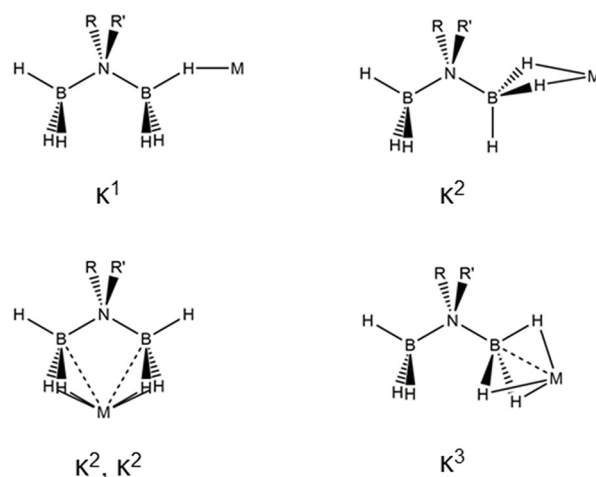


Figure 11. Depictions of the various binding modes present in the structures of the sodium aminodiboranates.

In one kind of $\text{Na}\cdots\text{BH}_3$ interaction, the crystal structures show that three hydrogen atoms on the boron atom form chemically significant contacts to the same sodium atom. Not surprisingly, for these κ^3 interactions, the $\text{Na}\cdots\text{B}$ contacts are

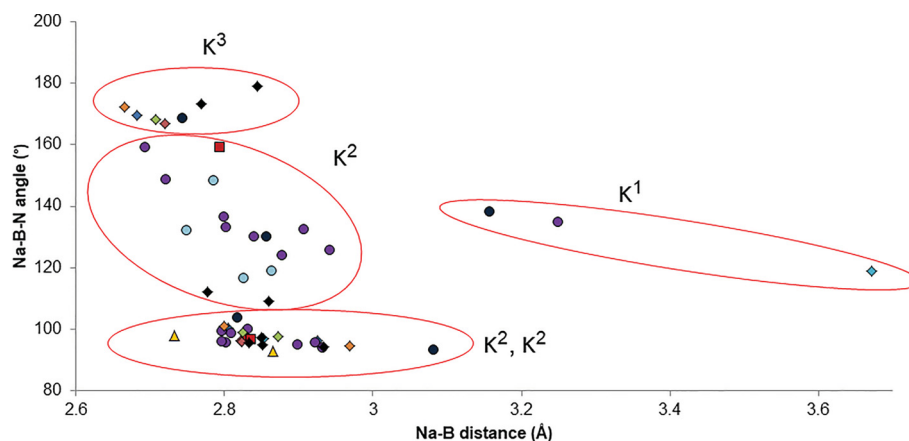


Figure 10. Plot of $\text{Na}-\text{B}-\text{N}$ angle vs $\text{Na}\cdots\text{B}$ distance in structures **1**, **1a–1c**, **3a–4a**, **6a–8a**, **9**, and **12** showing the different binding modes of the boron hydrides in each structure.

short (between 2.67 and 2.84 Å) and the Na–B–N angles are nearly linear (between 160 and 180°).

Another class of Na⋯BH₃ interactions is found in chelating aminodiboranate groups, in which both boron atoms bind symmetrically to the same sodium atom. In these interactions, the crystal structures show that two hydrogen atoms on each boron atom bridge to the sodium ion. With respect to the parameters for κ^3 interactions, these κ^2, κ^2 interactions are characterized by longer Na⋯B distances (between 2.73 and 3.08 Å) and more acute Na–B–N angles (between 93.0° and 103.6°). The two BH₃ groups within symmetrically chelating aminodiboranate anions have nearly identical Na⋯B distances and Na–B–N angles.

In some cases, however, chelating κ^2, κ^2 aminodiboranate groups bind unsymmetrically to the sodium ion: the two Na⋯B distances and the two Na–B–N angles are not equal, and these parameters change in a correlated way. For example, a difference of 0.1 Å in the Na⋯B distance corresponds with a difference of about 4° in the Na–B–N angle. Unsymmetric chelating interactions appear to be caused by bridging interactions of the chelating BH₃ units to an adjacent sodium ion. In structures **4a–8a**, the degree to which the symmetry is broken (as judged by the difference in Na⋯B distances between the two BH₃ units) increases as the bridging interaction becomes stronger, i.e., as the Na⋯B distance becomes shorter.

Next are non-chelating aminodiboranates in which each boron atom binds to a (different) sodium ion by means of two bridging hydrogen atoms. These κ^2 interactions display Na⋯B distances in the same range (between 2.72 and 2.94 Å) as seen for chelating κ^2, κ^2 interactions but have larger Na–B–N angles (between 109° and 159°).

An additional class of interactions is one in which only one hydrogen atom bridges between boron and sodium. These κ^1 interactions (present in compounds **1**, **1a**, and **12**) are characterized by a long Na⋯B distance (between 3.15 and 3.67 Å). The Na–B–N angles for these interactions fall between 109° and 139°.

Finally, several of the bridging interactions seem to be intermediate between the classes above, falling between κ^3 and κ^2 or between κ^2 and κ^1 . In these binding modes, one hydrogen atom on boron forms a contact with a sodium ion that is longer than the other contacts present but still short enough to be considered chemically significant (between 2.7 and 2.8 Å approximately).

The B–N–B angles within the aminodiboranate anions range from 109.0° to 113.8° (Table 3). The B–N–B angle is largest (111.9°–113.8°) when one R group is hydrogen and decreases as the R groups increase in size, as one would expect from steric considerations. In all of the structures containing the dimethylaminodiboranate anion, the B–N–B angle lies between 111.22 and 112.19°, which is similar to the angle seen when one group is H and the other is larger than methyl (such as Et or SiMe₃). The smallest angles (109°–109.87°) are seen when the substituents on nitrogen are two alkyl or silyl groups, at least one of which is sterically more demanding than a methyl group.

¹¹B NMR Spectra of Sodium Aminodiboranates. With one exception, the ¹¹B NMR spectra of the new sodium aminodiboranates consist of a single binomial quartet due to coupling with the three BH₃ hydrogen atoms. The exception is the sodium *cis*-2,6-dimethylpiperidinyldiboranate salt, **15**, whose ¹¹B NMR spectrum features two quartets due to the

Table 3. B–N–B Angles as a Function of Substituents on Nitrogen, Sorted by Increasing Size

NRR' group	B–N–B angle, °
H, Me	113.82
	113.80
H, Et	111.90
H, SiMe ₃	112.08
Me, Me	111.45
	111.61
	112.37
	111.22
	111.50
	112.19
Me, SiMe ₃	109.87
Et, Et	109.22
C ₄ H ₈	109.91
C ₅ H ₁₀	109.00

inequivalent chemical environments (axial vs equatorial) produced by the chair conformation of the 2,6-dimethylpiperidine ring.

The ¹¹B NMR shifts (Table 4) are additive, in that they can be estimated quite closely (about ±0.2 ppm) from the

Table 4. ¹¹B NMR Chemical Shifts as a Function of Substituents on Nitrogen

NRR' group	δ, ppm
H, H	−19.9
H, Me	−15.7
H, Et	−17.2
H, <i>i</i> -Pr	−19.3
H, <i>t</i> -Bu	−19.7
H, SiMe ₃	−19.2
Me, Me	−11.5
Me, Et	−13.1
Me, <i>i</i> -Pr	−14.6
Me, <i>t</i> -Bu	−14.6
Me, SiMe ₃	−14.8
Et, Et	−14.8
C ₄ H ₈	−12.7
C ₅ H ₁₀	−13.5
<i>cis</i> -C ₅ H ₈ Me ₂	−14.2, −25.1
<i>i</i> -Pr, <i>i</i> -Pr	−19.2
SiMe ₃ , SiMe ₃	−17.7

equation $\delta = -19.9 + \Delta\delta_1 + \Delta\delta_2$, where $\Delta\delta_1$ and $\Delta\delta_2$ are empirical parameters that describe the effects of the two substituents on nitrogen. Thus, approximate $\Delta\delta$ values are 0 (H), 4.2 (Me), 2.7 (Et), 0.8 (*i*-Pr), 0.6 (*t*-Bu), and 1.1 (SiMe₃). The pyrrolidide and piperidide rings change the chemical shift by an amount similar to two ethyl groups, which makes sense from a chemical point of view. From these substituent effects, we can conclude that more strongly electron donating substituents deshield the ¹¹B NMR shift, whereas more sterically bulky substituents shield the ¹¹B NMR shift.

CONCLUSIONS

We find that the synthetic method of Nöth and Thomas can be extended to prepare sodium salts of a variety of aminodiboranate anions with different alkyl substituents attached to

the nitrogen atom, provided that the substituents are not too sterically bulky. We also find that the synthetic method of Keller is more tolerant of sterically bulky substituents and also works for SiMe₃ substituents. As a result, Keller's method can be used to prepare sodium salts that cannot be made by the method of Nöth and Thomas.

Several of these new aminodiboranate salts have been crystallographically characterized. The structures of these salts are rather diverse, displaying several different kinds of cation–anion arrangements in the solid state. The chemically significant Na⋯B distances and Na–B–N angles vary over a wide range, corresponding to the several different kinds of Na⋯BH₃ interactions in the solid state. We find that we can identify four main kinds of Na⋯BH₃ interactions: non-chelating interactions that can be described as either κ^3 , κ^2 , or κ^1 and chelating interactions best described as κ^2, κ^2 . The chelating interactions are sometimes unsymmetrical, so that the two Na⋯B distances are not equal.

In addition, we found that the B–N–B angle of the ligand is the largest and the B–N distance is the shortest when the groups on nitrogen are small. The B–N–B angle decreases and the B–N distance increases as the R groups increase in size, as one would expect from steric considerations. These changes suggest that sterically bulky substituents on nitrogen weaken the B–N bonds. Finally, increasing the electron-donating ability of the substituents on nitrogen deshields the ¹¹B NMR shift, whereas increasing the steric bulk of the substituents shields the ¹¹B NMR shift.

The availability of these new sodium salts should make it possible to adjust the properties of aminodiboranate CVD precursors by varying the substituents on nitrogen. This flexibility offers the opportunity to design precursor molecules of a similar structure but with different volatilities, melting points, reactivities, and deposition onset temperatures. Because the unsubstituted parent aminodiboranate anion is carbon-free, it may be useful as a ligand in precursors for CVD depositions in which carbon contamination is an issue.^{19–26}

EXPERIMENTAL SECTION

All operations were carried out in vacuum or under argon using standard Schlenk techniques. All solvents were distilled under nitrogen from sodium/benzophenone immediately before use. Bis(2-methoxyethyl) ether (diglyme) and *N,N,N',N'*-tetramethylethylenediamine (tmeda) were distilled from sodium before use. 1,4,7,10-Tetraoxacyclododecane (12-crown-4), sodium metal, NH₃·BH₃, HNMe₂·BH₃, NaNH₂, and BH₃·THF (1.0 M) were used as received (Aldrich).

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 ¹H NMR data were obtained on a Varian Unity 400 instrument at 400 MHz or on a Varian Unity U500 instrument at 500 MHz. The ¹¹B NMR data were collected on a General Electric GN300WB instrument at 96 MHz, a Varian Unity Inova 600 instrument at 192 MHz, or a Varian Unity 400 instrument at 9.4 T. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (¹H or ¹³C{¹H}) or BF₃·Et₂O (¹¹B). X-ray crystallographic data were collected by the George L. Clark X-ray Laboratory at the University of Illinois. Melting points were determined in closed capillaries under argon on a Thomas-Hoover Unimelt apparatus. The synthesis of compound 1 was performed following the method described by Nöth and Thomas.² We have previously reported the synthesis and characterization of compounds 2–5, 7, 8, 3a, 4a, and 7a.¹²

Sodium *N,N*-Dimethylaminodiboranate Dioxane (1:1), Na(H₃B-NMe₂-BH₃)(1,4-dioxane), 1a. To Na(H₃B-NMe₂-BH₃) (100 mg, 1.1 mmol) was added 1,4-dioxane (4 mL). The solution was stirred for 10 min and evaporated to dryness under vacuum to yield a white solid. The residue was extracted with Et₂O (30 mL), the extract was filtered, and the filtrate was stored at –20 °C to yield colorless prisms. Anal. Calcd for C₆H₂₀B₂NO₂Na: C, 39.4; H, 11.0; N, 7.66. Found: C, 39.8; H, 11.7; N, 7.58. ¹H NMR (DMSO-*d*₆, 20 °C): δ 1.45 (1:1:1:1 q, ¹J_{BH} = 91 Hz, BH₃, 6 H), 2.15 (s, NCH₃, 6 H), 3.56 (s, OCH₂, 8 H). ¹¹B NMR (THF-*d*₈, 20 °C): δ –8.7 (q, ¹J_{BH} = 92 Hz, BH₃). IR (cm^{–1}): 2390 s, 2297 vs, 2246 s, 1302 s, 1212 s, 1168 vs, 1144 vs, 1114 s, 1087 s, 1046 m, 1029 m, 1016 s, 923 m, 904 m, 888 vs, 877 vs, 790 s, 615 s, 410 s.

[Bis(2-methoxyethyl)ether]sodium *N,N*-Dimethylaminodiboranate Na(BH₃-NMe₂-BH₃)(diglyme), 1b. To sodium *N,N*-dimethylaminodiboranate (300 mg, 3.17 mmol) in tetrahydrofuran (20 mL) was added bis(2-methoxyethyl)ether (0.5 mL, 3.5 mmol). The resulting solution was stirred for 2 h. The solvent was removed under vacuum, the residue was extracted with hot heptane (30 mL), and the extract was filtered and cooled to –20 °C. Small colorless crystals were observed after 24 h. Yield: 335 mg (46%). Mp. 49–50 °C. Anal. Calcd for NaC₈H₂₆NB₂O₃: C, 42.0; H, 11.5; N, 6.1. Found: C, 42.7; H, 11.8; N, 6.2. ¹H NMR (C₆D₆, 20 °C): δ 1.96 (1:1:1:1 q, ¹J_{BH} = 95 Hz, 6H, BH₃), 2.74 (s, 6H, NMe₂), 2.99 (s, 4H, OCH₂), 3.00 (s, 4H, OCH₂), 3.21 (s, 6H, OMe). ¹¹B NMR (C₆D₆, 20 °C): δ –11.2 (q, ¹J_{BH} = 90 Hz). IR (cm^{–1}): 2391 s, 2281 vs, 2234 vs, 2076 m, 1351 s, 1287 m, 1252 s, 1226 m, 1202 sh, 1179 vs, 1153 vs, 1132 s, 1106 vs, 1072 vs, 1014 vs, 944 m, 928 m, 906 w, 865 s, 839 s, 796 m.

(*N,N,N',N'*-Tetramethylethylenediamine)sodium *N,N*-Dimethylaminodiboranate Na(BH₃-NMe₂-BH₃)(tmeda), 1c. To sodium *N,N*-dimethylaminodiboranate (300 mg, 3.17 mmol) in tetrahydrofuran (20 mL) was added *N,N,N',N'*-tetramethylethylenediamine (0.5 mL, 3.36 mmol). The resulting solution was stirred for 2 h. The solvent was removed under vacuum, the residue was extracted with hot heptane (30 mL), and the extract was filtered and cooled to –20 °C. Small colorless crystals were observed after 24 h. Yield: 273 mg (41%). Mp. 83–85 °C. Anal. Calcd for NaC₈H₂₈N₃B₂: C, 45.6; H, 13.4; N, 19.9. Found: C, 46.1; H, 13.5; N, 19.7. ¹H NMR (C₆D₆, 20 °C): δ 1.87 (s, 4H, NCH₃), 1.93 (1:1:1:1 q, ¹J_{BH} = 89 Hz, 6H, BH₃), 2.05 (s, 6H, NMe₂), 2.65 (s, 12H, NMe₂ of tmeda). The BH₃ resonance in the ¹H NMR spectrum is partially obscured by the NMe₂ peaks of tmeda and [H₃BNMe₂BH₃][–], and the reported values are approximate. ¹¹B NMR (C₆D₆, 20 °C): δ –11.2 (q, ¹J_{BH} = 89 Hz). IR (cm^{–1}): 2372 m, 2299 vs, 2245 s, 1361 m 1296 s, 1254 w, 1206 m, 1195 m, 1175 s, 1159 vs, 1135 m, 1099 w, 1076 m, 1037 sh, 1026 vs, 950 s, 922 m, 907 w, 803 m, 786 s.

Bis(1,4,7,10-tetraoxacyclododecane)sodium *N,N*-Dimethylaminodiboranate Na(BH₃-NMe₂-BH₃)(12-crown-4)₂, 1d. To sodium *N,N*-dimethylaminodiboranate (300 mg, 3.17 mmol) in tetrahydrofuran (20 mL) was added 1,4,7,10-tetraoxacyclododecane (0.51 mL, 3.15 mmol). The resulting solution was stirred for 2 h. The solvent was removed under vacuum, the residue was extracted with hot tetrahydrofuran (30 mL), and the extract was filtered and cooled to –20 °C. Small colorless crystals were observed after 24 h. Yield: 1.17 g (82%). Mp. 185 °C (dec). Anal. Calcd for NaC₁₈H₄₄NB₂O₈: C, 48.4; H, 9.9; N, 3.1. Found: C, 49.1; H, 10.0; N, 3.1. ¹H NMR (C₆D₆, 20 °C): δ 1.39 (1:1:1:1 q, ¹J_{BH} = 92 Hz, 6H, BH₃), 2.09 (s, 6H, NMe₂), 3.57 (s, 32H, OCH₂). ¹¹B NMR (C₆D₆, 20 °C): δ –8.9 (q, ¹J_{BH} = 92 Hz). IR (cm^{–1}): 2336 m, 2301 vs, 2271 vs, 2196 vs, 2156 m, 2054 w, 1365 vs, 1302 s, 1291 s, 1248 s, 1167 vs, 1150 vs, 1136 vs, 1094 vs, 1022 vs, 916 vs, 849 s, 779 m.

Sodium *N,N*-Diethylaminodiboranate, Na(H₃B-NEt₂-BH₃), 6. To BH₃·THF (200 mL of a 1 M solution in tetrahydrofuran, 0.200 mol) at 0 °C was added dry diethylamine (0.200 mol) dropwise over 20 min. The solution was stirred for 1 h and then was slowly transferred to a separate flask containing 1 × 1 × 1 cm cubes of sodium (14 g, 0.61 mol). After the addition was complete, the mixture was heated to reflux until all of the diethylamine-borane had been consumed (as monitored by ¹¹B NMR spectroscopy). Typical reaction times were 70–80 h. The reaction mixture was cooled and

filtered. The colorless filtrate was taken to dryness under vacuum to give a sticky gray-white residue. The residue was washed with benzene (2 × 120 mL) and pentane (3 × 50 mL) and dried under vacuum to yield a free-flowing white powder. Yield: 4.68 g (38%). Anal. Calcd for $C_4H_{16}NB_2Na$: C, 39.1; H, 13.1; N, 11.4. Found: C, 39.0; H, 13.6; N, 11.1. 1H NMR (THF- d_8): δ 1.03 (t, $^3J_{HH} = 7.3$ Hz, 6H, β -Et), 1.05 (1:1:1:1 q, $^1J_{BH} = 90$ Hz, 6H, BH_3), 2.45 (q, $^3J_{HH} = 7.3$ Hz, 4H, α -Et). $^{13}C\{^1H\}$ NMR (THF- d_8): δ 10.4 (s, β -Et), 53.6 (s, α -Et). ^{11}B NMR (THF- d_8): δ -14.8 (q, $^1J_{BH} = 90$ Hz). IR (cm^{-1}): 2326 s br, 2256 s br, 1217 m br, 1164 m br, 1151 m br, 1130 m, 1049 m, 972 w, 845 w, 800 w, and 779 w.

(Dioxane)sodium *N,N*-Diethylaminodiboranate, $Na(H_3B-NEt_2-BH_3)(diox)$, 6a. To $Na(H_3B-NEt_2-BH_3)$ (0.100 g, 0.814 mmol) was added 1,4-dioxane (5.00 mL, 58.7 mmol). After the slurry had been stirred for 20 min, the solvent was removed under vacuum and the white residue was extracted with diethyl ether (2 × 20 mL). The extract was filtered, and the colorless filtrate was concentrated to ca. 5 mL and cooled to -20 °C to afford large colorless needles. Yield: 0.064 g (37%). Anal. Calcd for $C_8H_{24}NO_2B_2Na$: C, 45.6; H, 11.5; N, 6.64. Found: C, 45.6; H, 11.5; N, 6.69. 1H NMR (THF- d_8): δ 1.03 (t, $^3J_{HH} = 7.3$ Hz, 6H, β -Et), 1.18 (1:1:1:1 q, $^1J_{BH} = 92$ Hz, 6H, BH_3), 2.48 (q, $^3J_{HH} = 7.3$ Hz, 4H, α -Et), 3.56 (s, 8H, OCH_2). $^{13}C\{^1H\}$ NMR (THF- d_8): δ 10.5 (s, β -Et), 53.7 (s, α -Et), 67.8 (s, OCH_2). ^{11}B NMR (THF- d_8): δ -14.6 (q, $^1J_{BH} = 92$ Hz). IR (cm^{-1}): 2397 m br, 2295 br, 2249 br, 1637 m, 1617 m, 1377 s, 1295 m, 1258 m, 1195 br, 1164 br, 1149 br, 1116 br, 1084 w, 1050 m, 960 m, 889 m, 875 m, 798 w, 773 m, and 615 w.

(Dioxane)sodium Piperidinyldiboranate, $Na(H_3B-NC_5H_{10}-BH_3)(diox)$, 8a. To $Na(H_3B-NC_5H_{10}-BH_3)$ ¹² (0.100 g, 0.742 mmol) was added 1,4-dioxane (5.00 mL, 58.7 mmol). After the slurry had been stirred for 20 min, the solvent was removed under vacuum and the resulting white residue was extracted with ether (2 × 20 mL). The resulting clear solution was filtered, and the filtrate was concentrated to ca. 5 mL and placed in a -20 °C freezer overnight. After 17 h, the colorless needles were isolated and dried for 1 h at 0.1 Torr and 20 °C. Yield: 0.131 g (57%). Calc for $C_8H_{24}NO_2B_2Na$: C, 48.5; H, 10.9; N, 6.28. Found: C, 48.4; H, 10.9; N, 6.32. 1H NMR (THF- d_8): δ 1.25 (1:1:1:1 q, $^1J_{BH} = 91$ Hz, 6H, BH_3), 1.35 (apparent pentet, $^3J_{HH} = 6.0$ Hz, 2H, 4- CH_2), 1.63 (apparent pentet, $^3J_{HH} = 5.0$ Hz, 4H, 3- CH_2), 2.49 (t, $^3J_{HH} = 5.0$ Hz, 4H, 2- CH_2), 3.56 (s, 8H, OCH_2). $^{13}C\{^1H\}$ NMR (THF- d_8): δ 22.7 (s, 4- CH_2), 25.5 (s, 3- CH_2), 58.9 (s, 2- CH_2), 67.8 (s, OCH_2). ^{11}B NMR (THF- d_8): δ -14.6 (q, $^1J_{BH} = 91$ Hz). IR (cm^{-1}): 2355 m, 2396 s br, 2249 s br, 1376 m, 1310 w, 1295 w, 1258 m, 1203 m, 1184 m br, 1158 m br, 1113 m br, 1082 m, 1066 m, 1039 m, 1013 w, 998 w, 972 m, 956 m, 891 m, 872 s, 799 br, 721 br, 669 w, 617 m, 548 w.

Sodium *N*-Trimethylsilylaminodiboranate, $Na(H_3B-N(SiMe_3)_2-BH_3)$, 9. To $BH_3 \cdot THF$ (100 mL of a 1 M solution in THF, 100 mmol) was added a solution of $HN(SiMe_3)_2$ (10.4 mL, 50 mmol) in THF (10 mL). The mixture was stirred at room temperature for 6 days. The mixture was separated by distillation at reduced pressure. After the THF had been distilled off, the first fraction (50 mTorr/20 °C) consisted largely of μ -*N*-trimethylsilylaminodiborane (yield: 2.62 g; 46%). The second fraction (50 mTorr/45 °C) consisted largely of μ -*N,N*-bis(trimethylsilyl)aminodiborane (yield: 4.54 g, 49%). ^{11}B NMR (THF, 20 °C): ($SiMe_3$)₂ NB_2H_5 : δ -26.03 (td, $^1J_{BH} = 128$, $^2J_{BH} = 33$ Hz). ($SiMe_3$) HNB_2H_5 : δ -24.31 (td, $^1J_{BH} = 128$, $^2J_{BH} = 34$ Hz). NaH (1.66 g of a 60 wt % dispersion in mineral oil, 42 mmol) was washed with pentane (3 × 50 mL) and dried under vacuum for 30 min. The μ -*N*-trimethylsilylaminodiborane was dissolved in THF (30 mL) and the solution was transferred onto the NaH . After having been stirred for 21 h, the solution was filtered from the remaining NaH and the filtrate was taken to dryness in vacuum. The residue was extracted with Et_2O (2 × 20 mL), and the extract was filtered. The filtrate was taken to dryness in vacuum, and the residue was washed with toluene (30 mL) and pentane (3 × 30 mL) and dried under vacuum at room temperature overnight to afford a white solid. Yield: 3.3 g (40%). The microanalysis reflected the presence of some sodium *N,N*-bis(trimethylsilyl)aminodiboranate (compound 15) owing to an imperfect separation of the two

distillation fractions. 1H NMR (THF- d_8 , 20 °C): δ 0.12 (s, 9H, $SiMe_3$), 1.23 (1:1:1:1 q, $^1J_{BH} = 89$ Hz, 6H, BH_3), 1.73 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (THF- d_8 , 20 °C): δ 2.07 (s, $SiMe_3$). ^{11}B NMR (THF, 20 °C): δ -17.7 (q, $^1J_{BH} = 91$ Hz). IR (cm^{-1}): 3231 m, 2299 br, 2234 br, 1458 m, 1377 w, 1252 m, 1199 w, 1152 m, 1026 w, 995 w, 973 w, 848 s, 779 vw, 756 vw, 691 vw, 660 vw.

Sodium *N*-iso-Propyl-*N*-methylaminodiboranate, $Na(H_3B-N(i-Pr)Me-BH_3)$, 10. To $BH_3 \cdot THF$ (50 mL of a 1 M solution in THF, 50 mmol) at 0 °C was added *N*-iso-propyl-*N*-methylamine (2.4 mL, 23 mmol) dropwise with stirring. After several minutes, the solution was warmed, first to room temperature and then to 50 °C for 3 days. During this time gas was evolved to afford μ -(*N*-iso-propyl-*N*-methylamino)diborane, μ -(*i-Pr*) $MeNB_2H_5$. ^{11}B NMR (THF): δ -17.9 (td, $^1J_{BH} = 130$ Hz, $^2J_{BH} = 32$). In a separate flask, NaH (2.6 g of a 60 wt % dispersion in mineral oil, 65 mmol) was washed with pentane (50 mL), collected by filtration, and dried under vacuum. The μ -(*N*-iso-propyl-*N*-methylamino)diborane solution from the previous step was cooled to 0 °C and added to NaH . The resulting slurry was stirred for 4 h at room temperature. The slurry was filtered, and the colorless filtrate was taken to dryness under vacuum to afford a white solid. Coordinated solvent was removed by heating the solid under vacuum to 40 °C overnight. The white solid was dissolved in Et_2O (50 mL), the solution was filtered, and the colorless filtrate was taken to dryness under vacuum to afford a white powder. Yield: 2.57 g (90%). Mp. >275 °C. Anal. Calcd for $C_4H_{16}NB_2Na$: C, 39.1; H, 13.1; N, 11.4%. Found: C, 39.1; H, 13.1; N, 10.3%. The nitrogen content is low due to the presence of some silicone grease. 1H NMR ($MeCN-d_3$): δ 1.13 (d, $^1J_{BH} = 6.6$ Hz, 6H, CMe), 1.22 (1:1:1:1 q, $^1J_{BH} = 90$ Hz, 6H, BH_3), 2.12 (s, 3H, NMe), 2.66 (septet, $^1J_{BH} = 6.4$ Hz, 1H, $N-CH$). ^{11}B NMR ($MeCN-d_3$): δ -13.1 (q, $^1J_{BH} = 91$ Hz). IR (cm^{-1}): 2322 s, 2258 s, 1416 w, 1221 m, 1198 m, 1169 s, 1140 w, 1110 w, 1072 w, 1055 w, 1025 w, 972 w, 826 w, 799 w.

Sodium *N*-(*tert*-Butyl)-*N*-methylaminodiboranate, $Na(H_3B-N(t-Bu)Me-BH_3)$, 11. To $BH_3 \cdot THF$ (150 mL of a 1 M solution in THF, 150 mmol) at 0 °C was added *N*-(*tert*-butyl)-*N*-methylamine (5.0 mL, 41.7 mmol) dropwise with stirring. After several minutes, the solution was warmed, first to room temperature and then to 60 °C for 7 days. During this time, gas was evolved to afford μ -(*N*-*tert*-butyl-*N*-methylamino)diborane, μ -(*t-Bu*) $MeNB_2H_5$. ^{11}B NMR (THF): δ -20.14 (td, $^1J_{BH} = 128$, 32 Hz). The product diborane was isolated by vacuum distillation into a -78 °C ethanol/dry ice cooled trap as a solution in THF. In a separate flask, NaH (5.4 g of a 60 wt % dispersion in mineral oil, 135 mmol) was washed with pentane (50 mL), collected by filtration, and dried under vacuum. The μ -(*N*-*tert*-butyl-*N*-methylamino)diborane from the previous step was dissolved in THF (30 mL), and the solution was cooled to 0 °C and added to the NaH . The resulting slurry was stirred for 12 h at room temperature. The slurry was filtered, and the colorless filtrate was taken to dryness under vacuum to afford a white solid. Coordinated solvent was removed by heating the solid under vacuum to 50 °C overnight. The white solid was washed with toluene (50 mL) and pentane (50 mL) and then was dried under vacuum. The product contains small amounts of $NaBH_4$, which is difficult to separate from the product due to their similar solubility in diethyl ether. Yield: 3.83 g (67%). Anal. Calcd for $C_5H_{18}NB_2Na \cdot 0.1NaBH_4$: C, 42.6; H, 13.1; N, 9.90%. Found: C, 42.6; H, 13.3; N, 9.80%. 1H NMR ($MeCN-d_3$): δ 1.22 (1:1:1:1 q, $^1J_{BH} = 91$ Hz, 6H, BH_3), 1.23 (s, 9H, $C-Me$), 2.17 (s, 3H, NMe). ^{11}B NMR ($MeCN-d_3$): δ -13.8 (q, $^1J_{BH} = 91$ Hz). IR (cm^{-1}): 2285 s, 2260 s, 1392 w, 1230 m, 1195 s, 1096 m, 1035 w, 1013 w, 970 w, 845 w, 818 w.

Sodium *N*-Methyl-*N*-trimethylsilylaminodiboranate, $Na(H_3B-N(SiMe_3)Me-BH_3)$, 12. A solution of chlorotrimethylsilane (10 mL, 79 mmol) in Et_2O (200 mL) was frozen in liquid nitrogen, and then H_2NMe (100 mL of a 2 M solution in THF, 200 mmol) was transferred to the frozen solution. The solution was warmed to room temperature in a water bath and then was stirred for 4 h, during which time a white powder precipitated from the solution. The solution was filtered from the precipitate at 0 °C. To this solution was added $BH_3 \cdot THF$ (80 mL of a 1 M solution in THF, 80 mmol) with stirring. After 30 min, the solvent was removed under reduced pressure to provide a

white solid. Yield: 4.4 g (48%). ^{11}B NMR (THF, 20 °C): δ –17.01 (q, $^1J_{\text{BH}} = 98$ Hz). The crude amine–borane adduct from the previous step was dissolved in THF (20 mL), and to this solution was added $\text{BH}_3\cdot\text{THF}$ (40 mL, 40 mmol). The mixture was heated to reflux for 3 days. In a separate flask, NaH (1.6 g of a 60 wt % dispersion in mineral oil, 40 mmol) was washed with pentane (3 $\times$ 50 mL) and dried under vacuum for 30 min. The solution was transferred to the NaH and stirred overnight for 21 h. The solution was filtered, and the filtrate was taken to dryness in vacuum. The product, a white solid, was washed with toluene (1 $\times$ 30 mL) and pentane (3 $\times$ 30 mL) and dried under vacuum at room temperature overnight. Yield: 3.1 g (51%). The sample contained some diethyl ether and stopcock grease, which affected the microanalysis. ^1H NMR (THF- d_8 , 20 °C): δ 0.15 (s, 9H, SiMe_3), 1.20 (1:1:1:1 q, $^1J_{\text{BH}} = 90$ Hz, 6H, BH_3), 2.12 (s, 3H, NMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 20 °C): δ 3.92 (s, SiMe_3), 45.82 (s, NMe). ^{11}B NMR (THF, 20 °C): δ –14.4 (q, $^1J_{\text{BH}} = 91$ Hz). IR (cm^{-1}): 2724 vw, 2332 br, 2236 br, 1457 br, 1416 vw, 1377 m, 1254 w, 1216 w, 1249 w, 1164 w, 1080 m, 1021 m, 965 m, 843 br, 750 w, 772 w, 687 w, 648 m.

Sodium *cis*-(2,6-Dimethylpiperidinyl)diboranate, $\text{Na}[\text{H}_3\text{B}-\text{N}(\text{C}_7\text{H}_{14})\text{-BH}_3]$, 13. *cis*-2,6-Dimethylpiperidine-borane (3.8 g, 30 mmol) was heated to 180 °C, during which time the solid melted at 110 °C and began to evolve gas. A clear and colorless liquid, $(\text{C}_7\text{H}_{14})\text{N}=\text{BH}_2$, was distilled off through a heated still head (ca. 100 °C) to prevent condensation of the dimer $((\text{C}_7\text{H}_{14})\text{N}-\text{BH}_2)_2$, into a flask at –78 °C. $\text{BH}_3\cdot\text{THF}$ (20 mL of a 1 M solution in THF, 20 mmol) was added to the distillate, and the solution was heated to 50 °C until the conversion of $(\text{C}_7\text{H}_{14})\text{N}-\text{BH}_2$ (^{11}B NMR: δ 1.5, $^1J_{\text{BH}} = 160$ Hz) to *cis*-(2,6-dimethylpiperidino)diborane (^{11}B NMR: δ –16.7, td, $^1J_{\text{BH}} = 128$, $^2J_{\text{BH}} = 33$ Hz, δ –20.1, td, $^1J_{\text{BH}} = 128$, $^2J_{\text{BH}} = 33$ Hz) was complete. In a separate flask, NaH (0.75 g of a 60 wt % dispersion in mineral oil, 19 mmol) was washed with pentane (50 mL), collected by filtration, and dried under vacuum. The *cis*-(2,6-dimethylpiperidino)diborane solution was cooled to 0 °C and added to the NaH. The resulting mixture was stirred at room temperature for 3 h. The slurry was filtered, and the colorless filtrate was dried under vacuum to afford a white powder. Coordinated solvent was removed by heating the solid under vacuum to 50 °C for 3 days. The solid was dissolved in Et_2O (50 mL), and the solution was concentrated to ca. 40 mL and cooled to –20 °C. The resulting needles were collected and dried under vacuum. Yield: 1.56 g (32%). Mp. >275 °C. Anal. Calcd for $\text{Na}[\text{H}_3\text{B}-\text{N}(\text{C}_7\text{H}_{14})\text{-BH}_3]$: C, 51.6; H, 12.4; N, 8.60%. Found: C, 49.9; H, 12.2; N, 8.40%. ^1H NMR ($\text{MeCN}-d_3$): δ 0.91 (1:1:1:1 q, $^1J_{\text{HB}} = 88$ Hz, 3H, BH_3), 1.14 (m, 2H, *ax*-3- CH_2), 1.27 (1:1:1:1 q, $^1J_{\text{HB}} = 88$ Hz, 3H, BH_3), 1.27 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, *eq*-2-Me), 1.36 (m, 1H, *ax*-4- CH_2), 1.59 (d of apparent septets, $^2J_{\text{HH}} = 12.7$ Hz, $^3J_{\text{HH}} = 2.2$ Hz, 1H, *eq*-4- CH_2), 1.89 (apparent qd, $^2J_{\text{HH}} = 13$ Hz, $^3J_{\text{HH}} = 4.5$ Hz, 2H, *eq*-3- CH_2), 2.39 (m, 2H, *ax*-2-CH). The BH_3 resonance in the ^1H NMR spectrum is partially obscured by the other peaks in the spectrum. ^{11}B NMR ($\text{MeCN}-d_3$): δ –12.5 (q, $^1J_{\text{BH}} = 91$ Hz), –23.5 (q, $^1J_{\text{BH}} = 90$ Hz). IR (cm^{-1}): 2343 s, 2309 sh, 2260 s, 1329 w, 1300 w, 1275 m, 1266 m, 1209 sh, 1177 s, 1165 s, 1114 m, 1098 s, 1074 w, 1057 m, 1042 w, 1027 m, 976 m, 951 w, 918 w, 902 w, 868 w, 832 w, 802 w, 768 w.

Sodium *N,N*-Di(*iso*-propyl)aminodiboranate, $\text{Na}[\text{H}_3\text{B}-\text{N}(\text{i-Pr})_2\text{-BH}_3]$, 14. *N,N*-Di(*iso*-propyl)amine-borane (4.1 g, 35.7 mmol) was heated to 100 °C, which caused the white solid to melt to a colorless liquid (*i-Pr* $_2\text{N}=\text{BH}_2$) and evolve gas. The colorless liquid was distilled at 160 °C and ~1 atm into a Schlenk flask cooled to –78 °C. To the distillate at 0 °C was added $\text{BH}_3\cdot\text{THF}$ (32 mL of a 1 M solution in THF, 32 mmol). The mixture was warmed to room temperature and then stirred overnight to give a solution of μ -(*N,N*-di(*iso*-propyl)amino)diborane, μ -(*i-Pr*) $_2\text{NB}_2\text{H}_5$. ^{11}B NMR (THF): δ –20.8 (td, $^1J_{\text{BH}} = 128$, $^2J_{\text{BH}} = 33$ Hz). In a separate flask, NaH (1.8 g of a 60 wt % dispersion in mineral oil, 45 mmol NaH) was washed with pentane (50 mL), collected by filtration, and dried under vacuum. The μ -(*N,N*-di(*iso*-propyl)amino)diborane solution from the previous step was cooled to 0 °C and transferred onto the NaH, and the resulting mixture was stirred for 21 h at room temperature. The slurry was filtered, and the colorless filtrate was taken to dryness under

vacuum to afford a white solid. Coordinated solvent was removed by heating the solid under vacuum to 40 °C overnight. The white solid was dissolved in Et_2O (50 mL), the solution was filtered, and the colorless filtrate was taken to dryness under vacuum to afford a white powder. Yield: 3.62 g (67%). Analytically pure crystals can be grown by dissolving the powder in Et_2O , concentrating the solution under reduced pressure to saturation, and cooling to –20 °C. Mp. >275 °C. Anal. Calcd for $\text{C}_6\text{H}_{20}\text{NB}_2\text{Na}$: C, 47.8; H, 13.4; N, 9.29%. Found: C, 47.7; H, 13.1; N, 9.4%. ^1H NMR ($\text{MeCN}-d_3$): δ 1.02 (1:1:1:1 q, $^1J_{\text{BH}} = 91$ Hz, 6H, BH_3), 1.16 (d, $^3J_{\text{HH}} = 6.5$ Hz, 12H, C-Me), 2.96 (septet, $^3J_{\text{HH}} = 6.5$ Hz, 2H, N-CH). ^{11}B NMR ($\text{MeCN}-d_3$): δ –17.6 (q, $^1J_{\text{BH}} = 91$ Hz). IR (cm^{-1}): 2543 w, 2354 s, 2312 s, 2250 s, 2096 w, 1321 w, 1270 m, 1225 m, 1197 m, 1158 s, 1124 w, 1101 w, 1046 m, 1025 m, 975 m, 941 w, 924 w, 895 w, 822 w, 771 w.

Sodium *N,N*-Bis(trimethylsilyl)aminodiboranate, $\text{Na}(\text{H}_3\text{B}-\text{N}(\text{SiMe}_3)_2\text{-BH}_3)$ 15. *Method A.* NaH (3.33 g of a 60 wt % dispersion in mineral oil, 83 mmol) was washed with pentane (3 $\times$ 50 mL) and dried in vacuum for 30 min. A solution of μ -bis-*N,N*-(trimethylsilyl)aminodiborane (4.54 g, 24 mmol; prepared as described in the synthesis of compound 9) in THF (30 mL) was transferred onto the NaH, and the mixture was stirred for 23 h. The solution was filtered from the remaining NaH, and the filtrate was taken to dryness in vacuum. The residue was washed with toluene (30 mL) and pentane (3 $\times$ 30 mL) and dried under vacuum at room temperature overnight to afford the product as a white solid. Yield: 4.15 g (78%). The microanalysis reflected the presence of some sodium *N*-trimethylsilylaminodiboranate (compound 9) owing to an imperfect separation of the two distillation fractions. ^1H NMR (THF- d_8 , 20 °C): δ 0.20 (s, 18H, SiMe_3), 1.21 (1:1:1:1 q, $^1J_{\text{BH}} = 89$ Hz, 6H, BH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 20 °C): δ 1.87 (s, SiMe_3). ^{11}B NMR (THF, 20 °C): δ –19.3 (q, $^1J_{\text{BH}} = 91$ Hz). IR (cm^{-1}): 2333 br, 2250 br, 1458 s, 1376 m, 1247 s, 1054 s, 949 m, 840 br, 785 w, 762 w, 726 w, 681 m, 651 w, 501 w.

Method B. To $\text{BH}_3\cdot\text{THF}$ (100 mL of a 1 M solution in THF, 100 mmol) was added $\text{HN}(\text{SiMe}_3)_2$ (10.5 mL, 50 mmol). The mixture was heated to reflux until the conversion to both the μ -bis(trimethylsilyl)aminodiborane and μ -trimethylsilylaminodiborane was complete, as judged from a ^{11}B NMR spectrum of an aliquot. Typically, this step required 3 days. The mixture was separated by distillation at reduced pressure (30 mTorr/32 °C). In a separate flask, NaH (1.67 g of a 60 wt % dispersion in mineral oil, 42 mmol) was washed with pentane (3 $\times$ 50 mL) and dried under dynamic vacuum for 30 min. The μ -bis(trimethylsilyl)aminodiborane solution was transferred onto the NaH and stirred for 21 h. The solution was filtered from the remaining NaH, and the filtrate was taken to dryness in vacuum. The product, a white solid, was washed with toluene (1 $\times$ 30 mL) and pentane (3 $\times$ 30 mL) and dried under vacuum at room temperature overnight. Yield: 4.96 g (47%). The ^{11}B NMR data match that of $\text{Na}[\text{H}_3\text{B}-\text{N}(\text{SiMe}_3)_2\text{-BH}_3]$ prepared by method A.

Crystallographic Studies.²⁷ Single crystals of 1, 1a, 6a, and 8a were grown from diethyl ether, single crystals of 9 and 12 were grown by diffusion of pentane into diethyl ether, single crystals of 1b and 1c were grown from heptane, and single crystals of 1d were grown from tetrahydrofuran. All crystals were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled 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 S1.

Data were collected with an area detector by using the measurement parameters listed in Table S1. 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 set of unique data. The structures were solved using direct methods (SHELXL). Correct positions for all the non-hydrogen atoms were deduced from an E-map and subsequent least-squares refinement and difference Fourier calculations. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. Hydrogen atoms attached to boron were located in the

difference maps, and their positions were refined with independent anisotropic displacement parameters, unless otherwise noted. Hydrogen atoms attached to carbon were placed in idealized positions; the methyl groups were allowed to rotate about the C–N or C–O axis 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} . No correction for isotropic extinction was necessary. Final refinement parameters are given in Table S1. More details of the refinements can be found in the ESI.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01997>.

Selected bond distances and angles, NMR data, and details of crystallographic refinements (PDF)

Accession Codes

CCDC 2177369–2177377 contain 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

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