J|A|C|S
COMMUNICATIONS

Synthesis of the Long-Sought Unsubstituted Aminodiboranate $Na(H_3B-NH_2-BH_3)$ and Its *N*-Alkyl Analogs

Scott R. Daly, Brian J. Bellott, Do Young Kim, and Gregory S. Girolami*

The School of Chemical Sciences, University of Illinois at Urbana−Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received February 25, 2010; E-mail: girolami@scs.illinois.edu

Boranes and their derivatives have long been important compounds and are currently the subject of renewed interest owing to their potential as hydrogen storage materials.[1−9] For example, ammonia borane, $NH_3 \cdot BH_3$, has an especially high gravimetric hydrogen content of 19.6 wt % and can release multiple equivalents of H_2.[10−14] Related metal amidoboranes such as $M(NH_2-BH_3)$ or $M(NH_2-BH_3)_2$, where M is an alkali or alkaline earth metal, are also being explored as hydrogen storage materials.[15−18] In a different context, metal complexes of amino- and amidoboranes can serve as models of the binding and activation of alkanes and alkenes.[19−22]

One of the most interesting borane amine compounds is the "diammoniate of diborane" of stoichiometry $B_2H_6 \cdot 2NH_3$ first prepared by Alfred Stock in 1923.[23] Schlesinger and Berg[24] suggested that this compound should be formulated as the ammonium salt $[NH_4][H_3B-NH_2-BH_3]$, but the structure remained controversial for many decades until spectroscopic studies established that this compound is actually the borohydride salt $[H_3N-BH_2-NH_3][BH_4]$.[25] Interestingly, despite its historical importance, the $H_3B-NH_2-BH_3^-$ anion proposed by Schlesinger and Berg has never been prepared (although it has been the subject of a computation).[26] Here we report the synthesis of the unsubstituted aminodiboranate salt $Na(BH_3-NH_2-BH_3)$.

Reduction of dimethylamine−borane, $HNMe_2 \cdot BH_3$, with Na in refluxing tetrahydrofuran is known to generate the *N*,*N*-dimethylaminodiboranate salt $Na(H_3B-NMe_2-BH_3)$.[27] We find that this synthesis can be extended to prepare other aminodiboranates, including the previously unknown parent compound. In particular, reduction of $NH_3 \cdot BH_3$ with excess Na in tetrahydrofuran at room temperature yields a solution of the recently described[17,18] salt $Na(NH_2-BH_3)$, as shown by a signal at δ −21.9 in the ^{11}B NMR spectrum (Figure 1). When this mixture is heated to reflux, however, the unsubstituted aminodiboranate $Na(BH_3-NH_2-BH_3)$ is formed, along with a white byproduct that precipitates from the reaction solution. Filtration of the solution, removal of the solvent, and washing successively with benzene and pentane afford $Na(BH_3-NH_2-BH_3)(thf)_x$ (**1a**). Similar reactions with other amine−boranes afford $Na(H_3B-NHMe-BH_3)$ (**1b**), $Na(H_3B-NHEt-BH_3)$ (**1c**), $Na(H_3B-NMeEt-BH_3)$ (**1d**), $Na[H_3B-N(C_4H_8)-BH_3]$ (**1e**), and $Na[H_3B-N(C_5H_{10})-BH_3]$ (**1f**), where $N(C_4H_8)$ = pyrrolido and $N(C_5H_{10})$ = piperido.

$$4\ HNRR' \cdot BH_3 + 2\ Na \rightarrow 2\ Na(H_3B-NRR'-BH_3) + H_2 + 2\ HNRR'$$

The parent salt can also be generated by reaction of 2 equiv of $NH_3 \cdot BH_3$ with $NaNH_2$ in refluxing thf, which produces $Na(H_3B-NH_2-BH_3)$ in better yield (50%). This reaction also proceeds through the $Na(NH_2-BH_3)$ intermediate.

The ^1H NMR spectra of the new aminodiboranates all contain broad 1:1:1:1 quartets for the BH_3 hydrogen atoms, which are coupled to ^{11}B ($I = 3/2$) with $^1J_{BH} \approx 90$ Hz. The ^{11}B NMR spectra consist of binomial quartets with the same coupling constant (Figure 1). The shifts of δ −19.9 for $Na(H_3B-NH_2-BH_3)$, δ −15.7 for $Na(H_3B-NHMe-BH_3)$, and δ −11.5 for $Na(H_3B-NMe_2-BH_3)$ show that the ^{11}B NMR resonance is deshielded by 4.2 ppm for each NH group that is replaced with a NMe group and suggest that all these salts are in the same chemical class.

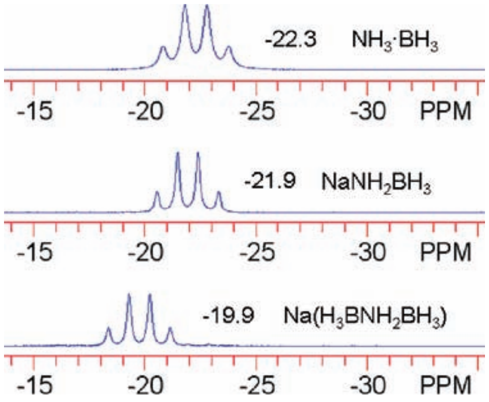

Figure 1. ^{11}B NMR spectra of (top) $NH_3 \cdot BH_3$, (middle) $Na(NH_2-BH_3)$ formed from $NH_3 \cdot BH_3$ and excess Na in thf at room temperature, and (bottom) $Na(H_3B-NH_2-BH_3)$ (**1a**) formed from $NH_3 \cdot BH_3$ and excess Na in refluxing thf.

Addition of dioxane to the aminodiboranate salts,[28] followed by extraction and crystallization from diethyl ether, affords the corresponding dioxane adducts (**2a**−**f**). Of these, $Na(H_3B-NHMe-BH_3)(dioxane)_{0.5}$ (**2b**), $Na(H_3B-NHEt-BH_3)(dioxane)$ (**2c**), and $Na[H_3B-N(C_4H_8)-BH_3](dioxane)$ (**2e**) form crystals suitable for X-ray diffraction studies.

The *N*-ethyl derivative **2c** crystallizes with 1 equiv of dioxane per sodium. The sodium atoms are arranged in pairs, each sodium

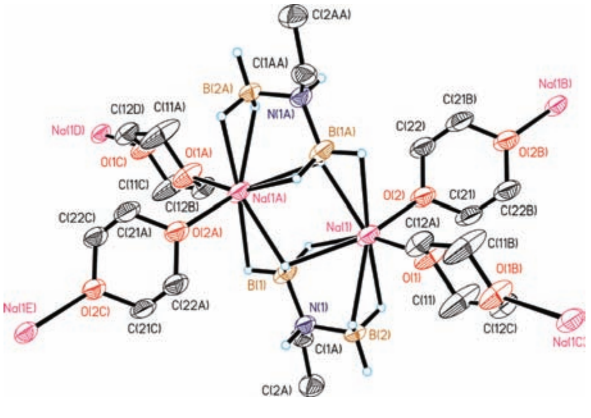

Figure 2. Molecular structure of $Na(H_3B-NHEt-BH_3)(dioxane)$, **2c**. Ellipsoids are drawn at the 35% probability level. Hydrogen atoms attached to carbon have been deleted for clarity.

10.1021/ja1016427 © 2010 American Chemical Society

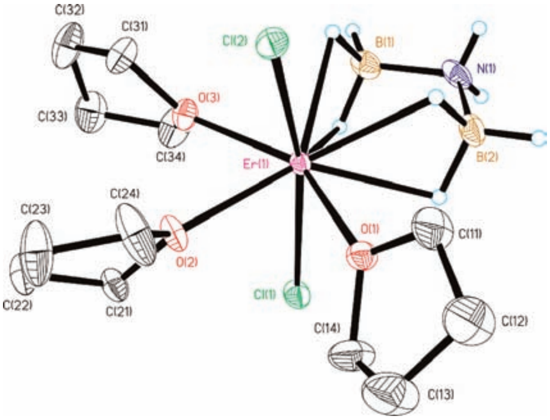

Figure 3. Molecular structure of $Er(H_3B{-}NH_2{-}BH_3)Cl_2(thf)_3$, **3**. Ellipsoids are drawn at the 35% probability level. The hydrogen atoms attached to carbon have been omitted for clarity.

atom being coordinated to one chelating $H_3B{-}NHEt{-}BH_3^-$ ligand, one BH_3 group from an adjacent unit, and two oxygen atoms from the dioxane ligands (Figure 2). The three boron and two oxygen atoms describe a trigonal bipyramidal arrangement about each Na atom, in which the oxygen atoms occupy one axial and one equatorial site. All of the BH_3 groups are bound to the Na atoms in a κ^2H fashion as indicated by the Na···B distances, which range from 2.720(3) to 2.823(3) Å. The dinuclear units in **2c** are connected into a network by the dioxane molecules, which bridge between Na atoms with Na−O distances of 2.333(2) and 2.362(2) Å. The crystal structure of the pyrrolidinodiboranate compound **2e** is very similar to that of **2c** (Figure S1).

The *N*-methyl derivative **2b** crystallizes with only 0.5 equiv of dioxane (vs 1 equiv in **2c** and **2e**). As seen in the structure of **2c**, pairs of sodium cations are connected together into dinuclear units by two *N*-methylaminodiboranate anions, which can be viewed as simultaneously chelating to one Na atom and bridging to the second (Figure S2). In **2b** there is only one Na−O interaction but two Na···B interactions with nearby dinuclear units. The Na···B distances range from 2.769(1) to 2.934(1) Å, and the Na−O distances are 2.335(1) Å. The borane hydrogen atoms, which surfaced in the difference maps, all interact with either one or two sodium atoms.

Although to date we have been unable to obtain X-ray quality crystals of the parent sodium salt $Na(H_3B{-}NH_2{-}BH_3)$ or its ether adducts, we have been successful in using it as a ligand for metal complexes. For example, treatment of $ErCl_3$ with $Na(H_3B{-}NH_2{-}BH_3)$ in tetrahydrofuran affords the new erbium complex $Er(H_3B{-}NH_2{-}BH_3)Cl_2(thf)_3$, **3**. This erbium complex provides crystallographic verification of the $H_3B{-}NH_2{-}BH_3^-$ motif (Figure 3). The aminodiboranate ligand chelates to the metal center by means of hydrogen atoms on the boron centers; each BH_3 unit forms a κ^2H interaction with the Er atom. The average B−N distance within the aminodiboranate anion is 1.561(5) Å, and the B−N−B angle is 110.8(2)°. The Er···B distances of 2.775(4) and 2.791(4) Å are similar to those observed for $Er(H_3B{-}NMe_2{-}BH_3)_3$ and $Er(H_3B{-}NMe_2{-}BH_3)_3(thf)$.[29,30]

Others have noted that the $-NH_2{-}BH_3^-$ group is isoelectronic with ethyl groups and can bind to metals to form agostic structures.[19] The $H_3B{-}NH_2{-}BH_3^-$ group is isoelectronic with propane and can similarly serve as a structural model for the binding of this alkane to metal centers.

The successful synthesis of the parent aminodiboranate anion resolves a 90 year old debate about the existence of this species. Although the aminodiboranates described herein are not likely to be useful hydrogen storage materials, they do have potential as ligands for chemical vapor deposition precursors.[29,31] The absence of carbon in $H_3B{-}NH_2{-}BH_3^-$ is significant in this regard, because carbon contamination is a problem in many CVD processes. The ability of the new sodium aminodiboranate salts to serve as ligands for CVD precursors is consequently under current investigation.

Acknowledgment. We thank the National Science Foundation (CHE07-50422) and the PG Research Foundation for support of this research, and Scott Wilson, Teresa Wieckowska-Prussak, and Danielle Gray for collecting the X-ray diffraction data.

Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Langmi, H. W.; McGrady, G. S. *Coord. Chem. Rev.* **2007**, *251*, 925–935.
(2) Orimo, S.-I.; Nakamori, Y.; Eliseo, J. R.; Zuettel, A.; Jensen, C. M. *Chem. Rev.* **2007**, *107*, 4111–4132.
(3) van den Berg, A. W. C.; Arean, C. O. *Chem. Commun.* **2008**, 668–681.
(4) Wang, P.; Kang, X.-D. *Dalton Trans.* **2008**, 5400–5413.
(5) Eberle, U.; Felderhoff, M.; Schueth, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6608–6630.
(6) Graetz, J. *Chem. Soc. Rev.* **2009**, *38*, 73–82.
(7) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294–1314.
(8) Lim, K. L.; Kazemian, H.; Yaakob, Z.; Daud, W. R. W. *Chem. Eng. Technol.* **2010**, *33*, 213–226.
(9) Yang, J.; Sudik, A.; Wolverton, C.; Siegel, D. J. *Chem. Soc. Rev.* **2010**, *39*, 656–675.
(10) Smythe, N. C.; Gordon, J. C. *Eur. J. Inorg. Chem.* **2010**, 509–521.
(11) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279–293.
(12) Xu, Q.; Chandra, M. *J. Alloys Compd.* **2007**, *446−447*, 729–732.
(13) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613–2626.
(14) Marder, T. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8116–8118.
(15) Zhang, Q.; Tang, C.; Fang, C.; Fang, F.; Sun, D.; Ouyang, L.; Zhu, M. *J. Phys. Chem. C* **2010**, *114*, 1709–1714.
(16) Chua, Y. S.; Wu, G.; Xiong, Z.; He, T.; Chen, P. *Chem. Mater.* **2009**, *21*, 4899–4904.
(17) Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. *Nat. Mater.* **2008**, *7*, 138–141.
(18) Xiong, Z.; Wu, G.; Chua, Y. S.; Hu, J.; He, T.; Xu, W.; Chen, P. *Energy Environ. Sci.* **2008**, *1*, 360–363.
(19) Forster, T. D.; Tuononen, H. M.; Parvez, M.; Roesler, R. *J. Am. Chem. Soc.* **2009**, *131*, 6689–6691.
(20) Tang, C. Y.; Thompson, A. L.; Aldridge, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 921–925.
(21) Alcaraz, G.; Vendier, L.; Clot, E.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 918–920.
(22) Chaplin, A. B.; Weller, A. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 581–584.
(23) Stock, A.; Kuss, E. *Ber. Dtsch. Chem. Ges. B* **1923**, *56B*, 789–808.
(24) Schlesinger, H. I.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 290–299.
(25) Schultz, D. R.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 4–8.
(26) Nguyen, V. S.; Matus, M. H.; Grant, D. J.; Nguyen, M. T.; Dixon, D. A. *J. Phys. Chem. A* **2007**, *111*, 8844–8856.
(27) Nöth, H.; Thomas, S. *Eur. J. Inorg. Chem.* **1999**, 1373–1379.
(28) Keller, P. C. *J. Chem. Soc. D* **1969**, 1465.
(29) Daly, S. R.; Kim, D. Y.; Yang, Y.; Abelson, J. R.; Girolami, G. S. *J. Am. Chem. Soc.* **2010**, *132*, 2106–2107.
(30) Daly, S.; Kim, D. Y.; Girolami, G. S., manuscript in preparation.
(31) Kumar, N.; Yanguas-Gil, A.; Daly, S. R.; Girolami, G. S.; Abelson, J. R. *Appl. Phys. Lett.* **2009**, *95* (144107), 1–3.

JA1016427