Single and Double Hydroboration of B-B Triple Bonds and Convergent Routes to a Cationic Tetraborane

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ABSTRACT: A compound with a boron-boron triple bond is shown to undergo stepwise hydroboration reactions with catecholborane to yield an unsymmetrical hydro(boryl)diborene and a 2,3-dihydrotetraborane. Abstraction of H+ from the latter compound produces an unusual cationic, planar tetraborane with a hydrogen atom bridging the central B3 moiety. Spectroscopic and crystallographic data and DFT calculations support a ‘protonated diborene’ structure for this compound, which can also be accessed via direct protonation of the corresponding diborene.

INTRODUCTION The study of boron hydrides has a rich history dating back to the early 20th century, when Alfred Stock’s pioneering research on the highly reactive cluster compounds led him to effectively invent the inert atmosphere technique underpinning much of modern inorganic and organometallic synthesis.1 Conclusive determination of the structures of these higher boranes upon the advent of X-ray crystallography2 resulted in the classification of “non-classical” multicentre bonding, and boron cluster chemistry grew into an established field in its own right.3–4 Classical, two-centre-two-electron bonds between boron atoms are comparatively rare, while well-defined chains of more than two boron atoms are limited to a handful of compounds.5–8 One of the more successful routes to such compounds thus far has involved addition reactions with unsaturated diboren species. In 2014 we reported on the hydroboration of diborenanes with catecholborane (HBcat) to form linear triboranes,9 while the equivalent reactions with boron triboranes (H3B) to form tetraboranes,10 including in the former case the first triborylboranes. We also recently reported the formation of unsaturated B2 chains in the form of diboryldiborenanes via reductive coupling of carbene-stabilized 1,1-dibromodiborenanes,13 and this class of compound also proved to be accessible in improved yields by the diboration of boron-boron triple bonds with B2Scat; and B2S2cat; (Scat = thiocatecholato).14

Over the last decade or so, significant attention has been paid to the relationship between hydrodiborenanes(6) that do not contain a formal boron-boron bond (i.e. B2H4 derivatives) and their classically B-B-bonded diborane(4) and diborene counterparts (Fig. 1). Matsuo, Tamaro and co-workers first reported the synthesis of stable diborane(6) dianions [(R)H2BH2(R)2]2– (B, Scheme 1) via two-electron reduction of diboranes (R)HB(μ-

H2BH(R) (A), where R is an extremely bulky aryl group.15–16 The same groups reported the abstraction of a hydride from one of these dianions to yield a monoanionic, hydride-bridged diborane(5) (C), which can be treated with Me3Si(OSO2CF3)2 to yield hydride-bridged diboranes(4).16 Wagner and coworkers then showed that such monoanions, C, (and indeed their diborane(6) precursors) can be reduced to diaionic diboranes [BnR2]2– (D) by using alkali metals to isolate a biphenylene-bridged diborene.17–19

The inherent electron deficiency of boron in diboron compounds can also be saturated by neutral Lewis bases. For example, neutral diboranes of the form L(R)B=B(R)L (I) are now accessible with a wide variety of bases and covalent substituents via Wurtz coupling of dihaloboranes or reduction of dihalodiboranes.3 Lewis base-stabilized dicaticionic, hydrogen bridged diboranes (F), formally dimers of borenium ions, have been reported by Curran and Vedejs20 and Ghadwal.21 A handful of neutral, base-stabilized dihydrodiboranes(4) (G) is known,22–26 though this is likely to increase with the recent development of transfer hydrogenation to diboranes.27 Very recently, the group of Yamashita reported the formation of a hydrogen-bridged tetraborane(6) (E, R = BR2) upon reductive coupling of the corresponding 1,1-dibromodiborane, presumably via radical hydrogen abstraction by a low-valent B3 intermediate.28 Surprisingly, this compound was shown to retain a significant degree of boron-boron multiple bonding between the central boron atoms, suggesting the contribution of a “doubly protonated diboryne” resonance structure. Herein, we report the preparation of a dihydrodiborane via double hydroboration of a boron-boron triple bond and its subsequent conversion to a cationic tetraborane(5). As well as displaying an interesting bonding situation in its own right, this latter compound represents a further synthetic bridge between key classes of diboron compounds.
The availability of a series of species with boron-boron triple bonds (J, Scheme 1) led us to consider the possibility of multiple hydroboration steps at the same molecule as a route to novel tetraboranes. Despite the highly reducing nature of diborynes, the first of which, (IDip)BB(IDip) (1^{IDip}), IDip = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, was reported in 2012, their reactivity is tempered by the shielding effect of the bulky carbene ligands. Small reductions in steric bulk and enhancement of the π-acceptor character of the NHC have both been found to enhance the reactivity. For example, while 1^{IDip} could not be hydrogenated to its corresponding dihydrodiborene, replacing the bulky IDip carbenes with the more π-acidic and somewhat less bulky ligand SIDep (= 1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidene) allowed clean addition of H₂ across the B-B triple bond at 80 °C.

We chose the diboryne 1^{SIDipMes} (Scheme 2) for the reactivity study towards catecholborane on the basis of its high reactivity towards B{cat} in diboration reactions. 

**RESULTS AND DISCUSSION**

Treatment of 1^{SIDipMes} with HB{cat} in benzene solution led to an immediate color change from red to purple. New signals in the ^{11}B NMR spectrum at 36.7 and 18.9 ppm suggested formation of diborone 2, which was isolated as a red powder after workup in 32% yield. The boron-bound hydrogen atom was observed in the ^{1}H NMR spectrum upon ^{11}B decoupling as a broad signal at 4.27 ppm. The ^{11}B NMR signal for the B{cat} group could not be unambiguously identified due to broadening and overlap with that of the central boron atom. The structure of compound 2 was determined by X-ray diffraction on single crystals grown from a saturated pentane solution (Figure 1). At 1.609(2) Å, the diborene B₁-B₂ distance is similar to that of previously reported diboryldiborones (1.582-1.627 Å). The B{cat} group is twisted significantly out of the diborene plane, as shown by the B-B-B-O torsion angle of 62.4(2)°, which suggests that there is negligible conjugation across the B₃ unit in the solid state. This is in contrast to the situation for certain diboryldiborones with smaller NHCs and probably originates from the steric bulk of the mesityl and diisopropylphenyl substituents. Conversely, the NHC at the H-substituted boron atom sits approximately coplanar with the diborene unit. These observations were supported by computation of the frontier orbitals by DFT (B3LYP/6-311G(d); Figure 2); the HOMO represents the HB=B(B{cat}) π-bond, whereas the LUMO is of B=B π-antibonding character and describes the backbonding from the B₂ unit to the NHCs, as expected for diborones. Unsymmetrical diborones are still relatively uncommon, and further reactivity studies on 2 will be the subject of future work.

**Scheme 1.** Isolated diboron hydrogen compounds. Arrow key: black = literature reported transformations; red = as yet unknown transformations; blue = reactions reported herein.

**Scheme 2.** Single and double hydroboration of compound 1^{SIDipMes}, and hydride abstraction from 3 to form the salt 4.
Diborenes have been shown to react with HBcat to yield hydroboration products, so we therefore treated 1SIDipMes with two equivalents of HBcat in the hope of achieving a second hydroboration. After the initial color change to violet indicating formation of 2, colorless crystals began to form within one minute. X-ray diffraction confirmed the formation of tetraborane 3 (Figure 3). Only the linear B₄-product was observed, indicating that the second HBcat addition occurs regioslectively. The observation of a single set of NMR signals for 3 (δ_{11B} = 45.2 (Bcat), –33.8 (BH)) also confirms the diastereoselectivity of the reaction in favor of the meso product. Compound 3 is a rare example of a tetraborane bound by classical two-centre two-electron covalent bonds. The central boron-boron distance is very large, at 1.842(2) Å, to the best of our knowledge exceeded by other analytical techniques, see below). The B1-B1’ bond is dramatically shorter than in precursor 3, at 1.635(5) Å, placing it in the range of diborene radical cations. The distance is also somewhat shorter than that in related neutral diboranes(5) (1.670(3) - 1.682(3) Å). IR spectroscopy confirmed the absence of terminal B-H bonds, supporting the X-ray structure, although the stretch associated with the bridging B-H-B unit, expected to fall in the fingerprint region of the spectrum, could not be unambiguously identified.

Compound 4 exists as two isomers in solution in CD₂Cl₂ as judged by ¹H NMR spectroscopy. The signals for the minor isomer broaden at 298 K, but sharpen significantly on cooling to 268 K, while the signals corresponding to the major species are largely unaffected by this temperature change. Measurement of a ¹H,¹H-ROESY spectrum at 268 K allowed observation of through-space coupling between the respective mesityl and disopropylphenyl residues, indicating anti (4a, major) and syn (4b, minor) conformers of the compound with respect to the orientation of the N-heterocyclic carbene (see Supporting Information for further details). Neither heating to 60 °C nor UV irradiation resulted in an alteration of the ratio of isomers.

Figure 1. Molecular structure of 2 with selected atomic displacement ellipsoids at 50% probability displaying the entire molecule (top) and a side view (bottom) showing the planarity of the B₃-NHC unit. All hydrogen atoms except H1 are omitted for clarity. Selected bond lengths (Å) and angles (°): B1-B2 1.609(2), B2-B3 1.690(2), B1-C1 1.553(2), B2-C2 1.571(2), B1-H1 1.15(1), B1-B2-B3 133.4(1), B1-B2-C2 116.9, B2-B1-C1 128.9(1).

Compound 3 reacted with a slight excess of methyl trifluoromethanesulfonate (MeOTf) at room temperature with immed-
We carried out DFT calculations at the B3LYP/6-311G(d) level in order to better understand the bonding situation in 4. Optimization of the structure confirmed that the planar configuration represents an energetic minimum with the hydrogen atom bridging the two central boron atoms. The frontier orbitals are displayed in Figure 2. The HOMO (and, to a lesser extent, the HOMO-8) is represented partially by lobes of pseudo-\(\pi\)-symmetry across the B-H-B unit, indicating involvement of the hydrogen atom in a 3c-2e bond. This motif was predicted by Lamertsma and Ohwada for hydrogen-bridged compounds\(^{15}\) and was observed by Yamashita and co-workers in their tetraphenylborane(6) compound with bridging hydrogen atoms.\(^{28}\) Furthermore, neutral diboranes(5) with a bridging hydrogen atom display an almost identical bonding mode across the B-H-B unit.\(^{28}\) The LUMO describes the \(\pi\)-bonding orbitals of the external B1-B2 units and is \(\pi\) antibonding between B1 and B1', resembling that of diboryldiboroles and Yamashita and co-workers' \(\pi\) linear tetraphenylborane(6). The energetic difference between the frontier orbitals is large, at 4.586 eV, which explains the colorless nature of 4, in contrast to both diboroles and diborole radical cations.\(^{2,36}\) The calculated Wiberg bond indices (WBIs) reveal a central boron-boron bond order of 1.131, indicating a modest degree of multiple bonding character, while the calculated WBI values for the B1-H1 and B1'-H1 bonds are 0.458 and 0.473, respectively. The external B1-B2 bonds in 4 have calculated WBI values of 0.956 and 0.962, respectively, and are thus in the expected range for single bonds. Natural population analysis (NPA) gives partial charge values of \(-0.221\) and \(-0.264\) for B1 and B1', respectively, and 0.158 for H1, suggesting a somewhat polar B-H bonding interaction. Of the possible resonance forms to describe the bonding in 4 (Scheme 3), this suggests a significant contribution from a “protonated diborole” structure, which is consistent with the crystallographically determined short B-B distance and the \(^{11}\)B NMR chemical shift of 24.9 ppm. Conversely, the \(^1\)H NMR chemical shift of the bridging hydrogen atom at \(-2.39\) (4a) and \(-2.32\) ppm (4b) is shifted dramatically upfield compared to Matsuo and Tamao’s anionic diborane(5) (\(\delta = 2.94\) ppm)\(^{1,14}\) and other neutral derivatives,\(^{34}\) being more akin to that of anionic derivatives\(^{17,19}\) and suggestive of high shielding.

![Figure 2](image)

**Figure 2.** Calculated LUMOs (top) and HOMOs (bottom) of compounds 2 (left) and 4 (right) (B3LYP/6-311G(d)).

Scheme 3. Possible resonance forms for compound 4. DFT calculations favor the right hand structure.

These observations concur with investigations by Tamao and co-workers on the compound EindB(μ-H)2BEind (Eind = 1,1,3,3,5,5,7,7-tetraethyl-s-hydrindacen-4-y1; WBIH = 1.533), for which one resonance description is a doubly protonated boron-boron triple bond. In the case of 4, the B1/B1′ NPA values are more negative, presumably as a result of σ-donation from both the boryl substituents and the flanking carbene ligands.

Having access to diborene 5 via a previously published route,14 we attempted to synthesize 4 via protonation (Scheme 4). Treatment of 5 with one equivalent of triflic acid (HOTf) in CD2Cl2 resulted in clean conversion to compound 4 as judged by NMR spectroscopy. This result adds to a growing body of work showing that judicious choice of substituents allows electron-rich boron compounds to shuttle H+ rather than H-.

Further addition of MeOTf to 4 led to no reaction, which is consistent with the bridging hydrogen atom having a partial positive charge and thus being unwilling to be abstracted as H+. Whereas neutral, H-bridged diboranes(5) have been shown to coordinate Cu(I) fragments,14 compound 4 showed no reactivity towards CuCl, probably as a result of significant electrostatic repulsion between the cationic species and the copper centre.

CONCLUSIONS In summary, we have described the first hydroborations of diborynes, yielding an unsymmetrical diborene and a neutral dihydrotetaborane. Abstraction of one hydride led to a cationic, hydride-bridged tetraborane that shows characteristics of a protonated diborene. Our efforts are currently focused on corroborating the last remaining links between classes of base-stabilized, classically bonded diboron hydride compounds.

ASSOCIATED CONTENT Supporting information including details of synthesis, analytical techniques and crystal structures in .cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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