Boron–Boron Double Bonds

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A Base-Stabilized Neutral B=B Bond: Closing a Gap by Filling the Void

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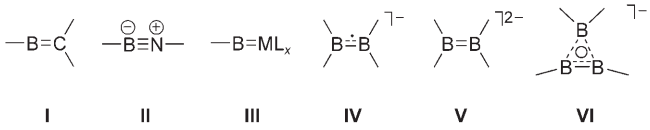
boron · donor–acceptor systems · Group 13 elements · multiple bonds

The unique diversity of organic chemistry is, among other things, largely dependent on the pronounced ability of the second-row elements carbon, nitrogen, and oxygen to form double and triple bonds, which provides an inexhaustible stockpile of reactivity and functionality. Consequently, main-group elements that are less readily engaged in multiple bonding have attracted enormous research efforts in this regard. During the last 30 years, stable electroneutral compounds with homonuclear low-valent bonding have been made accessible for all elements from Groups 13 to 15 except for boron (until very recently)[1] and aluminum.[2]

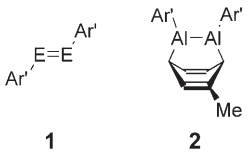
The inherently electron-deficient nature of Group 13 elements, especially boron, explains their preference to engage in multicenter bonding (e.g. in polyhedral borane clusters)[3] rather than to form stable π bonds. The high synthetic potential of unsaturated boron compounds led nonetheless to ongoing intense efforts in this regard, and a broad variety of heteronuclear multiple bonds involving boron has been realized. The chemistry of methyleneboranes **I**,[4] iminoboranes **II**,[5] and transition-metal borylene complexes **III**[6] (Scheme 1) is well developed; even one anionic derivative with a B–C triple bond has been reported.[7]



Scheme 1. Multiple-bonding motifs featuring boron.

The situation concerning B–B multiple bonds proved to be somewhat more delicate. Only charged derivatives with (partial) B–B π bonding have been isolated to date, presumably owing to their enhanced resistance towards oligomerization due to Coulomb repulsion. The EPR spectroscopic characterization of the radical anion of a diborane(4) with a partial homonuclear π bond **IV**[8] by Berndt and Klusik was followed by theoretical investigations by Schleyer and co-workers[9] on related dianionic diboraethenes **V**. Stable substituted derivatives of **V** were realized eventually by Power and co-workers through the reduction of the diborane(4) species Mes_2B–B(Ph)Mes (Mes = 2,4,6-$Me_3C_6H_2$) and Me_2N(Ph)B–B(Ph)NMe_2 in 1992;[10a–c] analogous tetraamino derivatives were later reported by Nöth and co-workers.[10d] The B–B distances (1.566–1.636 Å) were interpreted in terms of significant double-bond character. Furthermore, a broad variety of anionic compounds, in which the B–B bond is part of a cyclic π-electron system and hence exhibits partial double-bond character, has been reported.[11,12] Very recently, Berndt and co-workers isolated a derivative of the three-membered π- and σ-aromatic borate **VI**. In this compound, one regular two-center-two-electron bond and two supplementary three-center-two-electron bonds lead to the shortest B–B bond in a stable compound yet (1.483 Å).[13] However, as mentioned above, no isolable neutral acyclic derivatives with a B–B double bond have been reported to date.[1]

In fact, in Group 13 the increasing stability of the +I oxidation state going down the group allowed for the isolation of "dimetallenes" **1** featuring the extremely bulky terphenyl substituent Ar′ (Scheme 2), albeit with very long and exceedingly weak E–E bonds that readily dissociate in solution.[2a]



Scheme 2. Heavier "dimetallenes" **1** and trapping product **2** (E = Ga, In, Tl; Ar′ = 2,6-$Dip_2C_6H_3$, Dip = 2,6-$iPr_2C_6H_3$).

Employment of the same substituent allowed for the generation of Ar′-AlAl-Ar′, which owing to its extreme reactivity was only isolated as the Diels–Alder adduct with toluene **2**.[14] Attempts to generate the corresponding boron derivatives, that is, diborenes(2), to date only yielded CH and CC insertion products.[15]

A closer look at the electronic structure of the linear parent diborene(2) HB=BH readily reveals an explanation for the difficulties in accessing a stable derivative. The B=B moiety features orthogonal, hence degenerate, p_z and p_y

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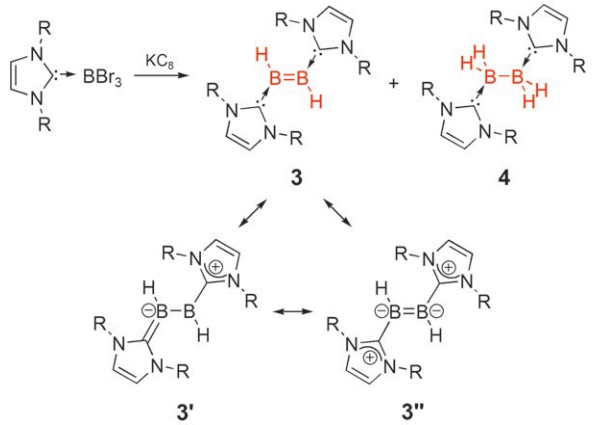
orbitals similar to those of acetylene HC≡CH, but unlike the latter only half-filled. Consequently, HB=BH should have a paramagnetic triplet ground state, which was predicted by theoretical studies[16] and convincingly verified by EPR spectroscopy experiments on photoionized B_2H_6 at 4 K in noble-gas matrices.[17] A possible approach to stabilize the singlet state of a neutral species with a B–B double bond was outlined by Barthelat and co-workers in 1987. Their calculations on the amino-substituted derivative $H_2NB{=}BNH_2$ showed that its singlet ground state is approximately 18 kcal mol^{-1} lower in energy than the triplet state.[18] Numerous enterprises have been undertaken by experimentalists to synthesize and characterize a stable diaminodiborene(2); in two cases, mass spectrometric data, ^{11}B NMR spectroscopy studies, and/or trapping reactions suggested the formation of diamino diborenes(2). Conclusive evidence, however, has not been supplied in these reports.[19]

Robinson and co-workers now adopted a different strategy for the stabilization of the singlet state of HB=BH, relying on the intramolecular coordination of a Lewis base to the vacant p_z orbitals of the diborene(2).[1] The reduction of the acid–base adduct of BBr_3 and an N-heterocyclic carbene with potassium/graphite yielded a mixture of products, from which the parent diborene(2) HB=BH and diborane(4) H_2B–BH_2 were isolated as their base-stabilized adducts **3** and **4**, respectively (Scheme 3). Both **3** and **4** contain two equivalents of an N-heterocyclic carbene and were isolated in moderate yields strongly depending on the stoichiometry of the reaction.[1]



Scheme 3. Synthesis of diborene(2) and diborane(4) carbene adducts **3** and **4** (R = Dip = 2,6-*i*$Pr_2C_6H_3$) and possible resonance forms **3′** and **3″**.

The structures in the solid state determined by single crystal X-ray diffraction exhibited a considerable shortening of the B–B bond in **3** (1.561 Å) as compared to that of **4** (1.828 Å), consistent with the presence of a reasonably strong π bond. Since the diborane(4) bis(carbene) adduct **4** is formally derived from **3** by the addition of dihydrogen, the steric and electronic situations are very similar, and the only apparent differences are the degree of hybridization of the boron atoms and the bond order of the B–B bond.

In the controversially discussed anionic systems $[ArGa{-}GaAr]^{2-}$, the coordination of the sodium counterions to the Ga–Ga bond and the aryl groups was found to induce the better part of the observed shortening of the bond in comparison with saturated systems, which served as an important argument against possible multiple-bond character.[20] Conversely, in the case of globally electroneutral **3**, the comparison with the ethane/ethylene system, for which a comparable shortening of the bond distance is known, is clearly justified, even though a contribution of the resonance form **3′** should certainly reduce the B–B bond order. Indeed, the B–C distances of **3** (1.543 and 1.532 Å) are approximately 0.04 Å shorter than the expected value for single bonds, which, however, could also be attributed to electrostatic attraction in resonance form **3″**. In any case, computational analysis of model compound **3a** (R = H) supports the notation of a B–B double bond. The π-bonding HOMO (highest occupied molecular orbital) is predominantly located on the boron atoms. The natural bond orbital and Wiberg bond indices analyses both show a lower bond order than 2.0, which, however, is readily explained by the π back-donation from the boron centers to the carbenic carbon atoms. A similar situation had been found by calculations on the related CO-stabilized HB=BH.[21]

The mechanism of the formation of **3** and **4** remains obscure for now, even though the proposed hydrogen abstraction from diethyl ether, which was used as a solvent, is plausible. The systematic introduction of the required amount of hydrogen might hold the key to a more selective synthesis, which would be highly desirable given the considerable synthetic potential of **3** and **4**. In particular, the reactivity of the HB=BH/carbene adduct **3** towards unsaturated organic compounds should be intriguing, given the possibility of both addition and hydroboration chemistry. Forthcoming results in this regard are eagerly awaited.

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