A Stable Doubly Hydrogen-Bridged Butterfly-Shaped Diborane(4) Compound

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The structures of hydrogen-substituted diboron compounds, B_2H_6 (**I**), B_2H_4 (**II**), and B_2H_2 (**III**), have been continuously studied for the complete understanding of chemical bonding.[1] Theoretical predictions of these compounds are summarized in Figure 1. Diborane(6) **I**, known as the most fundamental hydroboration agent,[2] is a typical electron-deficient compound with a pair of B−H−B 3-center, 2-electron (3c-2e) bonds.[3] Theoretical studies of the parent diborane(4) have proposed two forms, a staggered D_{2d} isomer **II** and a doubly H-bridged butterfly shaped C_{2v} isomer **II′**, with nearly the same energies.[4,5] The Lewis base adducts of the diborane(4) **II(2L)** have been experimentally studied.[6] The diborane(4) dianion **II(2−)** is isoelectronic with ethylene, which is related to a dilithio species **II(2−)′** with a planar geometry due to the B−H···Li+ interaction.[7] The C_{2v} isomer **II′** is considered to have one B−B σ single bond and two B−H−B 3c-2e bonds and is also closely related to a canonical "protonated B−B triple bond" (**II″**),[8] isoelectronic with a doubly proton-bridged acetylene $C_2H_4^{2+}$. The diborene(2) **III** adopts a linear geometry with two degenerate π orbitals like acetylene C_2H_2, but each π orbital is filled with one electron.[9] Its two-electron reduction form **III(2−)**, isoelectronic with acetylene, is related to the protonated B−B triple bond **II″** and also to a dilithio species **III(2−)′**.[10] The neutral B−B double bond compound **III** may be stabilized by the Lewis base adduct **III(2L)**.[11] In addition, some Lewis base stabilized B−B triple bond species (L)BB(L), L = CO and (BO)−, have also been spectroscopically and/or theoretically studied.[10,12]

As described above, the most characteristic feature of diboron chemistry, even in the smallest boron cluster, resides in the fact that the B−B single and multiple bond species are closely interrelated. In particular, the diborane(4) constitutes a rich chemistry related to all the B−B single, double, and triple bonds. Experimentally, however, only two types of unsaturated compounds have been isolated, both being related to the B−B double bond chemistry. Thus, one is the dilithium salts of the tetraaryl-, diamino(diphenyl)-, and tetraamino-diborane(4) dianions related to **II(2−)′**,[13] and the other is the neutral diborenes stabilized by *N*-heterocyclic carbenes **III(2L)**.[6a,14] We now report the isolation and characterization of a stable doubly hydrogen bridged butterfly shaped diborane(4), **II′** or **II″**, stabilized by bulky aryl groups, *i.e.*, 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) groups,[15] as the terminal substituents.

The experimental results are summarized in Scheme 1. The reduction of $EindBF_2$ using lithium powder in dry THF afforded the hydrogen-substituted diborane(4) dianion $[Li^+(thf)]_2[Eind(H)BB(H)Eind]^{2-}$ (**1**) as reddish purple crystals
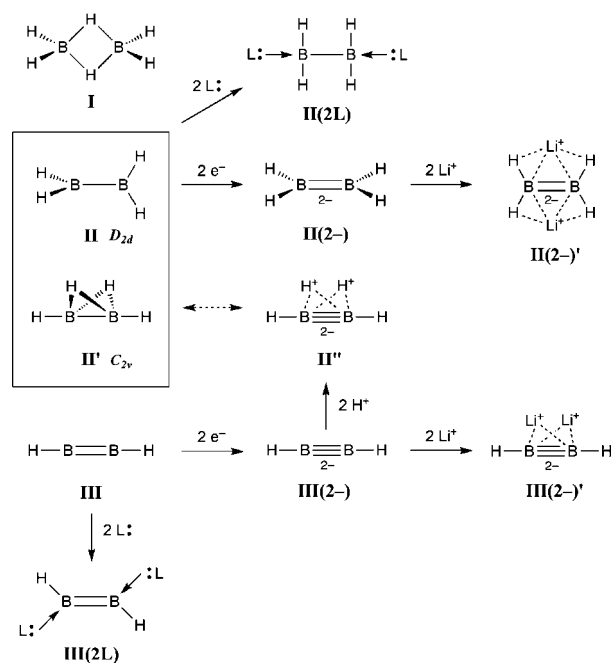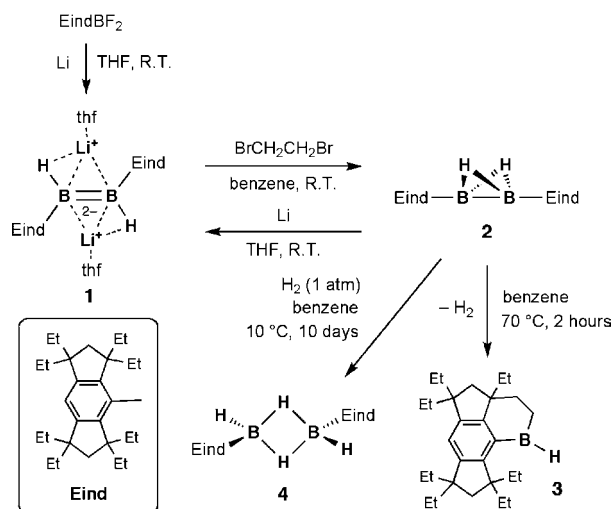

Figure 1. A schematic representation of diboron compounds.

Scheme 1

in a 23% yield. It was confirmed that the hydrogen atoms on the boron atoms originate from the ethyl groups of the Eind groups based on deuterium labeling experiments.[16] Compound **1** was characterized by NMR spectroscopy and X-ray crystal-

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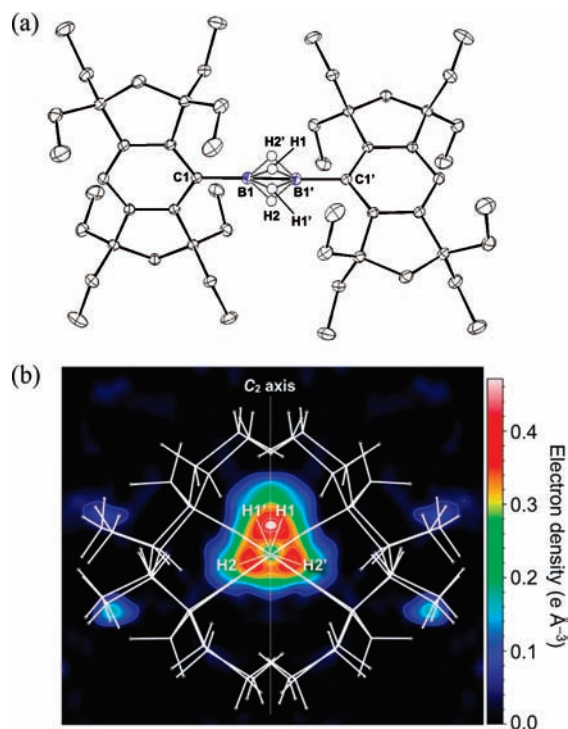§ Kyoto University.

Figure 2. (a) Molecular structure of **2** (50% probability level). Hydrogen atoms are not shown except for BH hydrogens. (b) Difference Fourier map of **2**. Electron density increases from blue to red. The peak heights are 0.47 and 0.42 e Å⁻³.

lography using synchrotron radiation (Figure S1). These experimental data are in agreement with the B−B double bond character together with the attractive B−H···Li⁺ interaction related to the **II(2−)′**, as predicted by Kaufmann and Schleyer.[6] An intriguing aspect is that **1** might be a candidate precursor for the H-substituted diborane(4), if an appropriate two-electron oxidation is applied. Thus, **1** was treated with 1,2-dibromoethane to cleanly form a neutral doubly H-bridged diborane(4), EindB(μ-H)$_2$BEind **2**. Recrystallization from hexane at −30 °C gave air-sensitive colorless crystals of **2** in a 72% yield. The crystals of **2** are stable at room temperature for more than 1 year in the absence of air but decompose at 133−134 °C under an argon atmosphere in a sealed tube.

The molecular structure of **2** was confirmed by X-ray crystallography [Figure 2a]. This molecule has a C_2 symmetry in the crystal with the axis passing through the center of the B−B bond. The two bridging hydrogen (μ-H) atoms are over the two positions, which have been located from the difference Fourier maps and isotropically refined with the occupancy factors of 0.5, thus giving a butterfly shaped B$_2$(μ-H)$_2$ unit with an interflap angle (φ) between the two B1−H1−B1′ and B1−H2−B1′ planes of 113(1)°, which is consistent with theoretical calculations (vide infra). The most notable feature of this molecule is the short B−B bond distance of 1.4879(7) Å, which is shorter than the neutral B−B double bond length [1.560(18) Å][6a] and the normal B−B single bond length (1.72 Å), but comparable to the computed B−B triple bonds (1.455−1.504 Å).[10] The geometry around the B−B bond in **2** is virtually linear with the C1−B1−B1′ bond angle of 178.92(4)°. These structural features indicate that the chemical bonding at the B atoms can be described as an sp-hybridization.

Experimental confirmations of the bonding mode of **2** were given by the electron density distribution analysis using single-
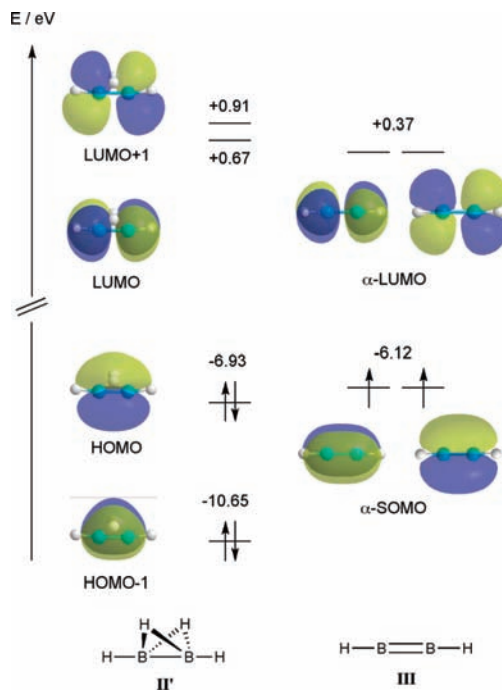
crystal X-ray diffraction. The data were analyzed by a multipole expansion method.[17] Figure 2b shows a difference Fourier map on the section perpendicular to the center of the B−B bond, including the C_2 axis. The difference in the electron density is based on the valence electrons arising from the 2s and 2p orbitals of the B atoms and the 1s orbitals of the H atoms. According to the peak height and the distance from the B atoms, the peaks are assignable as two sets of the two μ-H atoms, which are related by a 2-fold symmetry to each other. In addition, the large delocalization of the bonding electrons is clearly observed around the B−B bond.

DFT computations at the B3LYP/6-31G(d,p) level were carried out for diboron compounds using the Gaussian 03 program package.[18] The bonding analysis on the B$_2$(μ-H)$_2$ core is supported by the butterfly shaped C_{2v} structure **II′** with a φ angle of 104.7°. The B−B bond distance (1.463 Å) and the H−B−B bond angle (173.9°) are similar to those previously calculated.[7] The four pertinent MOs of **II′** are depicted in Figure 3 (left); there are two nondegenerate highest occupied π-like MOs (HOMO and HOMO−1) and two lowest unoccupied π*-like MOs (LUMO and LUMO+1). Although these energy levels differ from those of the triplet diborene(2) **III** having both two degenerate π and π* MOs [Figure 3 (right)], each MO found in **II′** and **III** is closely related to each other. Thus, the two singly occupied π MOs (SOMOs) of **III** have the correct symmetry to overlap with the group orbitals of the two μ-H atoms, producing the two π-like MOs for **II′**. The HOMO is represented by a 2p−2p π MO between the two B atoms incorporating the two 1s orbitals of the μ-H atoms in-phase, whereas the HOMO−1 is represented by the other, perpendicular to the former, 2p−2p π MO between the two B atoms incorporating the two 1s orbitals of the out-of-phase μ-H atoms. The energy levels of the HOMO and HOMO−1 in **II′** depend on the φ angle in the butterfly form.[16]

A similar butterfly geometry of the B$_2$(μ-H)$_2$ unit was also found by the computation of **2** with C_1 symmetry at the B3LYP/6-31G(d,p) level; the φ angle is 106.1°. The optimized B−B

Figure 3. A schematic representation of π-type MOs and energy levels for diborane(4) C_{2v} isomer (**II′**) and diborene(2) (**III**).

bond distance (1.485 Å) and the C−B−B bond angles (177.4° and 177.6°) well reproduce the experimental values. The distance between the two μ-H atoms in **2** is 1.797 Å, which is close to that in **II′** (1.801 Å), indicative of the absence of bonding between the two H atoms. The pseudo-π and π^* MOs are also found in **2**, while each MO splits into multiple MOs because of the interaction with the π orbitals of the Eind groups. The calculated electron density map of **2** also reproduces the Fourier map in Figure 2b.[16]

The Wiberg bond index (WBI)[19] provides further insight into the chemical bonding in **2**. The B−B bond order of 1.533 in **2** is similar to that in **II′** (1.673), which is higher than that in **III** (1.498). Thus, the multiple bonding character somewhat increases by the participation of the two μ-H atoms.

The natural population analysis (NPA) charge distribution[20] of **2** shows that the B−(μ-H) bonds polarize in a fashion of B(δ^-)−H(δ^+) with B(+0.043 and +0.074) and larger positive μ-H(+0.157 and +0.163). A charge separated structure is also observed for **II′** with B(−0.180) and μ-H(+0.151). These electronic configurations are consistent with a contribution from canonical form **II″**.

The doubly H-bridged structure of **2** has been confirmed to be maintained in solution as observed by the NMR studies. Thus, in the ^{1}H NMR spectrum of **2** in C_6D_6, a broad resonance at 2.94 ppm is observed for the BH groups. Based on the observed spin−lattice relaxation (T_1) time, 312(7) ms at 20 °C, the distance between the two H atoms was estimated as 1.77 Å in solution.[21] The ^{11}B NMR spectrum of **2** shows a broad resonance at $\delta = 6.4$ ppm, which is shifted upfield relative to that of **1** ($\delta = 16.5$ ppm). The chemical shifts calculated by the GIAO method support the doubly H-bridged structure of **2** in solution.[16]

Some reactions of **2** are also shown in Scheme 1. Compound **2** was cleanly converted into a fused borane **3** upon heating in benzene at 70 °C for 2 h with the evolution of molecular dihydrogen (H_2).[22] A benzene solution of **2** slowly reacted with 1 atm of H_2 gas to give the diborane(6) **4**, as observed for another diborane(4) B_2Cl_4.[23] The two-electron reduction of **2** with lithium metal in THF again quantitatively produced **1**. Thus, we can now easily perform the interconversion between the H-terminal diborane(4) dianion **1** and the H-bridged neural diborane(4) **2**, in which the H-binding modes may depend on the electron deficiency of the boron centers.

The availability of the Eind-stabilized **2** provides a new clue for the full understanding of the chemical bonding of diboron compounds as well as various transformations originating from the $B_2(\mu$-$H)_2$ moiety, which would open a new facet of borane chemistry.

Supporting Information Available: Experimental details, crystallographic data of **1** and **2** (CIF), details for calculations, and full listing for ref 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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