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# Boron−Boron $\sigma$-Bond Formation by Two-Electron Reduction of a H-Bridged Dimer of Monoborane

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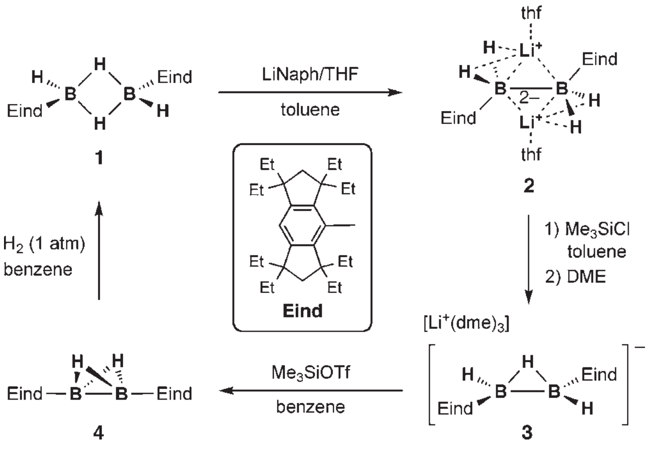
S *Supporting Information*

**ABSTRACT:** Diborane(6) as a H-bridged dimer of monoborane can be converted cleanly by two-electron reduction into diborane(6) dianion, which is isoelectronic with ethane, through B−B $\sigma$-bond formation when each boron atom has a bulky ligand on it. The existence of the B−B $\sigma$ bond is supported by the X-ray molecular structure [B−B bond length of 1.924(3) Å], NMR studies, magnetic susceptibility measurements, and DFT calculations. Stepwise hydride abstraction reactions of the diborane(6) dianion produce the corresponding H-bridged diborane(5) anion and doubly H-bridged diborane(4) without B−B bond scission.

Hydroboron compounds have played a vital role in the development of modern chemistry since their first isolation and characterization by Stock about a century ago.[1−3] Their structure and bonding accelerated the development of molecular orbital (MO) assessment of bonding character,[2] and they have proven useful as versatile reagents in organic synthesis.[3] The simplest stable borane is diborane(6), $B_2H_6$, whose bridging B−H−B three-center, two-electron (3c−2e) bonds marked a turning point in the history of how chemical bonding is perceived. Hydroboron derivatives of many kinds have since been prepared, attracting much attention from both experimentalists and theoreticians to completely understand how the electron deficiency of boron impacts its chemical bonding.[4−6]

Theory says that one-electron addition to electron-deficient group-13 boron species should give the corresponding anionic species, which are isoelectronic with their group-14 carbon counterparts. Thus, the B═B double-bond character of the dianionic diborane(4) species, $[B_2H_4]^{2-}$, which is isoelectronic with ethylene, $C_2H_4$, was predicted for the dilithium salt $Li_2B_2H_4$ by Kaufmann and Schleyer.[7] Subsequent isolation of a diborane(4) dianion by the two-electron reduction of a tetraaryldiborane(4) derivative was achieved by Power, providing clear evidence for B−B $\pi$-bond formation.[8] Similarly, one can envision that the introduction of two electrons into $B_2H_6$, a H-bridged borane dimer, would provide the $[B_2H_6]^{2-}$ dianion, which is isoelectronic with ethane, $C_2H_6$, with concurrent B−B $\sigma$-bond formation. However, since the first experimental approach toward the synthesis of dialkali metal salts of $[B_2H_6]^{2-}$ was reported by Stock in 1935,[9,10] all attempts to isolate such proposed molecules have met with failure. For instance, in 1994, Onak and Shore reported NMR spectroscopic evidence for the stepwise generation of $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$ as intermediates in the homogeneous reduction of $B_2H_6$, although further reaction led to the formation of $[B_3H_8]^-$ and $[BH_4]^-$.[11] Thus, it may be difficult to isolate clean diborane(6) dianion species because of undesirable clustering and disproportionation reactions.[12−16] Such adverse over-reactions would be completely suppressed by the introduction of a bulky protecting group on boron. We report here that the two-electron reduction of the substituted diborane(6) (Eind)HB($\mu$-H)$_2$BH(Eind) (**1**) (Eind = 1,1,3,3,5,5,7,7-tetraethyl-*s*-hydrindacen-4-yl) can be selectively achieved, leading to the formation of the dilithium diborane(6) dianion $[Li^+(thf)]_2[(Eind)H_2BBH_2(Eind)]^{2-}$ (**2**) as a stable B−B $\sigma$-bonded species (Scheme 1).[17] Thus, Stock's dream has been realized 76 years later by the installation of the bulky Eind groups on the two boron atoms.

**Scheme 1. Synthetic Cycle for Hydrodiboron Compounds**



Treatment of a toluene solution of diborane(6) **1** with 2 equiv of lithium naphthalenide (LiNaph) in THF produced air- and moisture-sensitive light-yellow crystals of the dilithium diborane(6) dianion compound **2** in 69% yield. Compound **2** was thermally stable in both solution and the solid state for months at

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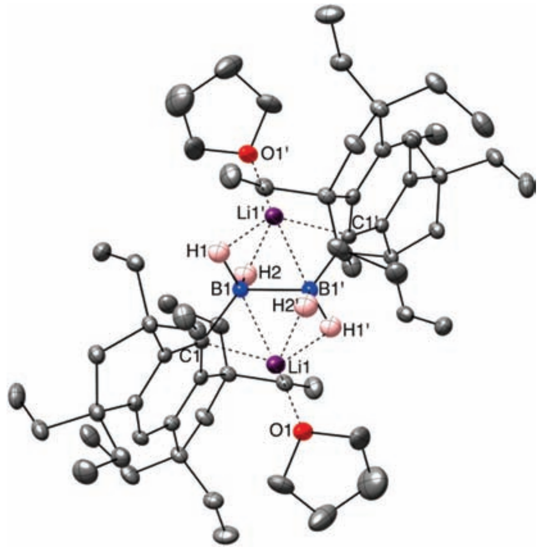


**Figure 1.** Molecular structure of **2** (50% probability ellipsoids). Hydrogen atoms have been omitted, except for the BH hydrogens. Selected atomic distances (Å) and bond angle (deg): B1−B1′, 1.924(3); B1−C1, 1.6662(19); Li1···B1, 2.354(3); Li1···B1′, 2.086(3); Li1···C1, 2.234(3); Li1···O1, 1.860(3); C1−B1−B1′, 122.22(13).

ambient temperature under a dry argon atmosphere. In the $^{11}$B NMR spectrum of **2** in benzene-$d_6$, only one resonance at −27.1 ppm was observed, which did not change significantly as a function of temperature. **2** was EPR-silent in both solution and the solid state. No detectable magnetic susceptibility was found in solution by the Evans method.[18,19] All of these observations indicate the diamagnetic character of **2**.

The molecular structure of **2** was confirmed by single-crystal X-ray crystallography (Figure 1). The dilithium salt **2** forms two-contact ion pairs in the crystal lattice, along with the attractive B−H···Li$^+$ interaction. This molecule has an inversion center about the midpoint of the B−B bond; the ethane-like structure has a staggered conformation in which all of the B−H bonds are terminal. The atomic distance between the two boron atoms is 1.924(3) Å, which is much longer than the length of a typical B−B single bond (1.72 Å) and even elongated relative to the typical B···B distance in diborane(6) derivatives (1.82 Å).[20] This long B−B distance suggests a weak interaction between two monoborane anion radicals, $[(\mathrm{Eind})\mathrm{BH}_2]^{-\bullet}$, that are connected by two lithium cations, but the diamagnetism of **2** supports the formation of a B−B σ bond. The B−B bond elongation is ascribed to the electrostatic Coulombic repulsion between the two anionic boron atoms.

To delineate the nature of the bonding in the diborane(6) dianion, density functional theory (DFT) computations at the B3LYP/6-31G(d,p) level were performed for **2** as a singlet using the Gaussian 03 program package.[21] The ethane-like structure was successfully reproduced with a B−B distance of 1.952 Å, which is comparable to the experimental value (see above). As shown in Figure 2, the HOMO of **2** is primarily localized as the B−B σ-bonding orbital. Its B−B bond order was calculated to be 0.905 on the basis of the Wiberg bond index (WBI).[22] The natural population analysis (NPA) charge distribution[23] of **2** shows that the two neighboring B atoms are negatively charged (−0.449). These electronic configurations are consistent with the presence of the B−B σ bond in dilithium dianion **2**. We also confirmed that the related counterion-free form, $[(\mathrm{Eind})\mathrm{H}_2\mathrm{BBH}_2(\mathrm{Eind})]^{2-}$ (**2′**), has a similar B−B σ-bonding nature in the ethane-like structure.[24] Thus, the addition of two electrons to **1** results in the formation of a σ bond between the two boron atoms, compensating for the electron deficiency of the boron centers, and converts the two B−H−B 3c−2e bonds into two terminal B−H bonds.

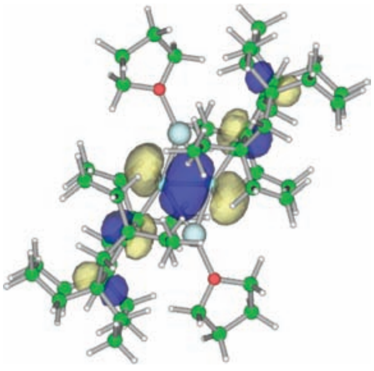


**Figure 2.** HOMO of **2**.

The dilithium diborane(6) dianion **2** can also be regarded as a bisadduct of lithium hydride (LiH) to the neutral diborane(4). Actually, stepwise hydride abstraction of **2** can be performed successfully without B−B bond scission. Thus, the addition of an excess amount of trimethychlorosilane ($\mathrm{Me_3SiCl}$) to a toluene solution of **2** led to the clean formation of a diborane(5) monoanion;[25] this was followed by ligand exchange from THF to 1,2-dimethoxyethane (DME), resulting in colorless crystals of $[\mathrm{Li}^+(\mathrm{dme})_3][(\mu\text{-H})(\mathrm{Eind})\mathrm{HBBH}(\mathrm{Eind})]^-$ (**3**) in 82% yield. The molecular structure of **3** determined by X-ray crystallography is shown in Figure 3. The diboron core of **3** possesses a unique single bridging hydrogen atom as well as two terminal hydrogen atoms. The B−B bond length of 1.655(2) Å is slightly larger than that in the previously reported Eind-substituted diborane(4) dianion $[\mathrm{Li}^+(\mathrm{thf})]_2[(\mathrm{Eind})\mathrm{HBBH}(\mathrm{Eind})]^{2-}$ [1.616(4) Å].[6] This singly hydrogen-bridged structure was also successfully reproduced by DFT calculations of the counterion-free form, $[(\mu\text{-H})(\mathrm{Eind})\mathrm{HBBH}(\mathrm{Eind})]^-$ (**3′**); the B−B distance of 1.643 Å indicates double-bond character (σ- and π-like bonds) between the two B atoms incorporating the bridging μ-H atom,[24] as predicted by Lammertsma and Ohwada.[26]

Further treatment of **3** with trimethylsilyl trifluoromethanesulfonate ($\mathrm{Me_3SiOTf}$) in benzene readily afforded the diborane(4) $(\mu\text{-H})_2(\mathrm{Eind})\mathrm{BB}(\mathrm{Eind})$ (**4**) in good yield. As previously reported, **4** was converted back to diborane(6) **1** upon exposure to $H_2$ gas. Thus, a transformation cycle involving a diborane(4), a diborane(5) anion, a diborane(6) dianion, and a diborane(6) has now been established through the use of the bulky Eind auxiliary.

This synthetic procedure is particularly useful for the elaborate molecular design of hydrodiboron compounds. The $^{11}$B-labeled deuterated diborane(4) $(\mu\text{-D})_2(\mathrm{Eind})^{11}\mathrm{B}^{11}\mathrm{B}(\mathrm{Eind})$ (**4-$^{11}$*B*,*d*$_2$**) (Figure 4), which is free from the highly neutron-absorbing $^{10}$B isotope and thus the best isotope-labeled form for single-crystal neutron diffraction studies,[27] was obtained in overall 12% yield starting from $^{11}\mathrm{BF}_3$ gas. Neutron data were collected on a large-sized single crystal of **4-$^{11}$*B*,*d*$_2$** with dimensions of 7 mm × 4 mm × 1 mm using the SXD single-crystal neutron diffractometer[28] (Figure 5). The experimental structural parameters, including

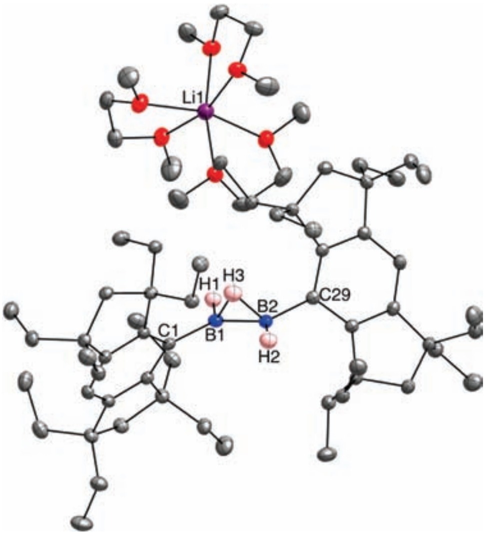
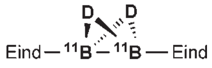


**Figure 3.** Molecular structure of **3** (50% probability ellipsoids). Hydrogen atoms have been omitted except for the BH hydrogens. Selected atomic distances (Å), bond angles (deg), torsion angle (deg), and dihedral angle (deg): B1−B2, 1.655(2); B1−C1, 1.6247(18); B2−C29, 1.6243(18); C1−B1−B2, 128.43(14); C29−B2−B1, 129.97(14); C1−B1−B2−C29, −178.98(14); B1−C1−H1/B2−C29−H2, 6.2(12).



$\mathrm{Eind{-}{}^{11}B\overset{D\;\;D}{-}{}^{11}B{-}Eind}$

**4-$^{11}B,d_2$**

**Figure 4.** $^{11}$B-labeled deuterated diborane(4).

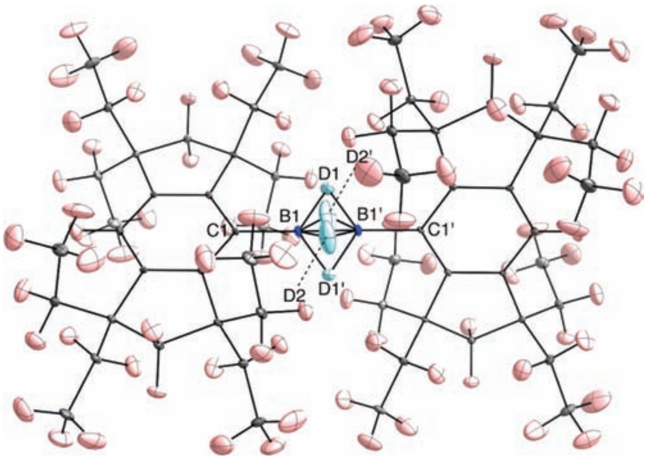


**Figure 5.** Molecular structure of **4-$^{11}B,d_2$** (50% probability ellipsoids) determined using single-crystal neutron diffraction. Selected atomic distances (Å), bond angle (deg), and dihedral angle (deg): B1−B1′, 1.483(3); B1−C1, 1.559(3); B1−D1, 1.383(14); B1−D2, 1.295(6); D1···D2, 1.796(13); C1−B1−B2, 178.8(2); B1−D1−B1′/B1−D2−B1′, 107.1(8).

the precise positions of the $\mu$-D atoms, are in excellent agreement with those previously predicted for **4** by theoretical calculations.[6]

To date, two types of synthetic methods for B−B bond formation at the laboratory level have been available: redistribution reactions of precursor boranes at higher temperatures and reductive coupling of appropriate boron halides.[29] We have demonstrated that B−B $\sigma$-bond formation via two-electron reduction of diborane(6) provides a new approach for the catenation of boron atoms, when a bulky group such as the Eind group is present on the boron atoms. The availability of a family of well-defined hydrodiboron compounds in quantity opens the door to the full experimental clarification of their electronic and bonding nature as well as their potential uses as new synthetic reagents and new building units in the field of functional materials.

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details; crystallographic data for **2**, **3**, and **4-$^{11}B,d_2$** (CIF); details of the calculations; and complete ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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