Diborenes

DOI: 10.1002/anie.201204449

Base-Stabilized Diborenes: Selective Generation and η^2 Side-on Coordination to Silver(I)**

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Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

The possibility of multiple bonding between main-group elements other than carbon has fascinated inorganic chemists. The quest for homoatomic Group 13 to 15 analogues of alkenes and alkynes has been pursued intensively during the last decades, and chemists were continuously faced with synthetic difficulties in generating such unusual low-valent main-group element species. Eventually, efforts were rewarded and multiple-bonded derivatives of the heavier Group 13 to 15 main-group elements are now well established.[1,2] By contrast, related diboron compounds have been considered inaccessible for a long time because of the electron-deficient nature of the boron atom and its inability to fill bonding orbitals. However, most recent experimental[3–6] and theoretical[7] studies in this area clearly demonstrated the opposite and today a small number of diboron species featuring bond orders higher than one are available (Figure 1). These molecules proved highly reactive and their generation and/or isolation required stabilization by 1) low-temperature matrix-isolation techniques[3] or 2) population of the empty π bonding orbital between the two boron centers by either reduction or coordination of a Lewis base.[4–6]

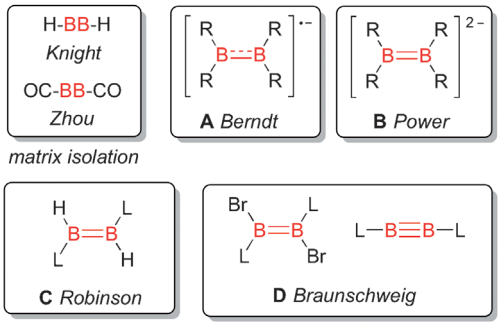

Figure 1. Examples of boron–boron multiple bonding (L = NHC).

Thus, Berndt et al. and Power et al. reported the isolation of mono- and dianionic **A** and **B**, which despite their negative charge feature multiple bond character with formal bond orders of 1.5 and 2, respectively.[4] First progress towards neutral multiple-bonded diboron species came from Robinson et al., who successfully exploited the concept of Lewis base stabilization of the boron centers by bulky N-heterocyclic carbene donors (NHC). Thereby, reduction of L:BBr_3 (L = NHC) resulted in the formation of doubly base-stabilized diborene L:(H)B=B(H):L and diborane L:$(H)_2$B–$B(H)_2$:L albeit in rather low yield.[5] In this case, hydrogen abstraction from the solvent by radical intermediates is evidently a competing factor during the B–B bond formation event. This "side-reaction" was subsequently avoided by our group employing B_2Br_4 with a preformed B–B bond as the precursor diborane(4). Accordingly, successive reduction of L:$(Br)_2$B–$B(Br)_2$:L selectively afforded the bromine-substituted diborene L:(Br)B=B(Br):L and the linear diborine L:B≡B:L with an unprecedented B–B triple bond.[6]

However, both approaches used to generate neutral diborenes have their synthetic drawbacks. While B_2Br_4 is rather difficult to prepare, reductive coupling of monoboranes L:BR_nHal_{3-n} (R = Ph, N*i*Pr_2; Hal = Cl, Br; $n = 0, 1$) suffers from a slow dimerization step because of the steric requirements of the NHC ligand. As a consequence, side reactions, such as hydrogen abstraction (see above)[5,8] or ligand C–H activation by intermediate borylene species readily occur,[8,9] which adversely affects selectivities and yields. The limited availability of diborenes L:(R)B=B(R):L also precluded any reactivity studies, and no information regarding the chemistry of the B–B double bond is available to date.

Since the interaction of boron-based ligands with transition-metal centers is a significant aspect of our research,[10] we set out to develop a more convenient access to diborenes and to subsequently evaluate their coordination chemistry. We reasoned that the reductive coupling approach established by Robinson is the most suitable with respect to a broad applicability. However, a careful design of the precursor molecules L:BR_nHal_{3-n} appears to be crucial to avoid unwanted side reactions. In our hands, NHC-stabilized mesityl and duryl boranes **1** and **2** combine all the features required for this purpose: 1) ease of preparation and handling; 2) a ligand sphere for which intramolecular C–H activation processes affording 5- or 6-membered boracycles are not feasible; 3) aryl substituents for kinetic stabilization of the resulting diborenes; 4) rather small NHC donor ligands to

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204449.

permit a fast dimerization step. Compounds **1** and **2** are readily isolated as colorless materials in 84% and 68% yield by simple gravity filtration from reaction mixtures containing the respective borane and *I*Me in Et_2O (*I*Me = 1,3-dimethylimidazol-2-ylidene; Figure 2).[11] Identification of **1** and **2**

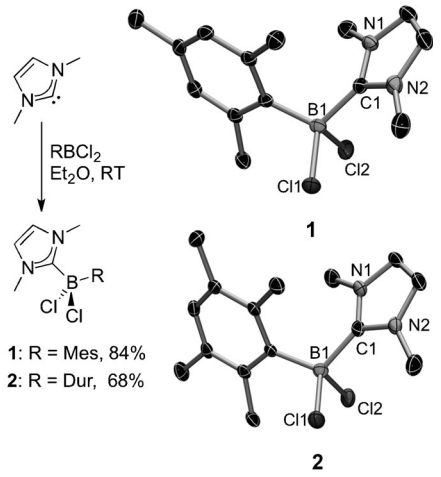
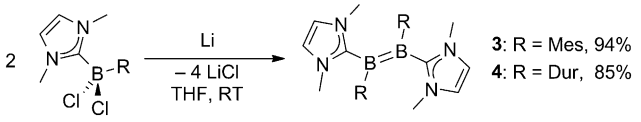


Figure 2. Left: Synthesis of **1** and **2**; Mes = 2,4,6-trimethylphenyl, Dur = 2,3,5,6-tetramethylphenyl. Right: Crystal structures of **1** and **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1** B1–C1 1.627(3), B1–Cl1 1.878(2), B1–Cl2 1.917(2); Cl1-B1-Cl2 108.56(13). **2** B1–C1 1.624(3), B1–Cl1 1.879(2), B1–Cl2 1.915(3); Cl1-B1-Cl2 107.48(15).

posed no difficulty, and ^{11}B NMR spectroscopy in solution (**1**: $\delta = 1.3$ ppm; **2**: $\delta = 1.4$ ppm) and X-ray diffraction (Figure 2) clearly confirmed adduct formation and the presence of tetracoordinate boron centers. Analysis of the solid-state structures of **1** and **2** afforded no surprises and all the parameters are reminiscent of other known NHC borane adducts.[5,8,9b,12]

Addition of excess lithium metal to THF solutions of **1** or **2** under ambient conditions spontaneously produced a dark red color indicating rapid formation of diborenes **3** and **4** (Scheme 1).[11] The reactions typically proceed quantitatively



Scheme 1. Synthesis of diborenes **3** and **4**.

within 50 min with high selectivity as judged by NMR spectroscopy of the reaction mixtures. Thus, the ^{11}B NMR signals of **3** ($\delta = 24.1$ ppm) and **4** ($\delta = 24.7$ ppm) are shifted downfield by approximately 23 ppm with respect to their precursors **1** and **2**. Hence, the chemical shifts strongly resemble those of the related species L:(H)B=B(H):L ($\delta =$ 25.3 ppm)[5] and L:(Br)B=B(Br):L ($\delta = 20.0$ ppm).[6] No evidence for the formation of side products resulting from either hydrogen abstraction or C–H activation is present, for which sharp doublet signals are usually found further upfield.[5,8,9a] The yields of isolated **3** (94%) and **4** (85%) are high, which further emphasizes the selective nature of this transformation. Moreover, reaction conditions are variable, and **3** and **4** are also formed selectively in other solvents, such as benzene or Et_2O and/or applying other reductants (Na, K, KC_8).

X-ray diffraction served to verify the higher bond order in diborenes **3** and **4** in the solid state (Figure 3).[11] The B1–B2

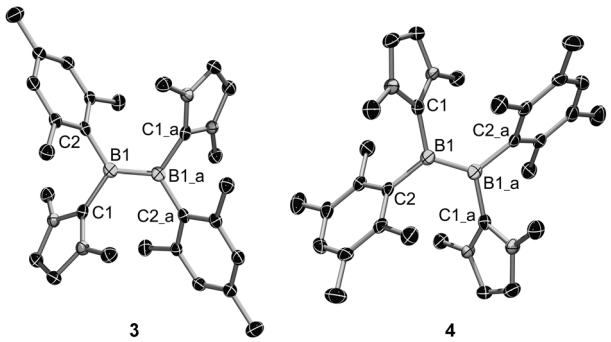


Figure 3. Crystal structures of **3** and **4**. Symmetry-related positions ($-x$, y, $0.5-z$) are labeled with _a. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3** B1–B1_a 1.593(5), B1–C1 1.569(3), B1–C2 1.606(3); C1-B1-B1_a 118.1(2), B1_a-B1-C2 128.6(2), C2-B1-C1 113.12(17). **4** B1–B1 a 1.590(5), B1–C1 1.567(4), B1–C2 1.609(4); C1-B1-B1_a 117.7(3), B1_a-B1-C2 127.1(3), C2-B1-C1 115.05(19).

bond lengths in **3** (1.593(5) Å) and **4** (1.590(5) Å) are essentially identical implying significant double-bond character in both species. Thus, B–B distances are similar to those found for the related diborenes L:(H)B=B(H):L (1.561(18) Å) and L:(Br)B=B(Br):L (1.546(6) Å),[5a] but notably shorter than those generally observed in dianionic diborenes of the type **B** (1.623–1.706 Å);[4] notable exceptions being dianionic tetra(amino)diboranes(4) (1.56–1.59 Å) described by Nöth et al.[13] The boron centers in **3** and **4** adopt a trigonal-planar geometry, which deviates only marginally from an ideal arrangement (**3**: $\Sigma = 359.82°$; **4**: $\Sigma = 359.85°$).

The intense red color of diborenes **3** and **4** is remarkable and has already been observed for L:(H)B=B(H):L,[5] while the bromine analogue L:(Br)B=B(Br):L is dark green in color.[6] We elucidated the electronic background for this photophysical behavior by a combined experimental and theoretical study using UV/Vis spectroscopy in Et_2O solution and time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-311G* level of theory.[11] The experimental UV/Vis spectra of **3** (Figure 4) and **4** feature three distinct absorption bands between $\lambda_{max} = 299$–538 nm (Table 1). The corresponding electronic excitations were subsequently identified by TD-DFT. Spectra were simulated by convoluting the oscillator strengths with Gaussian functions taking the half-bandwidths of 2500 cm^{-1}. Figure 4 shows the stick plot of the calculated oscillator strengths and the simulated spectra. The overall absorption profile of both systems is well reproduced theoretically. Both systems are very similar, only the data of **3** are depicted. Details on **4** can be found in the Supporting Information.

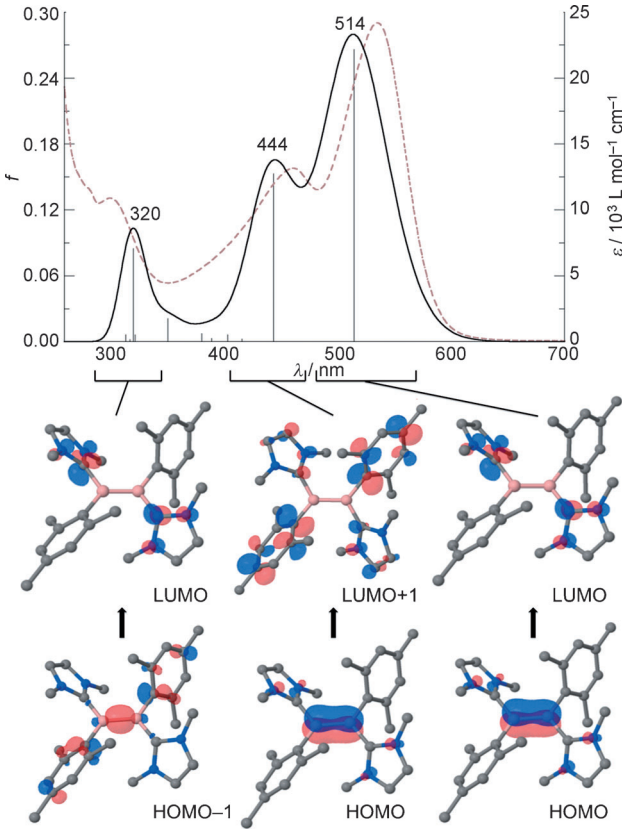


Figure 4. Experimental (-----) and calculated (——) absorption spectra of **3** and some selected transitions. f = oscillator strength.

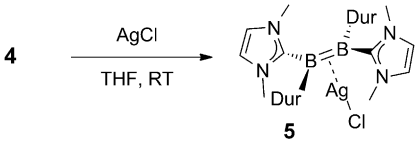
Table 1: Experimentally determined[a] and calculated UV/Vis parameters of **3** and **4**.

	λ [nm]	λ_{calcd} [nm]	ε [L mol^{-1} cm^{-1}]	Transition
3	535	514	10505	HOMO→LUMO
	461	444	5713	HOMO→LUMO+1
	300	320	4723	HOMO−1→LUMO
4	538	514	4126	HOMO→LUMO
	463	436	2200	HOMO→LUMO+1
	299	319	1914	HOMO−1→LUMO

[a] In Et_2O solutions at room temperature.

Close analysis of the computational results clearly validates the double-bond nature of the B–B bond. Thus, the HOMO is a B–B bonding orbital of π symmetry, while the HOMO−1 corresponds to B–B σ bonding. The LUMO is predominately composed of orbitals with p character located at the NHC ligand. The three main contributions to the observed spectra are due to transitions between HOMO→LUMO, HOMO→LUMO+1, and HOMO−1→LUMO.

Reaction of **4** with AgCl was used to evaluate the coordination chemistry of the B–B double bond and to generate olefin-type transition-metal complexes of diborenes. In general, the interaction between double bonds and transition metals is best described by the Dewar–Chatt–Duncanson model, which connects the synergetic concept of ligand→metal σ donation and metal→ligand π back donation.[14] For Ag^I, detailed studies on silver(I) alkene complexes have shown that π back donation is negligible in this case.[15] Addition of THF solutions of **4** to solid AgCl smoothly afforded the η^2 silver species **5** within 4 h under ambient conditions (Scheme 2).[11] ^{11}B NMR spectroscopy of the



Scheme 2. Synthesis of η^2 silver complex **5**.

reaction mixture indicated the gradual consumption of diborene **4** ($\delta = 24.7$ ppm) and the appearance of a new broad signal slightly upfield ($\delta = 18.1$ ppm). No other products are formed, even if more than one equivalent of **4** is applied. The steric bulk of diborene **4** clearly prevents coordination of a further double bond to the Ag^I center. This situation is in contrast to the corresponding Ag alkenes, in which neutral and cationic species with two or more coordinated double bonds are well established, in particular for small or chelating olefins.[15]

In the dark, yellow **5** is stable both in the solid state and in solution at −25 °C, but readily decomposes at room temperature and/or upon light exposure, within hours to afford elemental silver. Other decomposition products could not be identified. However, the lability of **5** provides a reasonable explanation for the rather low yield of isolated product, 28 %. The results of an X-ray diffraction study on **5** eventually verified the η^2 coordination mode of the diborene ligand (Figure 5).[11] Thus, the effect of side-on coordination of the B–B double bond system to the Ag^I center is small and the

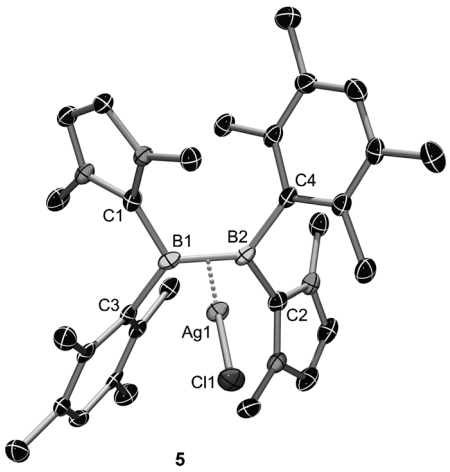


Figure 5. Crystal structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–B2 1.645(6), B1–C1 1.594(6), B1–C3 1.629(6), B2–C2 1.588(6), B2–C4 1.614(6), B1–Ag1 2.318(4), B2–Ag1 2.366(4), Ag1–Cl1 2.4104(10); B1-Ag1-B2 41.10(15), B2-Ag-Cl1 159.03(11), Cl1-Ag1-B1 159.69(12), Σ_{B1} 358.2, Σ_{B2} 358.7, Σ_{Ag1} 359.82.

planarity of the diborene ligand (B1: $\Sigma = 358.2°$; B2: $\Sigma = 358.7°$) is almost retained (cf. **4**: $\Sigma = 359.85°$). In addition, the B1–B2 bond length (1.645(6) Å) is only slightly elongated with respect to **4**. These findings further support the presence of an ideal η^2 coordination mode with pure σ donation character and little contribution of a boracyclopropane-like structure. As anticipated, the B1–Ag1 and B2–Ag1 distances (2.318(4) and 2.366(4) Å) are significantly longer than those found in the silver boryls of Yamashita and Nozaki et al. (2.118(2) and 2.122(4) Å), which are the only other examples for structurally characterized B–Ag bonding interactions.[16]

In summary, we have disclosed a new and highly selective access to neutral NHC-stabilized diborenes through reductive coupling of suitable monoborane precursors. Careful choice of the ancillary ligands was found to be critical to avoid well-known side reactions, such as hydrogen abstraction or C–H activation. The presence of B–B double bonds in diborenes **3** and **4** was clearly confirmed both experimentally (NMR spectroscopy, UV/Vis, X-ray crystallography) and theoretically (TD-DFT). With a convenient synthetic method in hand, we successfully assessed the coordination behavior of the B–B double bond, which allowed us to isolate the Ag^I species **5** featuring the diborene ligand in an unprecedented, olefin-like η^2 coordination mode. More detailed studies on the organic and organometallic reactivity of the B–B double bond are currently underway in our group.

Received: June 8, 2012
Published online: September 3, 2012

Keywords: boron · multiple bonds · N-heterocyclic carbenes · reduction · silver

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[11] See the Supporting Information section for full experimental, analytical, and crystallographic data as well as computational details. CCDC-885218 (**1**), -885219 (**2**), -885220 (**3**), -885221 (**4**) and -885222 (**5**) contain the crystallographic data to this article. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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