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Boron Chemistry

Single, Double, Triple Bonds and Chains: The Formation of Electron-Precise B−B Bonds

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boron · boron–boron bonds · boron-centered ligands · multiple bonding · transition metals

The construction of boron–boron bonds, despite the intense synthetic interest in diboranes and the high B−B bond enthalpy, is still difficult, uncontrollable, and unpredictable. Methods for the construction of B−B multiple bonds are rarer still. These problems have witnessed some progress in recent years; this Minireview attempts to provide a background to the history of B−B bond synthesis and summarize the recent results in the area.

1. Introduction

The chemistry of electron-precise chains of boron atoms (that is, B_xR_{x+2}) is leagues behind that of chains of carbon (organic chemistry) in terms of the stability and diversity of the products. There are a number of obstacles that stand in the way of the proliferation of these molecules, but the two most prominent are the stability and synthesis of the required B−B bonds. The homonuclear σ-bond enthalpy of boron ($D_0 = 293\ \mathrm{kJ\,mol^{-1}}$) approaches that of carbon ($D_0 = 345\ \mathrm{kJ\,mol^{-1}}$) and surpasses that of silicon ($D_0 = 222\ \mathrm{kJ\,mol^{-1}}$), two elements well known to form chains.[1] While relatively thermodynamically stable, breakage of the B−B bond is often promoted by the very stable bonds boron is able to form with oxygen (B−O: $D_0 = 536\ \mathrm{kJ\,mol^{-1}}$), nitrogen (B−N: $D_0 = 446\ \mathrm{kJ\,mol^{-1}}$) and carbon (B−C: $D_0 = 372\ \mathrm{kJ\,mol^{-1}}$) among others. Kinetically, the B−B bond also presents challenges, as the two empty boron-based p orbitals present excellent targets to nucleophiles; however this can be discouraged by the use of π-basic (for example dialkylamino or alkoxy) substituents attached to the boron atom. The importance of this concept, the partial population of the empty atomic orbital, was recently highlighted by Tiznado, Boldyrev, et al.,[2] whose computational survey of the geometries of boranes of the formula B_nH_{n+2} ($n = 2$–5) showed that boron avoids sp^2 hybridization, and that the longer the boron chain, the more the molecule will favor a non-classical structure. It is thus unsurprising that the vast majority of longer-chain boranes feature strongly π-basic amino substituents that can partially fill this orbital and alleviate the inherent electron deficiency of boron.

The number of methods developed for the synthesis of carbon–carbon bonds is now countless, and the construction of such bonds is now possible with extraordinary levels of control. In comparison, the synthesis of B−B bonds is unquestionably primitive. This is surprising when considering that the first examples of electron-precise B−B bond formation were reported almost a century ago (Figure 1) and the ever-increasing utility that diboranes are finding in organic chemistry.[3]

Stock's pioneering 1925 efforts involved exposing BCl_3 to an electrical arc between a Zn anode and an Al cathode under an atmosphere of N_2.[4] Aside from solid residue containing elemental boron and $ZnCl_2$, the gaseous components contained mostly unreacted BCl_3 and a small amount of B_2Cl_4. Later, Schlesinger and co-workers improved upon this synthesis by passing BCl_3 over a glowing discharge between two Hg electrodes.[5] Schlesinger and co-workers later observed the spontaneous conversion of B_2Cl_4 to B_4Cl_4 at around 0 °C.[6] The compound B_4Cl_4 could conceivably adopt either a classical (cyclotetraborane, with electron-precise B−B bonds) or non-classical (tetrahedrane) structure. Kleier and co-workers proposed a tetrahedrane–cyclotetraborane–tetrahedrane isomerization process on the basis of quantum-chemical calculations in 1980.[7] In 1979, Morrison and Davan reported a similar preparation of a mixture of B_2Cl_4 and B_4Cl_4 from BCl_3 using radio-frequency discharges.[8]

The report by Brotherton et al. in 1960 of reductive diaminohaloborane coupling offered the possibility of convenient large-scale synthesis of B−B bonds, thereby crucially demonstrating the importance of π-donor substitutents for stabilizing the products and intermediates in the process.[9] These two concepts of reductive coupling and π stabilization were to become the backbone of B−B bond formation for the next half century at least. Using these methods, the group of Nöth later presented the synthesis of electron-precise boron chains up to six atoms long in 1970,[10] and the synthesis of

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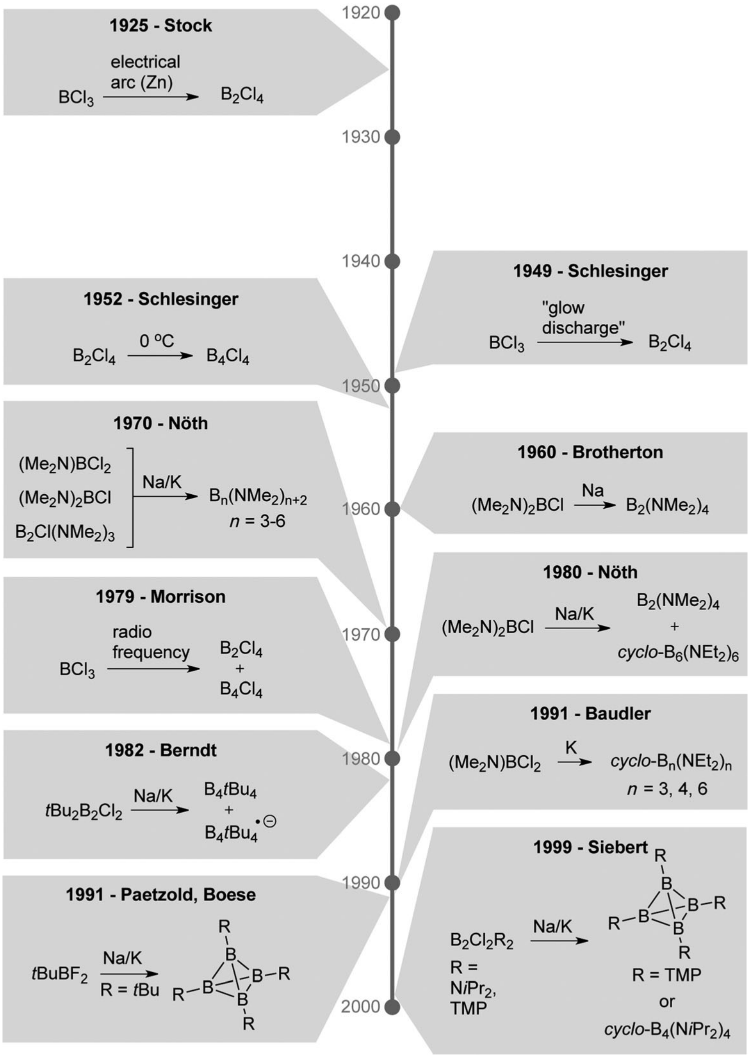

Figure 1. Milestones in the synthesis of electron-precise boron–boron single bonds during the 20th century.

a cyclohexaborane in 1980.[11] In 1982 Berndt and co-workers reduced dichlorodi-*tert*-butyldiborane(4) and obtained both the cyclic tetraborane B_4tBu_4 and the corresponding radical anion, $[B_4tBu_4]^{\bullet-}$, as determined by ESR spectroscopy.[12] The authors proposed a non-cluster butterfly structure of the B_4 ring of the latter based on the observed hyperfine coupling constant, and Paetzold et al. later provided structural confirmation of the tetrahedrane structure of B_4tBu_4.[13] The groups of Baudler and of Siebert reported the preparation of cyclotriboranes, -tetraboranes, and -hexaboranes by the

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reduction of haloboranes and dihalodiboranes(4), respectively.[14] The reduction of a dibromoborane with a large terphenyl substituent also allowed the group of Power to isolate an unusual diborate salt in 1999.[15]

Even now, the mechanism of the reductive coupling of haloboranes is uncertain. The two most likely mechanisms are 1) two-electron reduction of one borane leading to a boryl anion, followed by nucleophilic attack on a further haloborane (Path A, Figure 2); and 2) coupling of two boryl radical species generated by one-electron reduction of haloboranes (Path B). Examples of analogues of both key intermediates (boryl anions and boryl radicals) have now been isolated.[16] However, the presence of hydrogen-abstraction products in many of these reduction reactions is somewhat inconclusive given that both pathways involve radical generation.

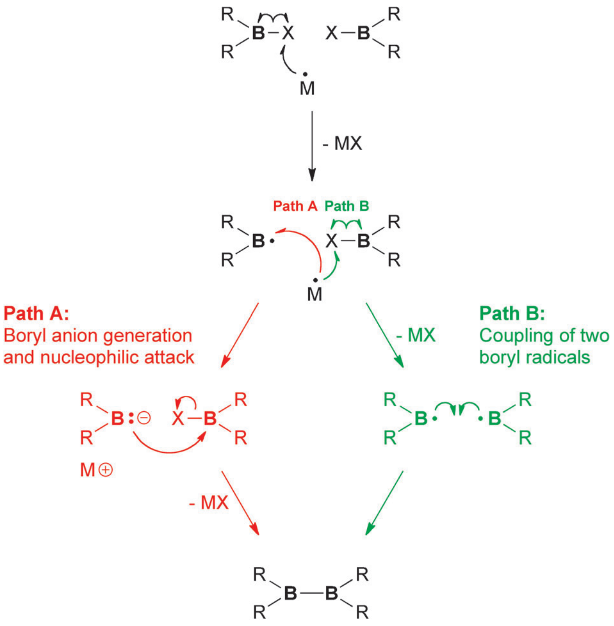


Figure 2. Two possible pathways for the reductive coupling of haloboranes.

It is clear from the above that reduction of haloboranes is by far the predominant method for the construction of electron-precise B–B bonds; however, this method comes with many disadvantages. The generation of reactive radical species during the reactions necessitates bulky and/or π-donating substituents at the boron center. Often, control of chain length, ring size, or even the selectivity for linear, cyclic, or polyhedral products is very poor. Many reductions thus provide a range of products that cannot withstand chromatography and must be separated by distillation or crystallization. This Minireview summarizes the recent efforts, by our group and others, to take B–B bond construction beyond simple haloborane reduction. Recent work on boron–boron multiple bonding, a field likewise dominated by reduction chemistry, is also discussed.

2. B–B Single Bonds by Borylene Coupling

In 2002, our report of coupling of two chloroborylene fragments (Figure 3 and Table 1) hinted at the potential for borylene-based B–B bond construction, yet it took another ten years to uncover the next example of such a reaction.[17] Irradiation of bridging chloroborylene complex **1** under a CO atmosphere resulted in the non-classical complex **2** (d_{BB}: 1.695(7) Å (X-ray), 1.676 Å (calcd.)), in which a B_2Cl_2 ligand forms a butterfly structure with the two manganese centers. Calculations by Pandey, Dewhurst, and Braunschweig showed that both the formation of a terminal chloroborylene intermediate and the dimerization of this chloroborylene are strongly exothermic processes in the presence of CO.[18] Later, Li, King, et al. theoretically predicted that B–B bonds would be present in the complexes $[\{(\eta^5\text{-}C_5H_5)Fe\}_2(\mu\text{:}\eta\text{-}B_2F_2)(\mu\text{-}CO)]$ (d_{BB}: 1.877 Å (B3LYP), 1.906 Å (BP86)) and $[\{(\eta^5\text{-}C_5H_5)(OC)_2Fe\}\{(\eta^5\text{-}C_5H_5)(OC)Fe\}(\mu\text{:}\eta\text{-}B_2F_2)]$ (d_{BB}: 1.850 Å (B3LYP), 1.878 Å (BP86)).[19] Subsequent attempts to induce B–B coupling of borylene ligands were unsuccessful; installation of two borylene ligands into one complex proved difficult to accomplish apart from in isolated, fortuitous instances.[20] The double borylene transfer from $[(OC)_5Mo\{BN(SiMe_3)_2\}]$ to $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ resulted in the first monometallic bis(borylene) complex, $[(\eta^5\text{-}C_5Me_5)Ir\{BN(SiMe_3)_2\}_2]$ (Table 1); however, the boron centers showed no sign of interaction, with linear Ir-B-N axes and a B–B distance of 2.358 Å.[21] Calculations by Pandey confirmed the negligible B–B interaction in this complex but predicted that the interaction would become more

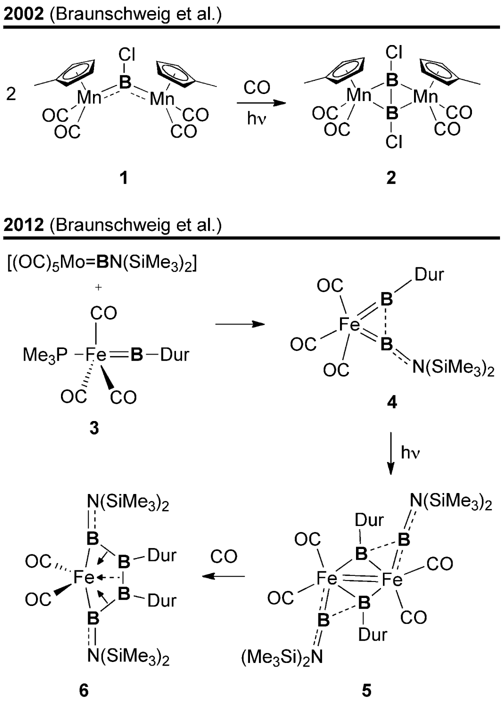
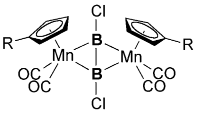
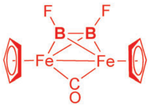
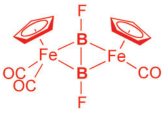
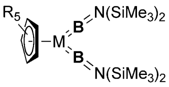
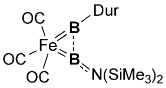
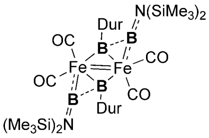
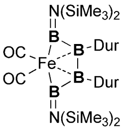


Figure 3. Construction of boron–boron single bonds based on borylene ligand coupling. Dur = 2,3,5,6-tetramethylphenyl.

Table 1: A comparison of selected structural, spectroscopic, and computational parameters for a variety of proximal multi(borylene) systems bound to transition metals.[a]

		d(B–B) [Å]	δ_B [ppm]	B–B bond index **W**iberg/**M**ayer
	R = Me	1.695(7)	142.4	–
	R = Me	1.676	168.9	–
	R = H	1.702	–	–
		1.877 (B3LYP) 1.906 (BP86)	–	–
		1.876 (B3LYP) 1.878 (BP86)	–	–
	M = Ir, R = Me	2.358	69	–
	M = Co, R = H	2.179	–	0.43 (M)
	M = Rh, R = H	2.373	–	0.49 (M)
	M = Ir, R = H	2.517	–	0.21 (M)
		1.982(3)	129, 78	–
		1.994	–	0.78 (W)
		2.102(3)	140, 86	–
	outer	1.792(6)/1.814(6)	86	–
	inner	1.686(6)	76	–
	outer	1.818/1.815	–	0.86/0.87 (W)
	inner	1.729	–	1.00 (W)

[a] Black: experimental results, red: theoretical results.

significant with the lighter Group 9 metals, and if the η^5-C_5Me_5 ligand was changed to the less electron-donating η^5-C_5H_5 ligand (Table 1).[22] However, we predicted that the most significant impediment to B–B coupling was the intense π donation from the boron-bound amino groups, and that a more promising strategy would be the use of borylene ligands without such π-basic substituents.

Over the past five years, we have established that the terminal alkylborylene complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mn(=BtBu)]$[23] unfortunately shows no inclination towards intermetal borylene transfer, instead preferring metathesis-type reactions[24] and addition of metal Lewis bases.[25] However, the recent synthesis of the iron arylborylene complex **3** (Figure 3)[26] prompted us to test this complex as a borylene acceptor with the powerful borylene transfer agent $[(OC)_5Mo\{BN(SiMe_3)_2\}]$.[20,27] With slight warming, the two borylene complexes reacted to form the unsymmetrical bis(borylene) iron tricarbonyl complex **4** (Figure 3), with slightly bent Fe-B-R axes (Fe-B-N 172.02(16)°, Fe-B-C 174.91(15)°) and a B–B distance of 1.982(3) Å (Table 1), which is considerably shorter than that of the negligible B–B bond in $[(\eta^5\text{-}C_5Me_5)Ir\{BN(SiMe_3)_2\}_2]$ (2.358 Å), but longer than that of the presumably "full" B–B bond of **2** (1.695(7) Å).[28] The calculated B–B distance (1.994 Å) and Wiberg Bond Index (WBI, 0.78) for **4** support this partial-bond description. Irradiation of **4** led to loss of one CO ligand from the molecule and dimerization to form the diiron (Fe=Fe) tetra(borylene) complex **5**. The durylborylene fragments act as bridging ligands in **5**, while the aminoborylene ligands remain terminally bound. The durylborylene ligands, now receiving π back-bonding from two electron-rich, formally zerovalent iron centers, are less inclined to interact with the aminoborylene ligands, and thus the B–B distances in this complex (2.102(3) Å) are considerably longer than those of the precursor **4**.

A recurring goal in our research, once we have an interesting boron–metal complex in hand, is to attempt to free the boron ligand from the metal to create metal-free boron species.[29] With this goal in mind, **5** was heated at 80 °C under a CO atmosphere to strip out the iron centers and perhaps liberate a boron-only heterocycle or cluster. This wish, in effect, came half-true: one iron center was lost (presumably as $[Fe(CO)_5]$), while the boron ligands catenated into a planar, four-boron "tiara" around the remaining iron in the complex **6** (Figure 3). The inner B–B segment of **6** forms a clear single bond (d_{BB}: 1.686(6) Å (X-ray), 1.729 Å (calcd); WBI: 1.00), while the outer B–B bonds are less complete (d_{BB}: 1.792(6), 1.814(6) Å (X-ray), 1.818, 1.815 Å (calcd); WBI: 0.86, 0.87; Table 1).[28] Calculations show that the HOMO of this molecule consists of an in-plane σ-bond network involving the four boron atoms and the iron center, while further bonding interactions consist of $\sigma_{BB} \rightarrow Fe$ sigma-bond donation to the metal that is strong for the outer B–B bonds and weaker for the central B–B bond. This donation to the metal is presumably the reason for the reduced B–B bond order observed for the outer bonds.

3. B–B Single Bonds by Borane Dehydrocoupling

The dehydrogenative coupling of amineboranes and aminoboranes is an intensively studied process owing to its relevance to the search for low-molecular-weight hydrogen

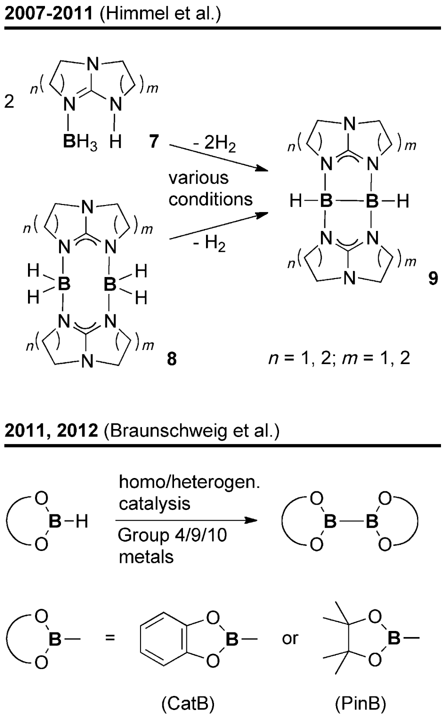


Figure 4. Recent (catalytic and non-catalytic) borane dehydrocoupling reactions from Himmel et al. and our group.

storage materials;[30] however, this process yields exclusively head-to-tail coupling products with B–N bonds, not B–B-bonded compounds. Since 2007 Himmel et al. have studied the reactivity of borane (BH_3) adducts of bicyclic guanidines (**7**, Figure 4) as an alternative system for aminoborane dehydrocoupling in which the boron atoms are preorganized to form B–B bonds instead of the regular B–N bonds.[31] These adducts lose dihydrogen and dimerize, forming compounds **8** with two BH_2 units spanning two guanidine bases, each boron unit becoming formally an imine-stabilized dihydroaminoborane. These diboron systems lose a further equivalent of dihydrogen to provide B–B-bound compounds **9** upon heating in refluxing toluene or with catalytic amounts of transition-metal complexes [{RhCl(COD)}$_2$] (COD = 1,5-cyclooctadienyl) or [$Ru_3(CO)_{12}$].

Despite the extensive use of diborane(4) reagents, such as bis(catechol)diborane(4) (Cat_2B_2) and bis(pinacol)diborane(4) (Pin_2B_2) in organic chemistry, the synthesis of these compounds relies, even now, on the reductive coupling of two diaminohaloboranes, a process that has seen little improvement since the report of Brotherton in 1960.[9] This pathway, despite involving many steps and creating six moles each of halide and amine byproducts per mole of product, is still the standard commercial synthesis of synthetically relevant diboranes(4). It was because of these disadvantages that we attempted to find a more direct and atom-efficient route to diboranes(4). Our initial attempts at dehydrocoupling of the hydroboranes catechol- and pinacolborane involved heating the boranes with homogeneous catalysts based on Group 10 transition metals of the general form [$MCl_2(P_2)$] (P_2 = chelating diphosphine), and were moderately successful, providing the coupled product with turnover numbers (TONs) of up to 160 (Figure 4).[32] Turning to heterogeneous catalysts led to an improvement in the TON to up to 350 (Pt on alumina). Upon noticing that increasing product concentration in the mixture led to decreased yields, we reasoned that the presumed oxidative addition of the product diborane onto a metal catalyst may in fact inhibit the catalysis. A method was thus devised in which the hydroborane could be continuously and selectively distilled out of the reaction mixture into a Soxhlet thimble containing the solid catalyst, thereby isolating the catalyst from the diborane product. This method led to an improvement of the TON measured by GC up to about 11000 (Pt on alumina, 20 h). Later, homogeneous and heterogeneous catalysts of Group 4 transition metals showed activity in the dehydrocoupling reaction, albeit with much lower TONs.[33]

In an attempt to understand the homogeneous catalytic process, mechanistic studies were undertaken using platinum phosphine complexes. An earlier study had uncovered a rapid scrambling process between the bis(catecholboryl) complex **10** (Figure 5) and an excess of substituted catecholdiborane(4) species Cat'_2B_2 (Cat′ = 4-*tert*-butylcatecholdiyl), leading to two new bis(boryl) Pt^{II} species **11** and **12**, as well as Cat_2B_2 and the mixed Cat′BBCat.[34] This reaction hinted at the possibility of higher-coordinate, higher oxidation state intermediates in the process. Using a two-coordinate Pt^0

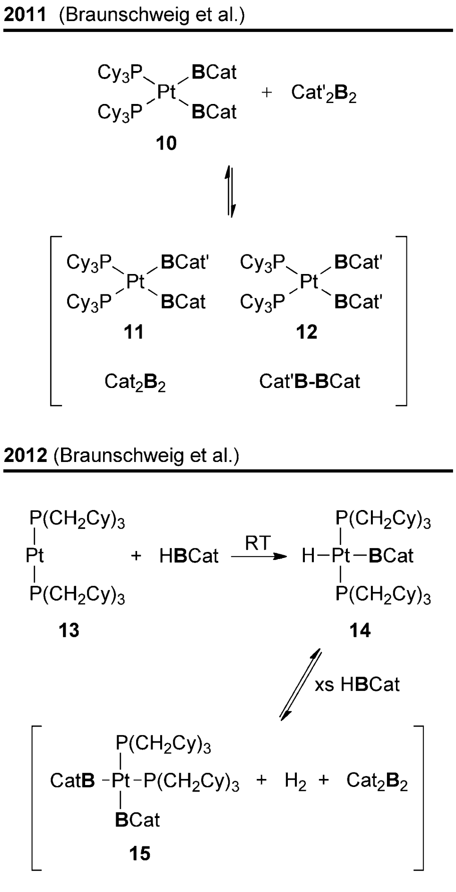


Figure 5. Mechanistic studies of relevance to the catalytic borane dehydrocoupling reaction.

precursor with a specially designed phosphine ligand with flexible steric bulk, $P(CH_2Cy)_3$ (**13**, Figure 5), the *trans* hydridoborane complex **14** could be isolated.[35] By adding an excess of hydroborane, the *cis*-bis(boryl) complex **15** could be detected in solution and confirmed by comparison of NMR spectroscopic data with an independently prepared sample. The final step in the process, the construction of the B–B bond and release of the product and dihydrogen, was also observed. Based on these reactions and DFT calculations, a mechanism was proposed which proceeds via a six-coordinate platinum dihydridobis(boryl) intermediate.

4. B–B Double and Triple Bonds

4.1. Early Work

The empty p orbital of boranes has for a long time been an irresistible target for reduction chemistry, in an attempt to satisfy the inherent electron deficiency of boron. In diboranes(4), the two empty p orbitals effectively represent an empty π-bonding orbital that, if filled, could increase the boron–boron bond order (Figure 6). In 1981 Berndt and co-workers published two reports on the one-electron reduction of boranes and diboranes in which the radical anions $[Np_2BBNp_2]^{\bullet-}$, $[Np(tBu)BB(tBu)Np]^{\bullet-}$, and $[(MeO)(tBu)BB(tBu)(OMe)]^{\bullet-}$ (Np = neopentyl) were isolated and characterized by EPR spectropscopy.[36] Later, the group of Power brought X-ray crystallography to bear on the similar radical anions **16**–**18** (Table 2), confirming that the reduction does result in a small amount of B–B bond contraction (**16**: 1.636(7) Å; **18**: 1.649(11) Å) compared to those of regular diboranes(4), which are usually around 1.7 Å in length.[37] In some cases, two-electron reduction of the diboranes(4) occurred, leading to the dianions **19** and **20** in which the two associated lithium cations are loosely bound to the boron substituents, and in **19**, to the boron atoms themselves. Despite the formally higher B–B bond order of **19** and **20** (2.0 vs. 1.5 in **16**–**18**), the B–B distances were not found to be significantly shorter (**19**: 1.636(11) Å; **20**: 1.627(9) Å).

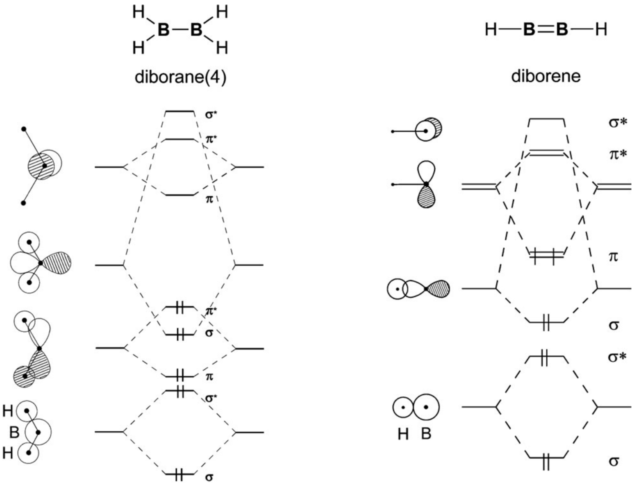
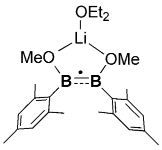
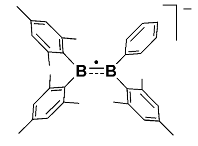
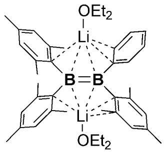
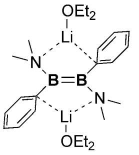


Figure 6. Full MO diagrams for diborane(4) (B_2H_4) and diborene (B_2H_2).

Table 2: Radical anions and dianions with B–B multiple bond character from Power et al.[a]

Radical anions	d(B–B) [Å]	δ_B [ppm]
 **16**	1.636(7)	–
 $K^+(DME)_3$ or $K^+(18C6)(THF)_2$ **17** **18**	1.649(11) (**18**)	–
dianions	d(B–B) [Å]	δ_B [ppm]
 **19**	1.636(11)	24
 **20**	1.627(9) (avg.)	33

[a] DME = 1,2-dimethoxyethane, 18C6 = [18]crown-6.

4.2. Recent Work

In 2007, Robinson and co-workers applied the promising technique of carbene stabilization[38] to the reduction of haloboranes and the synthesis of boron–boron multiple bonds.[39] By reduction of NHC-stabilized tribromoborane **21** (Figure 7; NHC = N-heterocyclic carbene) with potassium graphite, the neutral, bis(carbene)-stabilized diborene **23** was prepared and isolated. The very short B–B distance of **23** (1.561(18) Å, Table 3) was a clear sign that a double bond was present between these atoms. The full reductive dehalogenation of **21** to form a compound with a B–B triple bond was clearly one of the goals of this work; however, the observation of the resulting tetrahydrodiborane **22** as a byproduct suggested that this had been prevented by radical abstraction of hydrogen atoms from solvent.

The construction of a boron–boron triple bond has been a goal of chemistry for some time. The reduction of dihaloboranes with bulky, aryl substituents based on terphenyl groups was attempted by Power and co-workers in 1996; however, this led only to products of a formal borylene insertion into C–C bonds of the terphenyl substituents.[15] One

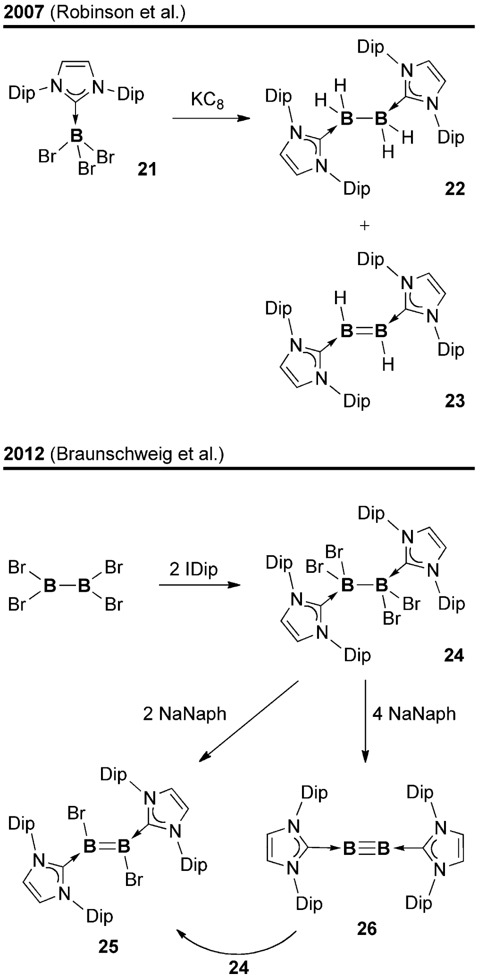
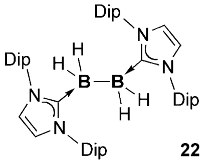
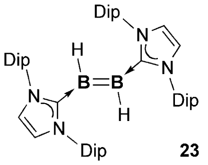
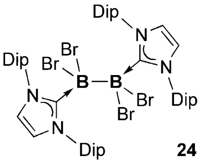
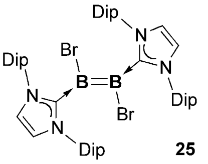
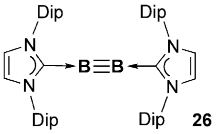
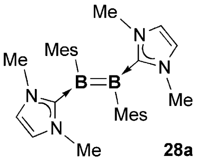
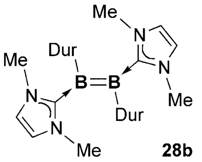


Figure 7. Synthesis of NHC-stabilized compounds with B–B double and triple bonds. Dip = 2,6-diisopropylphenyl, Idip = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene, NaNaph = sodium naphthalenide.

Table 3: B–B distances and ^{11}B NMR parameters for some carbene-stabilized diboranes, diborenes, and diborynes from Robinson et al. and our research group.

	d(B–B) [Å]	δ_B [ppm]
 **22**	1.828(4)	−31.6
 **23**	1.561(18)	25.3
 **24**	–	−4.8
 **25**	1.546(6)	20
 **26**	1.449(3)	39
 **28a**	1.593(5)	24.1
 **28b**	1.590(5)	24.7

year later, this strategy would prove successful in the synthesis of digallynes with Ga–Ga triple bonds by Robinson and coworkers,[40] and in 2006 was used by Power in the synthesis of dialuminynes ($Al\equiv Al$).[41] However in 2002, Zhou, Xu, and coworkers demonstrated an alternative concept, namely base-stabilization, using laser-vaporized boron atoms and CO.[42] This method was later to influence the conventional ambient-temperature synthesis of such molecules. They detected the B–B triply bonded species OCBBCO in an argon matrix at 8 K and provided computational evidence for a very short B–B distance in this molecule (1.453–1.468 Å). This work was followed by a report from Li and Wang on the gas-phase isolation of the dianionic molecule [OBBBBO]$^{2-}$ in 2008, which was calculated to have a B–B distance of 1.481 to 1.504.[43] These reports were accompanied by theoretical studies by the groups of Mavridis[44] and Frenking,[43b] which explored a range of donors for stabilizing the B$_2$ unit, such as noble-gas atoms, CO, CS, and N$_2$, thus confirming these short B–B distances.

In 2011, computational studies from the groups of Mitoraj[45] and Frenking[46] on $L\rightarrow B\equiv B\leftarrow L$ compounds extended the donor-stabilization concept to include more synthetically feasible and sterically tunable donor systems, such as phosphines, NHCs, and germylenes. For the carbene- and phosphine-stabilized systems, B–B distances were calculated to be in the range 1.45–1.470 Å. Having noted the hydrogen abstraction process that predominated in Robinson's reduction of an NHC–tribromoborane adduct, we reasoned that the elimination of the B–B bond formation step may promote the full reduction reaction in similar systems. Based on this hypothesis, we sought to reduce a similar NHC-stabilized system with a pre-formed B–B bond. Owing to the facile thermal decomposition of tetrahalodiboranes(4), the free carbene IDip (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) was added directly to a solution of tetrabromodiborane(4), prepared in situ, providing the bis(NHC) tetrabromodiborane(4) **24** (Figure 7).[47] Addition of two equivalents of the strong, soluble reducing agent sodium naphthalenide to **24** led to the corresponding bis(NHC)-stabilized dibromodiborene **25** with a B−B distance of 1.546(6) Å, which is comparable to that of the dihydrodiborene **23** of Robinson (Table 3). Alternatively, addition of four equivalents of sodium naphthalenide to **24** is accompanied by a shift of the ^{11}B NMR resonance to $\delta = 39$ ppm and the formation of the first compound with a boron–boron triple bond that is stable at ambient temperature, the diboryne **26**.[47,48] The B−B distance of **26** (1.449(3) Å) was found to be the shortest structurally confirmed B−B bond. As predicted by the above computational studies, the *trans* bending[49] of the $L\rightarrow B\equiv B\leftarrow L$ axis of **26** (C-B-B angles: 173.0(2), 173.3(2)°), which would signify triplet character of the molecule rather than true triple bonding, is small compared to that of dianionic dialuminynes[41] and digallynes.[40] Furthermore, a comproportionation reaction of equimolar amounts of **24** and **26** provided two equivalents of diborene **25**.

4.3. Coordination Chemistry of B−B Double Bonds

Two very recent publications from our laboratories have, for the first time, hinted at the coordination chemistry of both base-stabilized and non-stabilized boron–boron multiple bonds with transition metals. The first details the reductive coupling of two NHC-stabilized aryldichloroboranes **27** (Figure 8) with lithium to form the first diaryldiborenes **28**.[50] The duryl derivative, **28b**, reacted with silver(I) chloride to provide a side-on π-complex **29** with a B−B distance of 1.645(6) Å, corresponding to a bond lengthening of just over 3 % compared to the metal-free diborene **28b**. The trigonal-planar geometry of the boron atoms in doubly base-stabilized diborenes and their out-of-plane π orbital make them analogues of olefins, and thus the π complex **29** is a boron analogue of the well-known family of transition-metal π olefin complexes.

More recently, we were delighted to observe the clean two-electron reduction of the distorted σ-diboran(4)yl[51] complex **30** (Figure 8) with the Mg^IMg^I reducing agent **31**[52] developed by Jones. Although the yield is very low owing to facile decomposition and high solubility, the non-NHC-stabilized π diborene complex **32** was isolated and structurally and spectroscopically characterized.[53] In parallel to the NHC-stabilized diborene complex **29**, the unstabilized complex **32** can be seen as an analogue of a transition-metal π alkyne complex. Its near-linear C-B-B angles (166.0(8), 164.2(8)°), short B−B distance (1.510(14) Å), and perpendicular coordination of the B=B unit led us to present complex **32** as the first example of a complex in which π back-bonding from a transition metal (usually linked to bond weakening and activation) actually strengthens an attached element–element bond. Free diborenes are expected to be linear triplet species owing to their degenerate, half-filled, π bonding orbitals (Figure 6). However, the bending of the R-B-B-R axis effected by coordination to a transition metal breaks the degeneracy of these orbitals, leading to one filled and one empty bonding π orbital. In π diborene **32**, the filled π orbital donates electron density to the metal, while π back-bonding from the metal populates the empty π bonding orbital. It is this back-bonding interaction that strengthens the B−B bond. This concept was further explored by computation, and this back-bonding interaction was visualized (the HOMO−1 level in Figure 9).

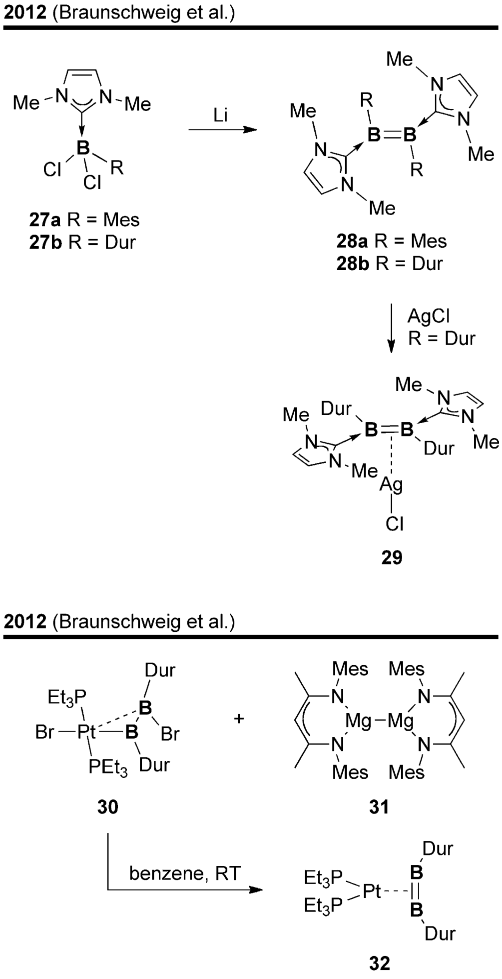


Figure 8. Coordination chemistry of both base-stabilized and non-stabilized B−B double bonds.

5. Summary and Outlook

New methods for the construction of boron–boron single bonds based on borylene coupling and borane dehydrocoupling have been described, including the metal-templated coupling of four boron atoms into a chain. Progress in the use of carbenes to stabilize compounds with boron–boron multiple bonding was also detailed, including the very recent synthesis of a compound with a boron–boron triple bond. The borane dehydrocoupling process is perhaps the only method covered in this review that currently approaches practical, large-scale utility. Although this reaction is superior to the standard commercial diborane synthesis in terms of number of steps and atom efficiency, the synthesis of the precursor hydroboranes requires a borane (BH_3) source, and makes this

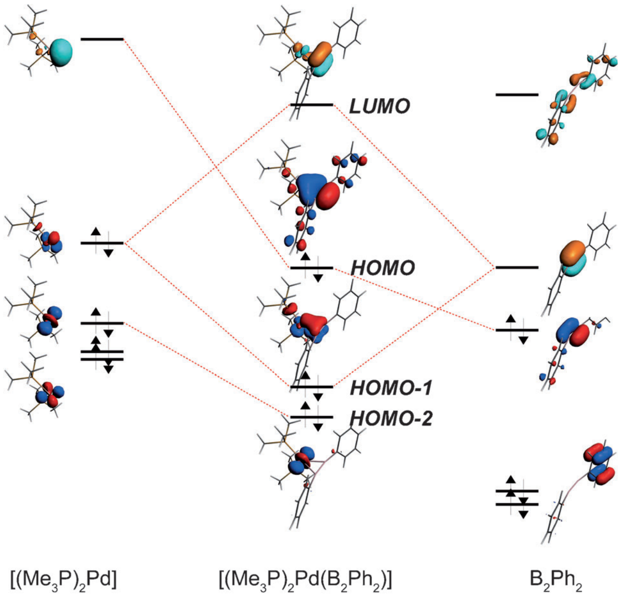


Figure 9. Molecular orbital diagram of model palladium π diborene complex [(Et$_3$P)$_2$Pd(B$_2$Dur$_2$)], showing the combination of pre-organized (that is, non-linear) diborene and palladium fragments. The non-linearity of the diborene fragment breaks the degeneracy of the two half-filled orbitals of a triplet free diborene, leading to a singlet state. The bond-strengthening back-bonding interaction is represented by the HOMO−1 level.

route currently nonviable. We hope the borylene coupling reaction can be extended to other systems and we are investigating the possibility of extending the boron chain and/or releasing it from the metal, as well as the long-term goal of synthesis of high molecular weight polyborylenes of the form (BR)$_n$. The diborenes of Robinson and our new triply bonded diboryne compound all promise rich further chemistry, and we hold great hopes for the exploitation of these fascinating molecules in the future.

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