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A Stable Neutral Diborene Containing a B═B Double Bond

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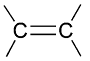
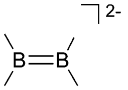
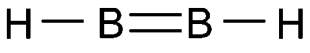
While carbon−carbon double bonds (**I**) are ubiquitous the corresponding multiple-bond chemistry of boron, the group 13 neighbor of carbon, is undeveloped.[1,2] Although the isoelectronic diboron dianions, $[R_2BBR_2]^{2-}$ (**II**), and their alkali metal salts were predicted two decades ago to be viable B═B double-bond candidates,[3] subsequent corroborating synthetic and structural efforts have been sparse.[4−6] *Neutral* diborenes(2), based on the parent (**III**), are less attractive boron−boron double-bond alternatives as they have been predicted to be highly reactive, with triplet ground states and two one-electron π-bonds.[7] Nevertheless, the synthesis and structural characterization of stabilized derivatives of (**III**) is a fascinating challenge.[1,8] The electron deficiency of the boron atoms in (**III**) invites complexation by Lewis base ligands (**IV**).



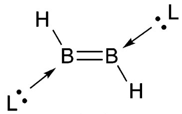
(**I**)



(**II**)



(**III**)



(**IV**)

The analogy between neutral ligated B═B double bonded compounds, (**IV**), and ethene derivatives (**I**) is compelling. Indeed, the isolobal relationship between CH and BCO groups has led to the extensive computational development of BCO chemistry.[9] Thus, OC(H)B═B(H)CO ((**IV**), L: = CO) and ethene are isolobal.[9c] The ethyne analogue, OCBBCO, has been characterized by FTIR in matrix isolation.[2] Other Lewis bases, L: in (**IV**), particularly bulky, sterically demanding N-heterocyclic carbene (NHC) ligands, are quite intriguing owing to their high stability and strong electron-donor capabilities.[10] We now report the experimental realization and molecular structure[11] of R(H)B═B(H)R (R = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$), **3**. Significantly, compound **3** is the first structurally characterized *neutral* diborene containing a B═B double bond. The nature of this B═B double bond is further delineated by density functional theory (DFT) computations.

We employed carbenes as stabilizing ligands in organo-group 13 chemistry over a decade ago with the synthesis and structural determination of R′:M$(CH_3)_3$ (R′ = :C{N(Pr^i)C(CH_3)}$_2$; M = Al, Ga).[12] Extending this work, we allowed $RBBr_3$, **1**,[11] to react with KC_8 in diethyl ether and isolated two products: **2**, $R(H)_2B-B(H)_2R$, as air-stable, colorless block crystals, and **3** as air-sensitive, orange-red sheet-like crystals (eq 1).

$$\underset{\mathbf{1}}{RBBr_3} \xrightarrow[Et_2O]{KC_8} \underset{\mathbf{2}}{R(H)_2B-B(H)_2R} + \underset{\mathbf{3}}{R(H)B{=}B(H)R} \quad (1)$$

The stoichiometric ratio of **1** to KC_8 has been observed to affect the yield of **3**. A higher yield of **3** (12%) was obtained with a stoichiometric **1**:KC_8 ratio of 1:5.4. Greater amounts of KC_8 decrease the yield of **3**. At a **1**:KC_8 ratio of 1:9, only **2** was isolated. The unexpected formation of **2** and **3** appears to involve the well-documented hydrogen abstraction from ethereal solvents[13] in the presence of alkali metals.[14−16]

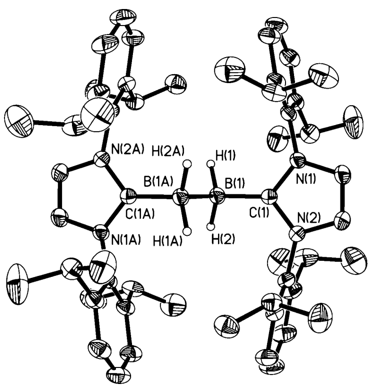


Figure 1. Molecular structure of **2** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbon omitted for clarity). Selected bond distances (Å) and angles (deg): B(1)−B(1A) 1.828(4), B(1)−C(1) 1.577(2), B(1)−H(1) 1.155(18), B(1)−H(2) 1.147(19); B(1A)−B(1)−C(1) 107.45(16), B(1A)−B(1)−H(1) 110.7(9), B(1A)−B(1)−H(2) 110.3(9), C(1)−B(1)−H(1) 108.9(9), C(1)−B(1)−H(2) 108.1(10), H(1)−B(1)−H(2) 111.3(13).

We also prepared the carbene:borane adduct, R:BH_3, **4**. The ^{11}B NMR resonances of **4** (RBH_3), **2** ($R(H)_2B-B(H)_2R$), and **3** (R(H)B═B(H)R) are −35.38, −31.62, and +25.30 ppm, respectively. The ^{11}B signal of **4** is a quartet (J_{BH} = 83.38 Hz), while **2** displays a singlet with shoulders ($w_{1/2}$ = 188 Hz) and **3** displays a broad singlet ($w_{1/2}$ = 946 Hz). The ^1H NMR imidazole resonances of **4**, **2**, and **3** are 6.31, 6.21, and 6.14 ppm, respectively.

X-ray structural analysis reveals that **2** has a center of symmetry about the $(H)_2B-B(H)_2$ core (Figure 1). The hydrides (B−H) in **2**, **3**, and **4** were located in the difference Fourier map. The B−B bond distance in **2** (1.828(4) Å) compares well to that computed for the CO-ligated analogue $OC(H)_2BB(H)_2CO$ (1.819 Å)[9c] and to those in an activated *m*-terphenyl based diborate (1.83(2) Å)[18] as well as a 2,3-diboratabutadiene dianion (1.859(8) Å).[19] However, the bond distance in **2** is longer than those in three-coordinate diboron compounds (1.682(16) to 1.762(11) Å).[17] The boron atoms in **2** reside in tetrahedral geometries. The N_2C_3 ring of the NHC ligand is almost perpendicular to the B−B−C plane with a N(1)−C(1)−B(1)−B(1A) torsion angle of −89.3°. The B−C bond distance in **2** (1.577(2) Å) is somewhat shorter than that in **1** (1.623(7) Å), but is similar to that in **4** (1.585(4) Å).

3 crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19). Each asymmetric unit contains two independent, and nearly identical, molecules of **3** (Figure 2; only one molecule of **3** is shown). The B−C bond distances, 1.547(15) Å (av), are marginally shorter than those of **1**, **2**, and **4**. Moreover, in contrast to **2**, one C_3N_2 carbene ring of **3** is nearly coplanar with the B_2H_2 core (N(1)−C(1)−B(1)−B(2) torsion angle, −13.8°), while the other is staggered more (N(4)−C(28)−B(2)−B(1) torsion angle, −30.0°). The

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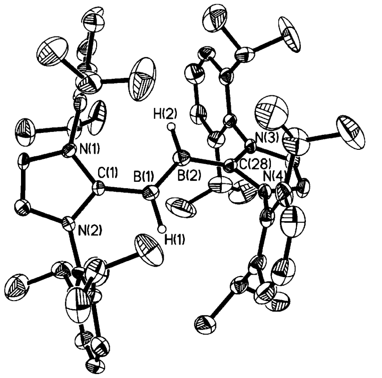

Figure 2. Molecular structure of **3** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbon omitted for clarity). Selected bond distances (Å) and angles (deg): B(1)−B(2) 1.561(18), B(1)−C(1) 1.543(15), B(1)−H(1) 1.14(2), B(2)−C(28) 1.532(15), B(2)−H(2) 1.13(2); B(2)−B(1)−C(1) 128.3(12), B(2)−B(1)−H(1) 124(4), C(1)−B(1)−H(1) 107(4), B(1)−B(2)−C(28) 126.1(12), B(1)−B(2)−H(2) 128(4), C(28)−B(2)−H(2) 105(4).

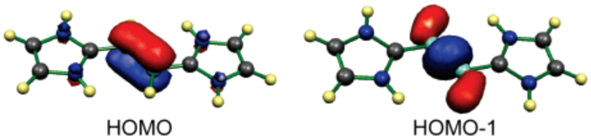

Figure 3. Representation of the HOMO and HOMO-1 orbitals of **3a**.

three-coordinate boron atoms in **3** adopt trigonal planar geometries. The most notable feature of **3**, however, is the B=B bond. The B=B bond distance of 1.560(18) Å (av) in **3** is not only considerably shorter than the B−B distance in **2** (1.828(4) Å), but also shorter than those reported for $[\text{Mes}_2\text{BB(Mes)Ph}]^{2-}$ (1.636(11) Å)[4] and for $[\{\text{Ph(Me}_2\text{N)BB(NMe}_2\text{)Ph}\}]^{2-}$ (1.627 Å (av)),[5] which purportedly contained a "strong B−B π-bond". Furthermore, the B=B bond distance in **3** compares well to those in dianionic tetra(amino)diborates (1.566(9) to 1.59(1) Å)[6] and to the computed B=B bond lengths for the OC(H)B=B(H)CO ((**IV**), L: = CO) analogue (1.590 Å)[9c] and for diborene(2), (**III**)[3] (1.498−1.515 Å). The computed B−B distance of 1.45 Å reported for OCBBCO, a compound "with some triple bond character", is shorter.[2,9c] Notably, the B−B bond distance difference of 0.27 Å between **2** and **3** is comparable to the corresponding difference (about 0.2 Å) between ethane and ethene. Likewise, the C−C bond distance difference of 0.1 Å between ethene and ethyne corresponds to the difference between **3** and OCBBCO (0.11 Å).[2,9c] Thus, the structural details of **3** are consistent with a B=B double bond.

The nature of **3** was investigated by performing B3LYP/6-311+G** DFT computations[20] on the simplified R(H)B=B(H)R (R = :C(NHCH)$_2$) model, **3a** (Figure 3). Both **3a** and the OC(H)B=B(H)CO ((**IV**), L: = CO) analogue[9c] are planar and have C_{2h} symmetry, whereas the corresponding R moieties in **3** are twisted because of the greater steric demands of the very bulky N(aryl) ligands. The computed B−B bond lengths in **3a** (1.591 Å) and (**IV**) (L: = CO) (1.590 Å)[9c] are virtually identical and are close to the error bound of the corresponding experimental distance of **3** (1.561 (18) Å). The B−C length (1.547 (15) Å (av)) of **3** also agrees with the computed value (1.531 Å) for **3a**. Perhaps due to reduced steric repulsion between the ligands, the B−B−C bond angle in **3a** (120°) is less than the average value in **3**, 126.7(12)°.

The HOMO of **3a** (Figure 3) is mainly a B−B π-bonding orbital involving the overlap of boron 2p orbitals, while the HOMO-1 has mixed B−B and B−H σ-bonding character. (A localized molecular orbital (LMO)[20] representation of the B−B σ bond is shown in the Supporting Information). Natural bond orbital (NBO) electron occupancies of the B−B σ- and π-bonding orbitals in **3a** are 1.943 and 1.382, respectively. The Wiberg and NLMO/NPA B−B bond indices, 1.408 and 1.656, respectively, also document the B=B double bond character in **3a**.

The computed boron−boron Wiberg bond indexes along the OC(H)$_2$B−B(H)$_2$CO (ethane-like), OC(H)B=B(H)CO ((**IV**), L: = CO) (ethene-like), and OCBBCO (ethyne-like) series, 0.870, 1.308, and 1.953, respectively, are instructive. The 1.0, 2.0, 3.0 unit bond-order values of the hydrocarbon series are not to be expected for the corresponding boron−boron analogues owing to the resonance contributions of Lewis structures. Nevertheless, the single-, double-, and triple-bond descriptions of boron−boron bonds discussed here are appropriate.

In summary, we have synthesized and characterized the first stable neutral diborene and computationally probed the nature of the novel boron−boron double bond. Related studies on the chemistry of boron−boron multiple bonds are ongoing.

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Note Added after ASAP Publication. After this paper was published ASAP September 21, 2007, production errors were fixed in the graphics showing structures (**I**)−(**IV**) and eq 1. The corrected version was published ASAP September 25, 2007.

Supporting Information Available: Complete ref 20, full details of the syntheses, computations, and X-ray crystal determination, including the cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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