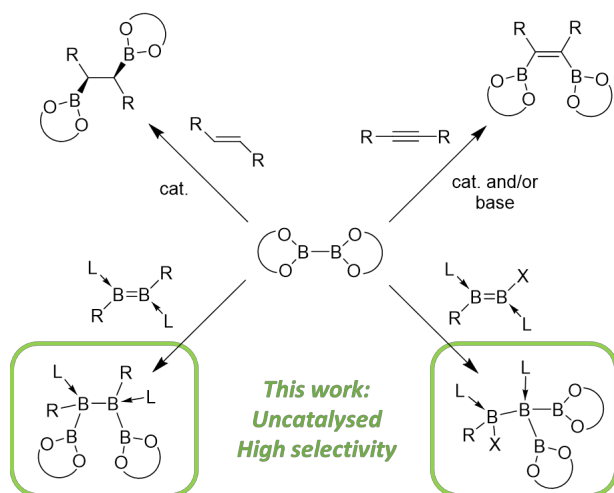


Construction of Linear and Branched Tetraboranes via 1,1- and 1,2-Diboration of Diborenes

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Abstract: Sterically unencumbered diborenes based on a benzylphosphine chelate undergo diboration reactions with bis(catecholato)diboron in the absence of a catalyst to yield tetraboranes. The symmetrical diborenes studied undergo 1,2-diborations, whereas an unsymmetrical derivative was found to yield a triborylborane-phosphine adduct as the result of a formal 1,1-diboration. A related borylborylene compound also underwent a 1,2-diboration to produce a borylene-borane adduct.

The chemistry of boron-boron bonds has traditionally been dominated by clusters with non-classical bonding modes.^[1] Boron's reluctance to display sp^2 -hybridisation causes the simple boranes (B_nH_{n+2}) to favour three-centre two-electron bonds over classical structures – an effect that is amplified as the size of the molecules increases.^[2] The study of electron-precise bonds between boron atoms had been a fringe pursuit ever since the first synthesis of B_2Cl_4 by Stock in 1925,^[3] but was propelled into the mainstream in 1993 by the discovery of transition-metal-catalysed diboration of unsaturated organic compounds (Scheme 1).^[4] Whereas B_2Cl_4 often undergoes uncatalysed 1,2-additions to alkenes and alkynes,^[5] the tetraalkoxydiboranes, $B_2(OR)_4$, utilised in these new catalytic processes, offered the advantages of considerably higher stability and tolerance of air and moisture.^[6]



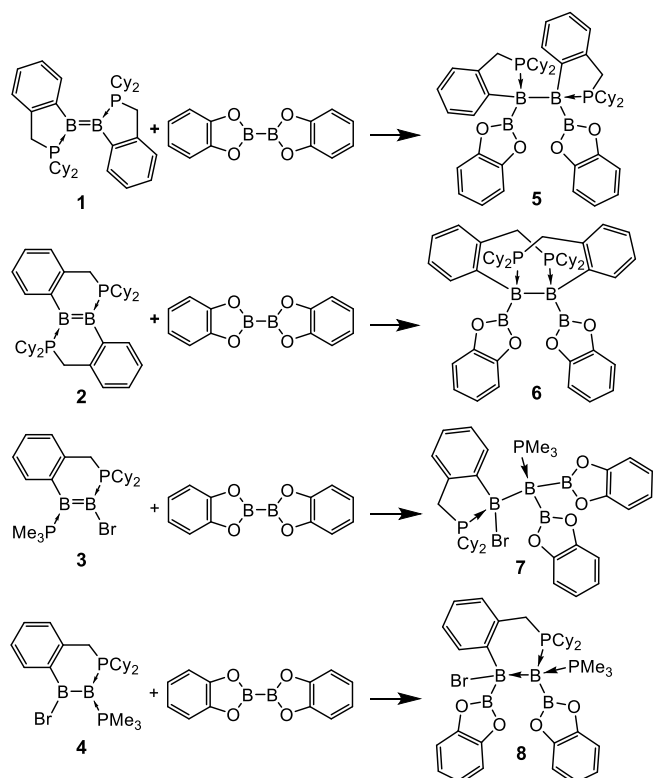
Scheme 1. Addition reactions of diboron compounds with alkenes, alkynes, and diborenes.

Despite the relatively high bond enthalpy of B-B σ -bonds ($D_0 = 293 \text{ kJ}\cdot\text{mol}^{-1}$), the construction of chains of boron atoms has proved challenging due to a lack of synthetic routes to the

compounds and the extremely high strength of B-O ($D_0 = 536 \text{ kJ}\cdot\text{mol}^{-1}$) and B-N ($D_0 = 446 \text{ kJ}\cdot\text{mol}^{-1}$) bonds.^[7] The fact that three-coordinate boron atoms also possess an empty p -orbital renders many such compounds susceptible to hydrolysis and other undesired reactions. Whereas the majority of routes to boron-boron bonds rely on harsh reductive coupling steps,^[8] dehydrocoupling of monoboranes^[9] and borylene coupling^[10] have both been successful in the preparation of new B-B bonds. Nöth obtained some linear oligoboranes (up to B_6) by the reduction of aminochloroboranes with alkali metals,^[8a] although these reactions were rather unselective. Otherwise, chains of more than two boron atoms are extremely rare. In 2012, we reported the on-metal catenation of borylene fragments into a B_4 chain,^[10a] and we recently reported the synthesis of metal-free B_4 chains in the form of diboryldiborenes via reductive coupling of two carbene-stabilised diboranes.^[11] The hydroboration of heteroaryl-substituted diborenes with catecholborane (HBCat, cat = catecholato) provided access to linear triboranes with electron-precise boron-boron bonds,^[9g] whereas use of 9-borabicyclo[3.3.1]nonane as the borane led to a B_3 arachno-cluster.^[12] These observations led us to consider the diboration of boron-boron multiple bonds as a route to extended boron chains. Here we report the 1,1- and 1,2-diboration of diborenes as a selective route to branched and linear tetraboranes.

We recently reported diborenes based on a benzylphosphine chelate (**1** and **2**, Scheme 2) that showed enhanced reactivity towards dienes compared to their non-chelated counterparts,^[13] on account of the fact that the aryl substituent is forced into a coplanar orientation with the B-B bond, reducing steric hindrance. Treatment of geminally-chelated isomer **1** with an equimolar amount of bis(catecholato)diboron (B_2cat_2) in benzene solution at room temperature resulted in a slow reaction. Monitoring of the reaction by NMR spectroscopy revealed a major product with a ^{31}P resonance at 46.4 ppm and ^{11}B resonances at -23 ppm and 44 ppm, alongside a second species ($\delta^{31}P = 33.3$ ppm). Complete conversion could be achieved in 20 h at 25 °C or 2 h at 60 °C, accompanied by decolouration of the solution, and diffusion of hexane into the resulting solution produced colourless crystals of the major product in 55% yield. X-ray diffraction confirmed the compound to be the linear tetraborane, **5** (Scheme 2, Figure 1), resulting from a 1,2-diboration of **1**. The Bcat groups display a gauche orientation with respect to the B1-B2 bond, which is consistent with a *syn*-addition across the diborene double bond. At 1.887(3) Å, the B1-B2 bond is the longest yet observed for a structurally characterised, unsupported, neutral diborane. It is also dramatically longer than in the corresponding dibromodiborane (1.749(7) Å),^[13] indicating that the Bcat substituents have a large influence. A plausible explanation would be that hyperconjugation of the B1-B2 σ -bonding orbital with the empty π -orbitals on B3 and B4 results in a reduction of the B1-B2 bond order. The compound also bears resemblance to a carbene-stabilised diborane reported by Stephan and co-workers, which had a calculated B-B distance of 1.901 Å and was shown to undergo homolytic cleavage of the B-B bond.^[14] The B1-B4 (1.680(3) Å) and B2-B3 (1.66(1) Å) distances are also slightly shorter than other catechol-derived $B(sp^2)$ - $B(sp^3)$ bonds.^[15]

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Scheme 2. Reactions of diborenes **1-3** and borylborylene **4** with B_2cat_2 .

Diborene **2**, in which the benzylphosphine substituent adopts a vicinal (1,2-chelating) configuration, is the more thermodynamically stable isomer of **1**. Compound **2** also reacted with B_2cat_2 , albeit more slowly, with 16 h at 60 °C required for complete conversion. The product of this selective reaction produced ^{11}B NMR signals at 46 and –28 ppm, while a single resonance was observed at 16.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Crystals suitable for X-ray diffraction were grown from a THF/pentane solution and confirmed the formation of tetraborane **6** (Scheme 2, Figure 1). The bridging benzylphosphine enforces an almost eclipsed geometry about the B1-B2 bond, resulting in a torsion angle between the two Bcat groups of 19.2(2)°. The central B-B bond (1.856(4) Å) is slightly shorter than that in **5**, but still at the upper end of the range for diboranes(**6**). The B-P bond lengths of both **5** and **6** fall between 1.94–1.95 Å, which is somewhat shorter than those of recently reported diboranes based upon this system with alkyl substituents in place of the Bcat moieties (B-P = 1.96–2.00 Å),^[13] indicating more Lewis acidic boron centres. In this regard, it is interesting to note the retention of conformation of the benzylphosphine substituents in these reactions; the 4,5-diboracyclohexenes formed from Diels-Alder reactions of **1** and **2** with dienes resulted in an equilibrium mixture of vicinally- and geminally-substituted diboranes, regardless of the starting diborene.^[13] Interconversion is possible between **5** and **6**, as heating **6** for longer periods (3 d at 60 °C) results in the formation of traces of **5** (< 5%), but this is evidently less facile for boryl-substituted than alkyl-substituted diboranes.

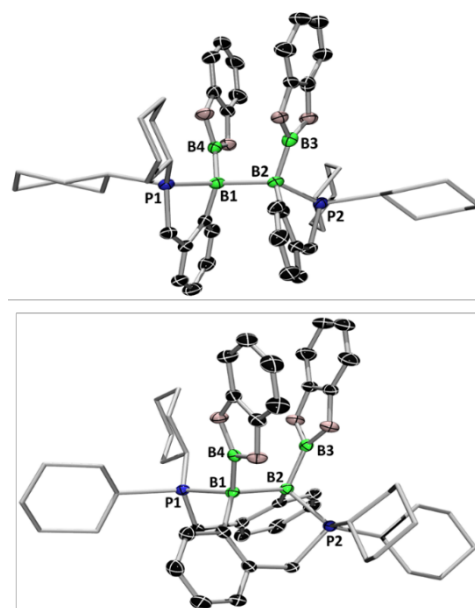


Figure 1. Molecular structures of compounds **5** and **6**, with selected atomic displacement ellipsoids at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and torsion angle (°): **5**: B1-B2 1.887(3), B2-B3 1.66(1), B1-B4 1.680(3), B1-P1 1.948(2), B2-P2 1.949(2); **6**: B1-B2 1.856(4), B2-B3 1.684(4), B1-B4 1.690(4), B1-P1 1.940(3), B2-P2 1.941(2), B4-B1-B2-B3 19.2(2).

Several reports have shown that desymmetrisation of diboranes(**4**)^[15a, 16] results in increased reactivity in small molecule activation,^[17] borylation and diboration reactions,^[18] and intramolecular rearrangement processes.^[19] We have recently reported benzylphosphine-substituted unsymmetrical diborene **3** and its *gem*-isomer **4** (Scheme 2),^[20] which displays borylborylene characteristics, and we were keen to explore the reactivity of these unsymmetrical compounds towards diboranes. Treatment of **3** with B_2cat_2 led to an instantaneous reaction, even at –30 °C, with conversion complete before NMR spectra could be recorded. The reaction was highly selective, with the product displaying three ^{11}B NMR signals at 44, –2 and –39 ppm and two signals in the $^{31}P\{^1H\}$ NMR spectrum at 31.1 and 2.7 ppm. Removal of volatiles under vacuum and washing the product with pentane afforded the pure compound in 84% yield, and recrystallisation from Et₂O produced crystals suitable for X-ray diffraction (Figure 2). Rather than the expected 1,2-addition product, the product was shown to be the triborylborylene **7**, the result of a formal 1,1-diboration at one of the boron atoms. The benzylphosphine chelate reverts to a geminal coordination at the terminal boron atom, while the central boron atom is coordinated by PMe_3 . The B1-B2 bond distance (1.80(1), 1.81(1) Å, two independent molecules in the unit cell) is shorter than those of **5** (1.887(3) Å) and **6** (1.856(4) Å), and thereby in the expected range for an sp^3-sp^3 diborane, while the P1-B2 distance (1.911(8), 1.926(8) Å) is relatively short for a P-B dative bond, an indication of the high Lewis acidity of the central boron atom.

Borylborylene **4** also underwent a rapid reaction with B_2cat_2 at –30 °C, producing an ^{11}B NMR spectrum similar to that of **7** ($\delta^{11}B = 42, -5, -37$ ppm). The major ^{31}P NMR signals appeared at 13.3 and –1.6 ppm, with several smaller signals also present. Recrystallisation from benzene/hexane yielded colourless needles, which still displayed two sets of ^{31}P and 1H NMR signals upon solvation in THF-*d*₆, corresponding to an equilibrium mixture of isomers (see below). Single-crystal X-ray diffraction allowed identification of the product as the simple 1,2-diboration product **8**. Compound **8** is formally a borylene-borane adduct, as both phosphines remain coordinated to B1. The B1-B2 bond (1.797(4) Å) is in the range of a typical sp^3-sp^3 σ -bond, while both phosphines have relatively short distances to B1 (B1-P1 = 1.921(2) Å, B1-P2 = 1.926(3) Å). One of the minor products of this reaction, a further isomer, 1,2-diboryldiborane(**6**) **9**, was also

identified by X-ray diffraction on colourless blocks obtained from evaporation of the solvent from the crude reaction mixture (see Supporting Information). Heating a benzene solution of **8** for three days at 60 °C results in unselective conversion to a number of species, including **7**, indicating the facile isomerisation of these compounds.

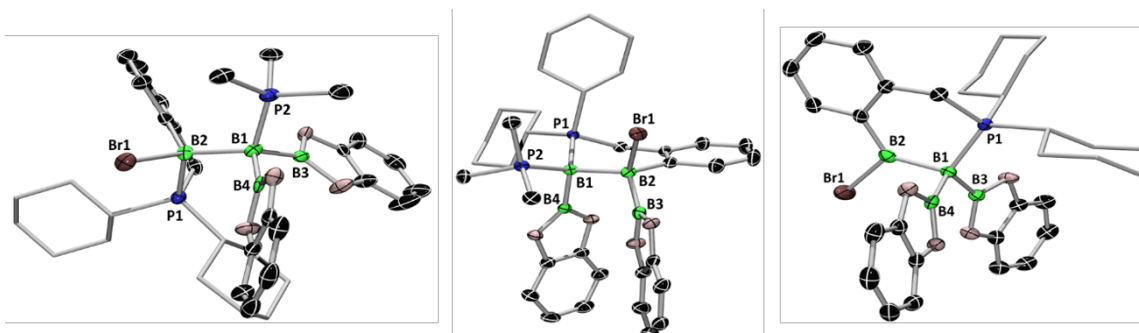


Figure 2. Molecular structure of compounds **7**, **8** and **10**, with selected atomic displacement ellipsoids at the 50% probability level. Solvent molecules (where present) and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): **7** (two independent molecules in asymmetric unit): B1-B2 1.80(1), 1.81(1), B1-B3 1.69(1), 1.69(1), B1-B4 1.69(1), 1.66(1), B2-P1 1.964(7), 1.986(7), B1-P2 1.911(8), 1.926(8); **8**: B1-B2 1.797(4), B2-B3 1.708(4), B1-B4 1.695(4), B1-P1 1.921(2), B1-P2 1.926(3); **10**: B1-B2 1.685(4), B1-B3 1.694(4), B1-B4 1.675(4), B1-P1 1.903(3).

Due to the large number of possible isomers and the evident rearrangement processes occurring, we sought further confirmation for the identities of **7** and **8** as the major reaction products by NMR spectroscopy. All of the new compounds described display broadened signals in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra due to the proximity of the phosphorus and boron nuclei. Broadband ^{11}B -decoupling of the $^{31}\text{P}\{^1\text{H}\}$ spectra of **7** and **8** led to significant sharpening of the signals, allowing determination of the ^{31}P - ^{31}P coupling constants. We then performed CW-decoupling triple resonance experiments, varying the ^{11}B decoupler offset to the values of the respective signals (Figure 3), in order to suppress $^1\text{J}_{\text{PB}}$ coupling and determine the connectivity of the molecules. For compound **7**, decoupling at 44.6 ppm (B3 and B4) had no effect on the linewidth; decoupling at -1.6 ppm (B2) led to sharpening of the ^{31}P resonance for the PCy_2 group at 31.1 ppm (the ^{31}P NMR signals were unambiguously assigned by ^1H , ^{31}P -

COSY experiments) while the signal at 2.7 ppm remained broad; setting the decoupling offset at -38 ppm (B1) caused the PMe_3 ^{31}P resonance at 2.7 ppm to sharpen. These observations are thus fully consistent with the structure of **7** determined by X-ray diffraction.

Compound **8** displays two sets of resonances in solution, which were determined by a ^{31}P , $^{31}\text{P}\{^1\text{H}, ^{11}\text{B}\}$ -EXSY experiment to be in rapid exchange on the NMR timescale. Selective ^{11}B -decoupling at 44 ppm or -4 ppm had no discernible effect on the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure 3), whereas decoupling at -37 ppm caused all four ^{31}P resonances to sharpen. This observation is consistent with the crystal structure of **8**, in which both phosphines are coordinated to B1. We therefore assigned the minor product ($\delta^{31}\text{P} = 16.2, -3.7$ ppm, $\approx 8\%$ by integration) as the diastereomer of **8**, which probably forms as a result of facile association/dissociation of one of the phosphines from boron.

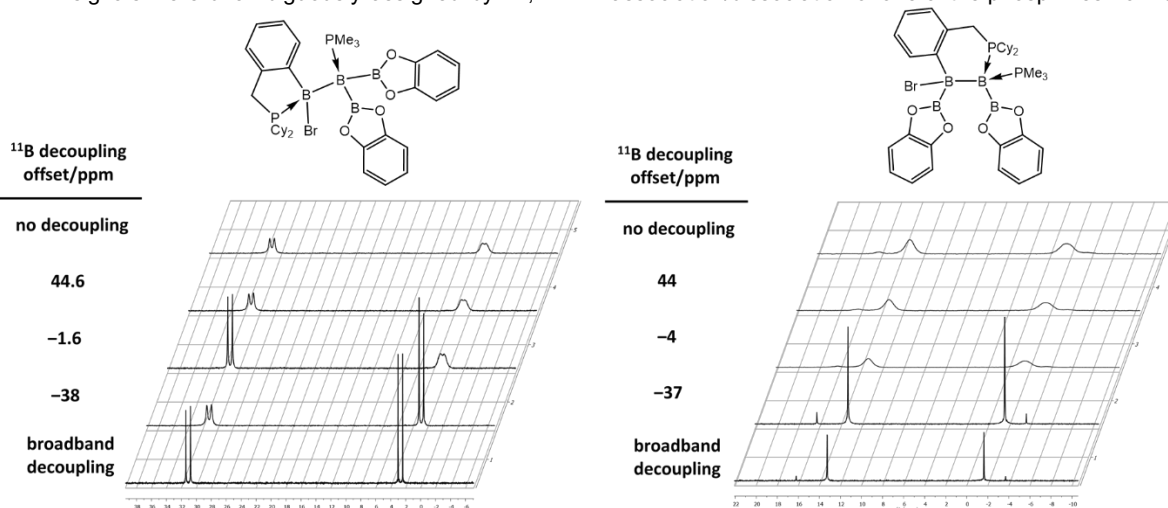
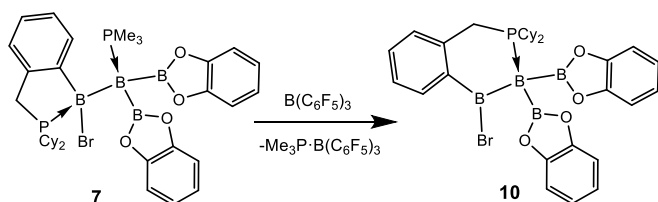


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds **7** (left) and **8** (right, mixture of diastereomers) with selective ^{11}B decoupling.

The mechanism of the unexpected formation of **7** from **3** remains unclear. The reactions of the other diborenes with B_2cat_2 give us no reason to doubt that the initial step involves a 1,2-addition of the diborane across the double bond, from which point at least two further rearrangements are necessary to form **7**. We

are currently undertaking computational studies to clarify this mechanism and will report on the results in due course.



Scheme 3. Abstraction of PMe_3 from compound **7**.

Having isolated borane-phosphine adduct **7**, we hoped to abstract PMe_3 with an appropriate Lewis acid and isolate the free triborylborane. Treatment with $\text{B}(\text{C}_6\text{F}_5)_3$ in benzene led to rapid precipitation of $\text{Me}_3\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$, and clean conversion to a new species by NMR spectroscopy. However, the presence of a high-field signal in the ^{11}B NMR spectrum at -36 ppm suggested retention of the triborylborane-phosphine moiety, while a low-field signal at 85 ppm indicated the presence of a three-coordinate borane. X-ray diffraction on single crystals grown from benzene/hexane solution confirmed the structure as that of compound **10** (Scheme 3, Figure 2), in which the benzylphosphine group had reverted to a 1,2-chelating conformation, with the phosphine now coordinated to the central boron atom (B1). This preferential coordination to B1 rather than B2 indicates a high Lewis acidity of the triborylborane, as previous observations suggest that the 1,1- and 1,2-chelating conformations of the benzylphosphine group are energetically similar.^[13] This can be ascribed to the lack of π -donating substituents at B1, which is now bonded to three trigonal boron atoms. At 1.685(4) Å, the B1-B2 bond of **10** is considerably shorter than that of **7**, as a result of the sp^2 hybridisation of the B2 atom, while the B1-P1 distance is very short (1.903(3) Å), again indicative of a strong interaction.

Despite the high reactivity of the low-valent diboron species **1-4**, especially the unsymmetrical derivatives, towards B_2cat_2 , they are remarkably inert towards the other diborane frequently applied in addition chemistry, bis(pinacolato)diboron (B_2pin_2). Treatment of diborene **3** with B_2pin_2 in C_6H_6 gave no reaction, and upon heating to 80 °C, the only observed reaction was the previously reported conversion to **4**, which was also found to be inert towards the B_2pin_2 under these conditions. The lower reactivity of B_2pin_2 has previously been noted in copper-catalysed diboration reactions,^[21] and has been ascribed to the lower Lewis acidity of boron in comparison to B_2cat_2 .^[22] In the present case, it is likely that the less electrophilic B-B bond of B_2pin_2 is less susceptible to attack by the highly electron-rich diborene. However, given that the products **5-8** are relatively ‘crowded’, steric factors may also be at play.

In conclusion, we have reported the diboration of sterically unhindered diborenes with B_2cat_2 to form both linear and branched tetraboranes under mild conditions in the absence of a catalyst. Whereas the symmetrical diborenes **1** and **2** yield their simple 1,2-diboration products, unsymmetrical diborene **3** undergoes a formal 1,1-diboration to form a triborylborane as its phosphine adduct, whereas borylborene **4** reacts via 1,2-diboration to a borylene-borane adduct. We are currently working towards further expansion of networks of electron-precise boron-boron bonds.

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