

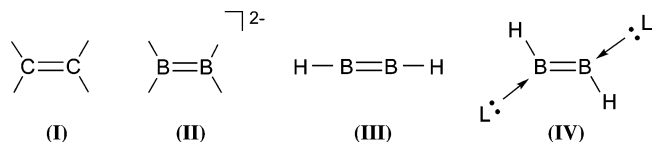
A Stable Neutral Diborene Containing a B=B Double Bond

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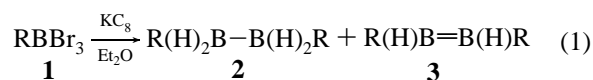
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While carbon–carbon double bonds (**I**) are ubiquitous the corresponding multiple-bond chemistry of boron, the group 13 neighbor of carbon, is undeveloped.^{1,2} Although the isoelectronic diboron dianions, $[R_2BBR_2]^{2-}$ (**II**), and their alkali 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**).



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 structure¹¹ of R(H)B=B(H)R (R = :C{N(2,6-Pr₂C₆H₃)CH₂})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 $R':M(CH_3)_3$ ($R' = :C\{N(Pr^i)C(CH_3)_2\}_2$; $M = Al, Ga$).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).



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-

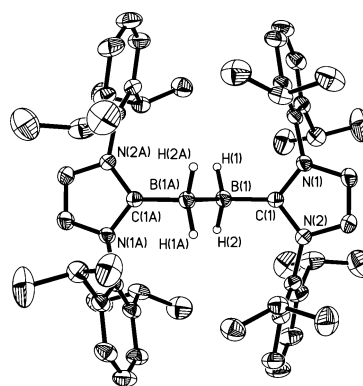


Figure 1. Molecular structure of **2** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbon omitted for clarity). Selected bond distances (Å) and angles (deg): B(1)–B(1A) 1.828(4), B(1)–C(1) 1.577(2), B(1)–H(1) 1.155(18), B(1)–H(2) 1.147(19); B(1A)–B(1)–C(1) 107.45(16), B(1A)–B(1)–H(1)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

documented hydrogen abstraction from ethereal solvents¹³ in the presence of alkali metals.^{14–16}

We also prepared the carbene:borane adduct, R:BH₃, **4**. The ¹¹B NMR resonances of **4** (RBH₃), **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 ¹¹B 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 N₂C₃ 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 C₃N₂ carbene ring of **3** is nearly coplanar with the B₂H₂ 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

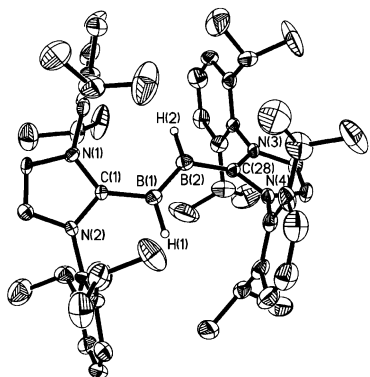


Figure 2. Molecular structure of **3** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbon omitted for clarity). Selected bond distances (Å) and angles (deg): B(1)–B(2) 1.561(18), B(1)–C(1) 1.543(15), B(1)–H(1) 1.14(2), B(2)–C(28) 1.532(15), B(2)–H(2) 1.13(2); B(2)–B(1)–C(1) 128.3(12),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

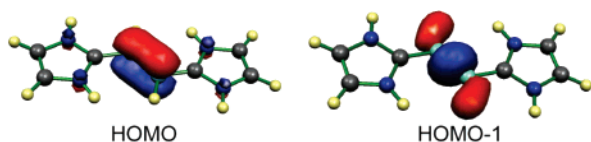


Figure 3. Representation of the HOMO and HOMO-1 orbitals of **3a**.

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 [Mes₂BB(Mes)Ph]^{2–} (1.636–(11) Å)⁴ and for [{Ph(Me₂N)BB(NMe₂Ph)]^{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 computations²⁰ 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)₂B–B(H)₂CO (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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