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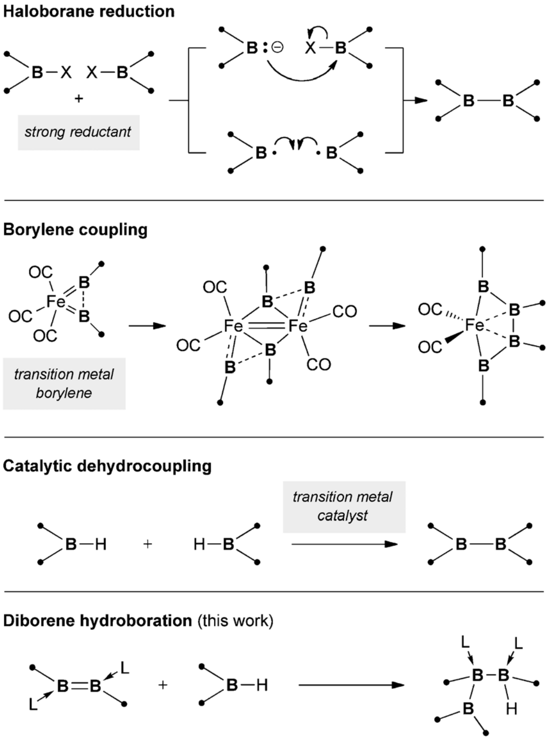
Direct Hydroboration of B=B Bonds: A Mild Strategy for the Proliferation of B−B Bonds**

Holger Braunschweig, Rian D. Dewhurst, Christian Hörl, Ashwini K. Phukan, Florian Pinzner, and Stefan Ullrich*

Abstract: *Synthetic access to electron-precise boron chains is hampered by the preferential formation of nonclassical structures. The few existing strategies for this involve either strongly reducing reagents or transition-metal catalysts, both with distinct disadvantages. The synthesis of new furyl- and thienyl-substituted diborenes is presented, along with their direct hydroboration with catecholborane (CatBH) to form a new electron-precise B−B bond and a B_3 chain. The reaction is diastereoselective and proceeds under mild conditions without the use of strong reducing agents or transition-metal catalysts commonly used in B-B coupling reactions.*

The ability to form homonuclear chains of atoms is restricted to a remarkably small set of elements. Of the elements of the first two rows of the periodic table, only carbon is able to form long, stable homonuclear chains, a phenomenon favored by the high homonuclear σ-bond enthalpy of the element ($D_0 = 345\,\mathrm{kJ\,mol^{-1}}$).[1] Boron is a potential candidate for chain formation, having a D_0 value only slightly lower than carbon ($293\,\mathrm{kJ\,mol^{-1}}$); homonuclear boron-only chains and rings of up to six atoms have been reported.[2–4] The formation of nonclassical boron clusters in many cases hampers attempts to form long chains of sp^2 boron atoms, although the use of electron-donating amino or bulky aryl groups effectively circumvents this cluster formation. However, it is notoriously difficult to selectively form such B−B bonds, despite their apparent stability.[5] It is clear that the barrier preventing the preparation of long chains of "BR" (R = amino, aryl) repeat units is less the stability of the electron-precise B−B bonds but rather a distinct lack of mild, functional-group-tolerant synthetic methods for their preparation.



Scheme 1. Known routes for the construction of electron-precise B−B bonds, and the new diborene hydroboration route described in this work (bottom).

Haloborane reduction is the classical method of B−B bond creation,[6–8] and forms the basis of the industrial synthesis of commercially available diboranes(4) (Scheme 1). However, these reactions often proceed in low yields, produce a number of byproducts stemming from over-reduction and radical reactivity, and require very strong reductants, thus limiting their functional group tolerance. The recently reported catalytic dehydrocoupling of hydroboranes[9–16] is a highly efficient method for the creation of B−B bonds, but is thus far limited to the use of monohydroboranes, precluding any boron chain growth. Borylene coupling,[17] although very mild, is to date limited in scope, requires a transition-metal template, and currently lacks a mechanism for releasing the formed B_4 chain.

The hydroboration of carbon–carbon double bonds, which was discovered in the 1950s by H. C. Brown[18] and later expanded by the discovery of transition-metal-catalyzed hydroboration,[19–22] is a mild and selective way to create carbon–boron bonds for subsequent derivatization of the carbon atom. The reaction now allows C=C, C=O, C=N, and C≡C bonds, to be functionalized with control of both regio- and stereochemistry. Recently, Sekiguchi and co-workers have also presented the hydroboration of the silicon–silicon

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[*] Prof. Dr. H. Braunschweig, Dr. R. D. Dewhurst, Dipl.-Chem. C. Hörl, Dr. A. K. Phukan, F. Pinzner, S. Ullrich
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: h.braunschweig@uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/Braunschweig/
Dr. A. K. Phukan
Department of Chemical Sciences, Tezpur University
Napaam 784028, Assam (India)

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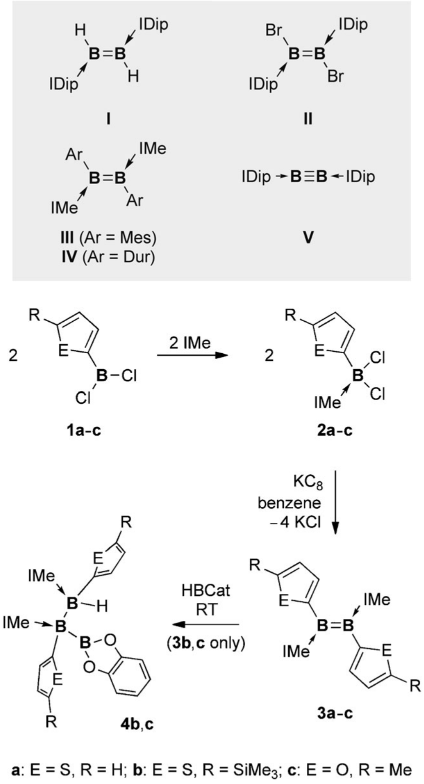
triple bond of a disilyne compound.[23] With a documented desire to develop mild B−B coupling strategies,[5] we envisaged the extension of hydroboration to B=B bonds to create a new boron–boron bond and a chain of three boron atoms. Work on the synthesis of diborene molecules from Robinson et al. and our laboratories has so far yielded a few stable examples (**I**–**IV**; Scheme 2).[24–26] However, these are sterically bulky and accordingly kinetically inert, being resistant to further reaction apart from with very harsh reagents (for example, reduction to form the diboryne compound **V**; Scheme 2)[26] or very small metal complexes such as AgCl.[25] To promote the diborene hydroboration reaction, we sought to reduce the steric bulk of the diborene partner, while also increasing its electron density, by using smaller five-membered heterocyclic substituents (2-thienyl, 2-furyl) instead of bulky alkylated aryl groups. Furthermore, we recently observed that 2-thienyl groups were able to remain coplanar with borolyl rings when bound to the boron atom, indicating some degree of conjugation with the borole.[27,28] We had hoped that the addition of 2-thienyl and 2-furyl substituents to diborenes would induce similar coplanarity and conjugation with the B=B bond, thus providing electron density to the B=B π system and leading to sterically more accessible diborenes. Herein we present the synthesis and characterization of diborenes **3a**–**c** (Scheme 2) substituted with heterocyclic moieties (thienyl, furyl). The first examples of hydroboration of the B=B double bonds of these diborenes are reported, which is a new pathway for the formation of electron precise B−B bonds without the use of strong alkali metal reductants or transition-metal catalysts.



Scheme 2. Previously reported and new results. Above: Published neutral diborenes **I**–**IV** and the neutral diboryne **V** derived from **II**. Below: Synthesis of base-stabilized diborenes **3a**–**c** and the hydroboration of **3b**,**c** to provide triboranes **4b**,**c**. IDip: 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene; IMe: 1,3-dimethylimidazole-2-ylidene; Mes: 2,4,6-trimethylphenyl; Dur: 2,3,5,6-tetramethylphenyl.

The preparation of the Lewis acid-base adducts **2a**–**c** is accomplished by addition of an *N*-heterocyclic carbene (IMe, 1,3-dimethylimidazol-2-ylidene) to a solution of the respective dihaloboranes (**1a**–**c**) at low temperature in good yields (**2a** 85, **2b** 92, **2c** 91%; Scheme 2). The ^{11}B NMR resonances of **2a**–**c** (**2a** $\delta = -1.68$, **2b** −1.67, **2c** −1.67 ppm) clearly indicate the presence of four-coordinate boron centers. In contrast to the precursors to diborenes **III** and **IV** (Scheme 2), the reductive coupling of the precursors **2a**–**c** with lithium metal in THF leads only to low yields (<10%) of the desired diborenes. However, by using KC$_8$ in benzene as reducing agent, the yields of isolated product are much higher (**3a** 82, **3b** 89, **3c** 67%). The resulting deep purple (thienyl) or red (furyl) compounds were characterized by multinuclear NMR spectroscopy and their ^{11}B NMR resonances (**3a** $\delta = 21.3$, **3b** 22.4, **3c** 18.7 ppm) fall between that of the dibromodiborene **II** ($\delta = 20.0$ ppm)[26] and those of the diaryldiborenes **III** ($\delta = 24.1$ ppm) and **IV** ($\delta = 24.7$ ppm).[25] Experimental UV/Vis spectra of all three diborenes display three absorption maxima between 300–550 nm (Supporting Information, Figures S1–S3). Despite small bathochromic shifts, the absorption bands of **3a**–**c** (**3a**: 293, 477, 543 nm; **3b**: 293, 492, 562 nm; **3c**: 289, 409, 547 nm) correspond well to the absorption maxima observed and calculated for **III** (300, 461, 514 nm) and **IV** (299, 463, 538 nm) (Table 1).[25] As in the previously reported diborenes **III** and **IV**, TD-DFT calculations on the new diborenes **3a**–**c** reproduce these band energies very well (Table 1), and show that the bands

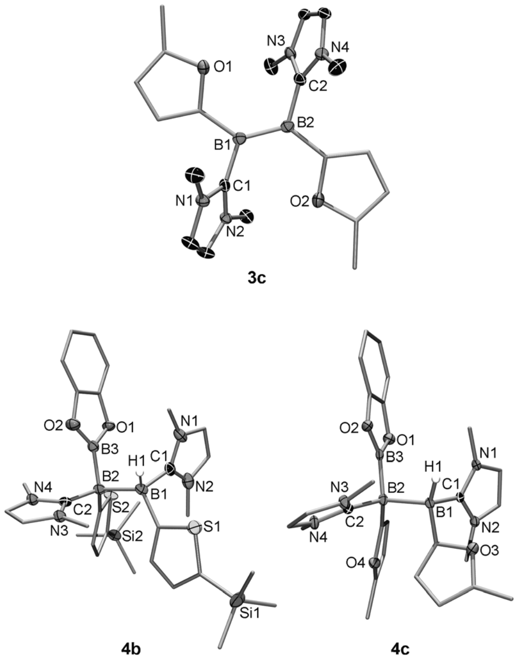
Table 1: Key UV/Vis bands of diborenes **III**, **IV**, and **3a**–**c**, and their assignment to electronic transitions.[a]

	λ_{exp}	ε	λ_{calcd}	Transition orbitals
σ(BB)→π(carbene) transition				
III[25]	300	4723	320	HOMO−1→LUMO
IV[25]	299	1914	319	HOMO−1→LUMO
3a	293	5553	310	HOMO−1→LUMO
3b	293	5332	312	HOMO−1→LUMO
3c	289	2131	310	HOMO−2→LUMO
π(BB)→π(carbene/aryl) transition				
III[25]	461	5713	444	HOMO→LUMO+1
IV[25]	463	2200	436	HOMO→LUMO+1
3a	477	6342	451	HOMO→LUMO+1
3b	492	4612	474	HOMO→LUMO+1
3c	409	2535	385	HOMO→LUMO+3
π(BB)→π(carbene) transition				
III[25]	535	10505	514	HOMO→LUMO
IV[25]	538	4126	514	HOMO→LUMO
3a	543	7025	550	HOMO→LUMO
3b	562	6037	561	HOMO→LUMO
3c	547	2824	567	HOMO→LUMO

[a] Wavelengths (λ) are given in nm; molar extinction coefficients (ε) are given in L mol^{-1} cm^{-1}.

correspond to essentially the same transitions in all of the compounds (although the orbital labels differ in some cases). These bands are assigned to the σ(BB)→π(carbene) (289–300 nm), the π(BB)→π(carbene/aryl) (409–492 nm), and the π(BB)→π(carbene) (535–562 nm) transitions. Depictions of the orbitals involved in these transitions can be found in the Supporting Information.

The solid-state structure of **3c** shows both the B=B bond character and the coplanarity of the furyl substituents with the B=B bond (Figure 1). The B=B distance in **3c** (1.585(4) Å) is very similar to those found in **III** (1.593(5) Å) and **IV** (1.590(5) Å), but considerably longer than that of the dihalo derivative **II** (1.546(6) Å). The coplanarity appears to be accompanied by some conjugation of the heterocycle with the B=B system, in that the B−C$_{\text{Furyl}}$ distances in **3a** (1.560(4), 1.565(4) Å) are significantly shorter than the B−C$_{\text{Aryl}}$ distances in **III** (1.606(3) Å) and **IV** (1.609(4) Å). The observed furyl–diborene coplanarity is analogous to the aforementioned coplanarity of thienyl, furyl, and pyrrolyl groups with boroles.[27,28] The occurrence of this coplanarity between both boroles and diborenes and a range of heterocycles suggests that boron-connected heterocyclic groups prefer to stay coplanar with boron-containing π systems despite steric pressure to the contrary, a phenomenon which may become very useful in the search for conjugated boron-containing materials.



3c

4b

4c

Figure 1. Solid-state structures of diborene **3c** and hydroboration products **4b** and **4c**. The molecules of **4b** and **4c** depicted are, in each case, one of two enantiomers present as a racemate in the sample. Ellipsoids are set at 50% probability. For clarity, all of the hydrogen atoms (except H1 of **4b** and **4c**) and some ellipsoids have been removed. Selected bond lengths [Å] for **3c**: C1–B1 1.577(4), B1–B2 1.585(4), B2–C2 1.589(4); angles between furan planes and mean plane of the central B_2C_4 unit: 5.08° and 2.52°. Selected bond lengths [Å] and angles (°) for **4b**: C1–B1 1.620(4), B1–B2 1.838(4), B2–B3 1.686(4), B2–C2 1.628(3); B1-B2-B3 100.67(18). Selected bond lengths [Å] and angles (°) for **4c**: C1–B1 1.611(2), B1–B2 1.838(2), B2–B3 1.676(2), B2–C2 1.616(2); B1-B2-B3 103.85(11).

The room-temperature addition of the well-known hydroboration reagent catecholborane (HBCat) to **3b** and **3c** led to distinct color changes from deep purple/red to yellow, and in both cases a pure yellow solid was obtained from the mixtures (**4b**,**c**) in good yields. The ^{11}B NMR spectra of both compounds showed one broad high-frequency resonance (**4b** $\delta=43.3$, **4c** 44.2 ppm), one sharp low-frequency doublet (**4b** $\delta=-22.6$ ppm, $J_{\text{BH}}=78.1$ Hz; **4c** $\delta=-24.0$ ppm, $J_{\text{BH}}=79.4$ Hz) and one sharp low-frequency singlet (**4b** $\delta=-24.9$, **4c** −28.1 ppm). The high-frequency resonance indicates the presence of the BCat group, while the doublet signal is a clear indicator of a tetrahedral boron atom bearing one hydrogen atom. However, only in the ^{1}H NMR spectrum of **4b** was a resonance observed that could be assigned to the boron-bound hydrogen atom, namely an unresolved quartet at $\delta=3.60$ ppm. The ^{29}Si NMR spectrum of **4b** confirmed that two distinct magnetic environments of Si exist in the molecule. Unequivocal evidence for the connectivity of **4b** and **4c** came from single-crystal X-ray crystallography, which in both cases revealed doubly-base-stabilized triborane compounds resulting from the addition of the H−B bond of HBCat to the B=B bond of **4b** and **4c** (Figure 1). Unsurprisingly, the (formerly diborene) B−B distances of the hydroboration products **4b** (1.838(4) Å) and **4c** (1.838(2) Å) are much longer than the B=B bond of **3c** (1.585(4) Å) owing to the reduced bond order between the two boron atoms. These distances are even significantly longer than B−B bonds in diboranes(4), reflecting the sp^3 hybridization of the corresponding boron atoms in **4b** and **4c**.[29] The B(sp^2)–B(sp^3) distances are accordingly shorter (**4b** 1.686(4), **4c** 1.676(2) Å). Notably, the B−C$_{\text{carbene}}$ distances in **4b** (1.620(4), 1.628(3) Å) and **4c** (1.611(2), 1.616(2) Å) are significantly longer than those of the diborene **3c** (1.577(4), 1.589(4) Å), reflecting reduced π delocalization and/or the increase in coordination number of the attached boron atoms.

The number of signals observed in the NMR spectra for **4b** and **4c** indicate that only one diastereomer of these molecules is formed in the reaction, which presumably exists as a racemate of two enantiomers. The connectivity of the triboranes and the absence of an alternative diastereomer leads to the assumption that the diborene hydroboration process is a concerted *syn* addition, in accordance with the mechanism of classical and catalytic olefin hydroboration reactions.[18–23] However, the dissociation of a IMe substituent and the concomitant isomerization to the thermodynamically more stable diastereomer cannot be unequivocally ruled out.

In conclusion, we have presented the synthesis of new base-stabilized diborenes, and the diastereoselective hydroboration of the B=B bonds of two of these compounds to give unprecedented bis(NHC)-stabilized triboranes. The reaction occurs at room temperature, without catalysts, strong reductants, or any other additives. This new diborene hydroboration is one of only a few strategies for the construction of classical B−B bonds, and we envisage the potential of the reaction for the construction of longer chains of boron atoms or polymers.

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