Borenium Cations

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Synthesis, Structure, and Reactivity of a Dihydrido Borenium Cation**

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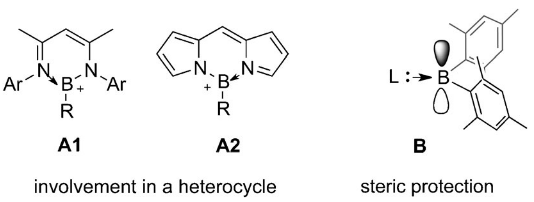
Dedicated to Professor Wolfgang Petz

According to the Nöth terminology, borenium cations are singly charged B^{III}-derived cationic species possessing a trigonal environment around boron.[1] As expected on the basis of these structural features, borenium cations are very potent electrophiles. This reactivity has recently found application in the borylation of aromatic and heteroaromatic rings, which has sparked great attention owing to its synthetic potential to directly provide aryl boronate esters and other Suzuki–Miyaura coupling partners.[2]

Despite this fact, there are only few persistent compounds containing borenium cations that have been isolated. Their preparation relies on two main approaches (Scheme 1): the embedding of the boron center in a heterocyclic scaffold with a bidentate monoanionic LX^- ligand[3] (in **A**) or the use of a strong σ-donor monodentate ligand L in concurrence with two bulky aromatic substituents that mainly provide steric protection (in **B**).[4]



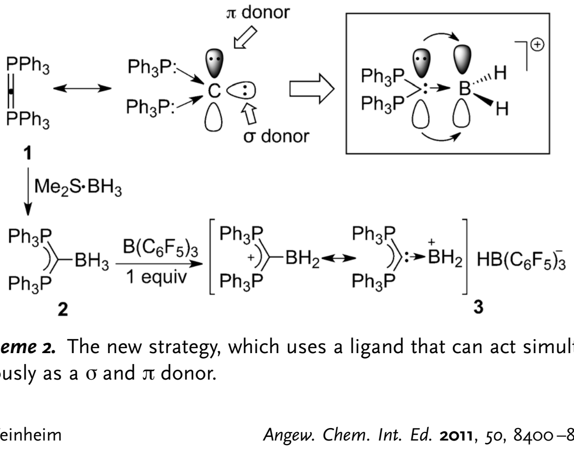
Scheme 1. Main strategies for the preparation of borenium cations.

However, neither of these procedures allows for the preparation of some seemingly simple compounds. For example, the parent borenium structure, the dihydrido cation $[L\rightarrow BH_2]^+$, has still not been isolated. It cannot be made by the chelating ligand approach because that would require at least two available coordination sites at the boron atom.[5] Furthermore, owing to the missing steric protection from the hydride substituents, all attempts to isolate it by hydride abstraction from $L\rightarrow BH_3$ adducts were unsuccessful, regardless of the nature of the ligand L employed (amines, pyridines, phosphines). In light of low-temperature multinuclear NMR spectroscopy and reactivity data, it has been postulated that the transient dihydridoborenium cation generated does not accumulate in these reactions, but rather undergoes rapid trapping by the borane adduct employed as starting material, thus producing a hydride-bridged cationic dimer that resists abstraction of a second hydride.[6]

The analysis outlined above indicates that a novel synthetic strategy toward the isolation of compounds containing the elusive dihydrido borenium cation has to be developed. In this regard, we envisaged that the use of a monodentate neutral ligand that is capable of simultaneous σ and π donation may provide sufficient stabilization to attenuate the reactivity of dihydrido borenium cations to a level that allows their isolation.

To put this design concept into practice, we considered hexaphenylcarbodiphosphorane **1** as the ligand that may fulfill the necessary electronic requirements. Computational investigations by Tonner and Frenking on the nature of this and related compounds have revealed that they should be considered to contain two phosphine ligands coordinated to a central zero-valent carbon atom that retains its four valence electrons, which are thus all available for donation.[7] This view was later confirmed experimentally.[8] However, in most of the reported examples, the central carbon atom donates two electron pairs to two different electrophiles, one pair to each, whereas the donation of two electron pairs to the same acceptor has been clearly underrepresented (Scheme 2).[9]

Thus, we allowed carbodiphosphorane **1** to react with borane–dimethylsulfide and isolated adduct **2** as a bright



Scheme 2. The new strategy, which uses a ligand that can act simultaneously as a σ and π donor.

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yellow solid in quantitative yield (Scheme 2).[10] The solution of **2** becomes colorless upon treatment with one equivalent of $B(C_6F_5)_3$. The ^{11}B NMR spectrum indicated the generation of the borohydride anion $HB(C_6F_5)_3^-$ ($\delta = -24.0$ ppm; $^1J(^1H,^{11}B) = 92$ Hz), while complete consumption of $B(C_6F_5)_3$ was confirmed by ^{19}F NMR spectroscopy. Furthermore, the original ^{11}B NMR resonance of **2** ($\delta = -22.7$ ppm; $^1J(^1H,^{11}B) = 84$ Hz) disappeared and a new broad signal at $\delta = 56.6$ ppm emerged. Moreover, no ^1H NMR signal consistent with a hydride-bridged structure could be observed, whereas a broad triplet at $\delta = 5.38$ ppm ($^1J(^1H,^{11}B) = 29$ Hz) was clearly visible. All of these data suggest the formation of the dihydrido borenium borohydride **3**, an interpretation that was validated by X-ray crystallographic analysis.

Figure 1 depicts the ORTEP diagram of **3**, which is, to the best of our knowledge, the first isolated compound containing a dihydridoborenium cation. In this molecule, the boron atom adopts a trigonal planar environment, which allows the π lone pair of the central carbon atom to overlap with the empty p orbital at boron. As a result, the C1–B1 distance in **3** (1.5030(17) Å) is shorter than the C–B single bonds reported for other borenium cations (1.62–1.58 Å).[12] It should be noted however that it is longer than in typical C=B bonds (1.35–1.45 Å)[13] while it compares quite well with the C–B distances reported for borabenzenes (1.50–1.47 Å), where the C–B bond order is 1.5.[14] Thus, the π interaction, although essential for the stability of **3**, might not be very strong.

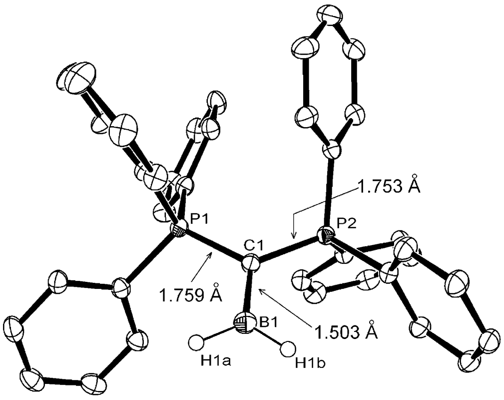


Figure 1. Crystal structure of **3**. Hydrogen atoms not directly bonded to boron and the $HB(C_6F_5)_3$ anion are omitted for clarity; ellipsoids are set at 50% probability. Sum of angles around B1 360.0°, torsion angle P1-C1-B1-H1a 1.6°.[11]

In an attempt to clarify the electronic nature of **3**, density functional calculations at the B3LYP/6-31G* level were performed. The optimized structure closely matches the experimental X-ray data. According to natural population analysis, each phosphorus atom bears a large positive charge (+1.74 e), while on boron the positive charge is much smaller (+0.25 e). Interestingly, the central carbon atom directly bonded to boron still carries quite a large negative charge (−1.39 e). Furthermore, inspection of the frontier orbitals reveals that the highest occupied molecular orbital (HOMO) is the C–B π-bonding orbital that is strongly polarized toward the carbon atom (see Figure 2; Mulliken populations 50 % at C and 11 % at B). This explains the calculated low Wiberg bond index between these two atoms (1.21), which is consistent with the recorded distances from crystallography. Energy decomposition analysis indicates that σ donation contributes about twice as much to the stability of the C=B bond as π donation (see the Supporting Information for details).

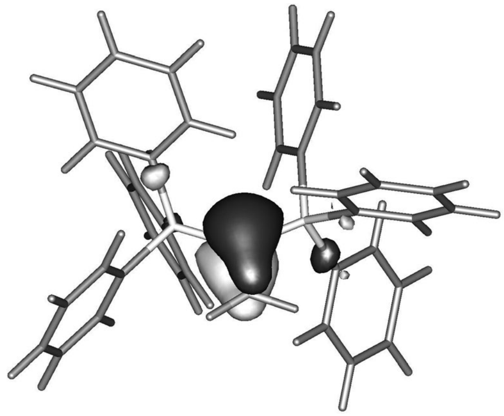
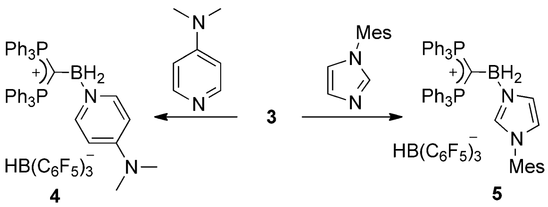


Figure 2. DFT optimized geometry of **3** with a plot of the HOMO.

Compound **3** readily reacts with 4-dimethylaminopyridine (DMAP) or 1-mesitylimidazole to yield the corresponding boronium cations **4** and **5**, respectively (Scheme 3). The X-ray structure of **4** (Figure 3) is quite informative. After coordination of DMAP, the C1–B1 distance in **4** (1.6376(16) Å) adopts a value that is typical for a C–B single bond. Noteworthy are the distances between the central carbon and the flanking



Scheme 3. Reactivity of **3** toward nucleophiles.

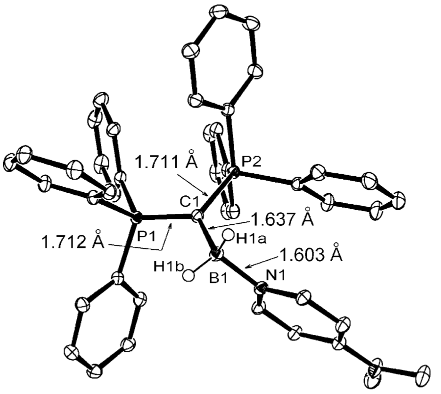
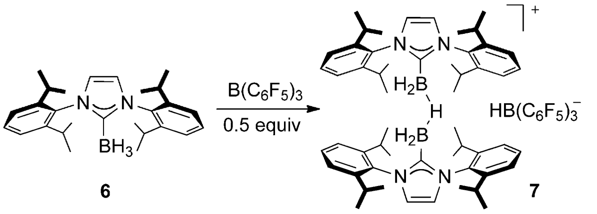


Figure 3. Crystal structure of **4**. Hydrogen atoms not directly bonded to boron and the $HB(C_6F_5)_3$ anion are omitted for clarity; ellipsoids are set at 50% probability.[11]

phosphorus atoms, which are now shorter than in **3**. This suggests that the excess π electron density on the central carbon, which can no longer be donated to boron, is now back-donated to the two surrounding phosphine ligands, thereby increasing the computed C–P bond order from 1.00 in **3** to 1.10 in **4**.

To better understand the properties of **3**, cyclic voltammetry experiments were carried out. Compound **3** undergoes an irreversible reduction at −2.67 V (vs. Fc/Fc$^+$), a value that is much more negative than that of other borenium cations and similar to the reduction potential of neutral triarylboranes.[15] This result again reflects the strong donor ability of **1**. Its outstanding qualities as a ligand are better appreciated when hydride abstraction from carbene–borane **6** is attempted (Scheme 4).[16] Adduct **6** contains an N-heterocyclic carbene ligand, which is a bulky σ donor;[17] these two properties should help to stabilize the borenium cation that could plausibly be formed after hydride abstraction. However, even in this case, reaction of **6** with $B(C_6F_5)_3$ only consumed half the equivalent of the hydride abstractor. Repetition of the reaction with the appropriate stoichiometry afforded crystalline **7**, the structure of which was determined by X-ray analysis (Scheme 4 and Figure 4).[18] The formation of **7** implies that strong σ donation alone is not enough to prevent trapping of the transient borenium cation by its unreacted precursor.[19] Therefore, the anticipated stabilizing influence of additional π electron density donation plays an essential role for the actual isolation of compounds containing dihydridoborenium cations.



Scheme 4. Formation of a two-electron three-center bond by coordination of borane adducts to borenium cations.

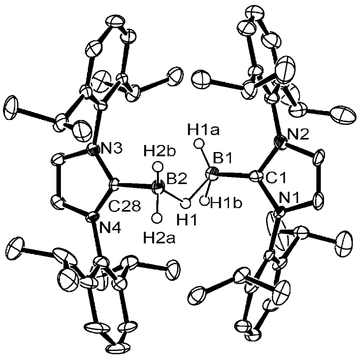


Figure 4. Crystal structure of **7**. Hydrogen atoms not directly bonded to boron and the $HB(C_6F_5)_3$ anion are omitted for clarity; ellipsoids are set at 50% probability.[11] Only one of the two cations from the unit cell is depicted. Averaged bond lengths [Å]: B–B 2.32(3), B–H 1.09(6), B–H(bridge) 1.37(5), and B–C(carbene) 1.62(4).

In summary, the synthesis of the first isolable compound containing a dihydridoborenium cation moiety has been achieved by the use of a new strategy that utilizes carbodiphosphoranes as monodentate ligands acting simultaneously as stabilizing σ and π donors. Moreover, the bonding situation and reactivity of the resulting borenium cation have been studied. We now plan to extend this strategy to the isolation of other highly electrophilic species based on boron or other elements.

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