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 tetaboranes. The symmetrical diborenes studied under 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 sp3-hybridisation causes the simple boranes (BnH2n−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 B4Cl2 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 B2Cl4 often undergoes uncatalysed 1,2-additions to alkenes and alkynes,[5] the tetaalkoxydiboranes, B2(OR)4, utilised in these new catalytic processes, offered the advantages of considerably higher stability and tolerance of air and moisture.[6]

Despite the relatively high bond enthalpy of B–B σ-bonds (D0 = 293 kJ·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 (D0 = 536 kJ·mol−1) and B–N (D0 = 446 kJ·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 B3) by the reduction of aminochloroboranes with alkali metals,[9a] 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 B3 chain,[10a] and we recently reported the synthesis of metal-free Bn chains in the form of diboryldiborenes via reductive coupling of two carbene-stabilised diboranes.[11] The hydroboration of heteroaryl-substituted diboranes with catecholborane (HBcat, cat = catecholato) provided access to linear triboranes with electron-precise boron-boron bonds,[12] whereas use of 9-borabicyclo[3.3.1]nonane as the borane led to a B6 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] This is facilitated by 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 (B2cat) in benzene solution at room temperature resulted in a slow reaction. Monitoring of the reaction by NMR spectroscopy revealed the major product with a 31P resonance at 46.4 ppm and 11B resonances at −23 ppm and 44 ppm, alongside a second species (δ31P = 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 substituents 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(sp2)-B(sp3) bonds.[15]

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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 Bcatz, 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($^1$H) 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 diboran(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 diboran(4), 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.

**Scheme 2. Reactions of diboranes 1-3 and borylborene 4 with Bcatz.**

Borylborene 4 also underwent a rapid reaction with Bcatz, at –30 °C, producing an $^{11}$B NMR spectrum similar to that of 7 ($^{11}$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 $^1$H NMR signals upon solvation in THF-$d_8$, 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$^3$ o-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(8) 9, was also

Several reports have shown that desymmetrisation of diboran(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 diborane 3 and its gem-isomer 4 (Scheme 2),[20] which displays borylborene characteristics, and we were keen to explore the reactivity of these unsymmetrical compounds towards diboranes. Treatment of 3 with Bcatz 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($^1$H) 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 upon solvation in THF-$d_8$ produced crystals suitable for X-ray diffraction (Figure 2). Rather than the expected 1,2-addition product, the product was shown to be the triborylborene 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. Borylborene 4 also underwent a rapid reaction with Bcatz, at –30 °C, producing an $^{11}$B NMR spectrum similar to that of 7 ($^{11}$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 $^1$H NMR signals upon solvation in THF-$d_8$, 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$^3$ o-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(8) 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.

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 $^{11}\text{B}$-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 $^{31}\text{P}-^{31}\text{P}$ coupling constants. We then performed CW $^{11}\text{B}$ decoupling triple resonance experiments, varying the $^{11}\text{B}$ decoupler offset to the values of the respective signals (Figure 3), in order to suppress $^{1}J_{PB}$ 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 $^{31}\text{P}$ resonance for the PCy$_2$ group at 31.1 ppm (the $^{31}\text{P}$ NMR signals were unambiguously assigned by $^{1}H$, $^{31}\text{P}$-COSY experiments) while the signal at 2.7 ppm remained broad; setting the decoupling offset at $-38$ ppm (B1) caused the PMe$_3$ $^{31}\text{P}$ 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 $^{31}\text{P},^{31}\text{P}\{^{1}\text{H},^{11}\text{B}\}$-EXSY experiment to be in rapid exchange on the NMR timescale. Selective $^{11}\text{B}$-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 $^{31}\text{P}$ 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.

The mechanism of the unexpected formation of 7 from 3 remains unclear. The reactions of the other diborenes with Bcat 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.
Having isolated borane-phosphine adduct 7, we hoped to abstract PMe₆ to an appropriate Lewis acid and isolate the free triborylborane. Treatment with B(C₂F₅)₃ in benzene led to rapid precipitation of Me₂P·B(C₂F₅)₃, and clean conversion to a new species by NMR spectroscopy. However, the presence of a high-field signal in the ₁¹B NMR spectrum at –36 ppm suggested retention of the Me₂P·B(C₂F₅)₃, or a boron-phosphine complex. 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 studies suggest that the 1,1- and 1,2-chelating conformations of the benzylphosphine group are energetically similar.[15] 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 sp² hybridisation of the B2 atom, while the B1-P 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 B₂cat, they are remarkably inert towards the other diboran frequently applied in addition chemistry, bis(pinacolato)diboron (B₂pin₂). Treatment of diboranes 3 with B₂pin in CH₂Cl₂ gave no reaction, and upon heating to 100 °C, the on-obtained compound was the previously reported conversion to 4, which was also found to be inert towards the B₂pin₂ under these conditions. The lower reactivity of B₂pin₂ has previously been noted in copper-catalysed diboration reactions,[11] and has been ascribed to the lower Lewis acidity of boron in comparison to B₂cat₂.[22] In the present case, it is likely that the less electrophilic B-B bond of B₂pin₂ is less susceptible to attack by the highly electron-rich diborane. 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 hindered diboranes with B₂cat₂ to form both linear and branched tetraboranes under mild conditions in the absence of a catalyst. Whereas the symmetrical diboranes 1 and 2 yield their simple 1,2-diboration products, unsymmetrical diboranes 3 undergoes a formal 1,1-diboration to form a triborylborane as its phosphine adduct, whereas borylborylene 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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