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A Stable but Highly Reactive Phosphine-Coordinated Borenium: Metal-free Dihydrogen Activation and Alkyne 1,2-Carboboration**

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: *Borenium cations have been found to be valuable analogues of boranes as a result of their cationic character which imparts high electrophilicity. Herein, we report the synthesis, characterization, and reactivity of a new type of borenium cation employing a naphthyl bridge and a strong intramolecular P→B interaction. The cation reacts with H_2 in the presence of $PtBu_3$ (frustrated Lewis pair (FLP) approach) but also on its own. The mechanism of the reaction between the borenium cation and H_2 in the absence of $PtBu_3$ has been investigated using deuterium-labeling experiments and DFT calculations. Both experiments and calculations imply the side-on coordination of H_2 to the B center, followed by heterolytic splitting and B−C bond cleavage. An uncommon syn 1,2-carboboration has also been observed upon reaction of the borenium ion with 3-hexyne.*

The last decade has witnessed an upsurge of interest in Lewis acidic boron-containing compounds, whose archetypal derivative is $B(C_6F_5)_3$. In addition to their role as co-catalysts in transition-metal-catalyzed reactions, boranes have shown versatile reactivity on their own or when associated with Lewis bases in so-called frustrated Lewis pairs (FLP). In particular, they enable the activation of strong σ bonds, such as H−H and H−Si, under metal-free conditions.[1,2] Such activity is possible as a result of the high electrophilic character of boron which typically requires electron-withdrawing substituents such as perfluorinated aryl groups.

As a result of their cationic character, borenium ions $(R_2B{\leftarrow}L)^+$ are valuable analogues of boranes.[3] Intra- and intermolecularly stabilized boreniums have been developed and the nature of the Lewis base has been modified to include pyridines, amines, N-heterocyclic carbenes (NHC), N-heterocyclic carbene olefins (NHO), carbodiphosphoranes, and phosphines.[4–6] Accordingly, the variety of stable boreniums has been considerably extended and our understanding of their electronic structure has progressed significantly. However, little is known about their reactivity, although the results obtained recently in H_2 activation with NHC-stabilized boreniums hold much promise.[7]

In this context and given the scarcity of phosphorus-coordinated boreniums (compared to those involving N and C donors), we set out to prepare new borenium derivatives of type **A** (Figure 1). Related neutral compounds **B**[8] and **C**[9] have been investigated recently. The naphthyl bridge was shown to impart unique properties and to enforce a strong P→B interaction despite steric shielding. Herein we report the synthesis, characterization, and reactivity of a phosphorus-stabilized diaryl borenium of type **A**. The reactivity of this borenium with H_2 and 3-hexyne has been explored. Most remarkable are the reactions observed in the absence of external base, namely H_2 splitting with B−C cleavage and *syn* 1,2-carboboration.

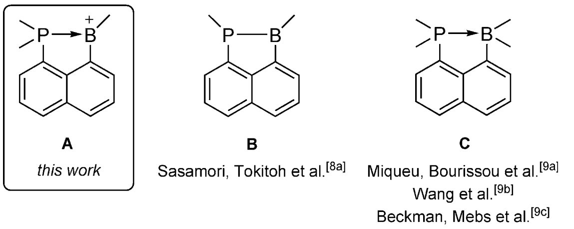

Figure 1. Naphthyl-bridged P/B derivatives.

The phosphine-bromoborane **2**-Br was prepared in two steps from 1-diphenylphosphino-8-iodonaphthalene (**1**; Scheme 1).[10] In line with previous reports,[9] the naphthyl bridge enforces a strong intramolecular P→B interaction.

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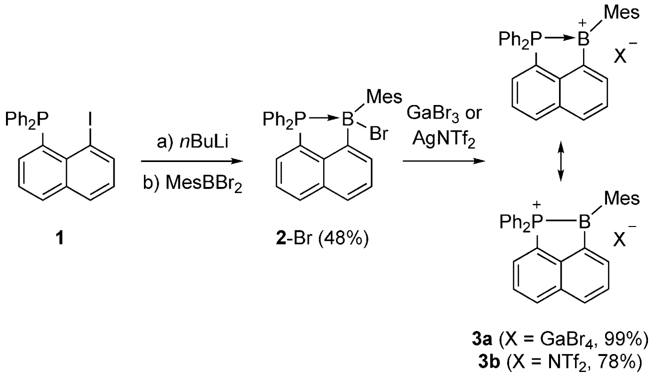
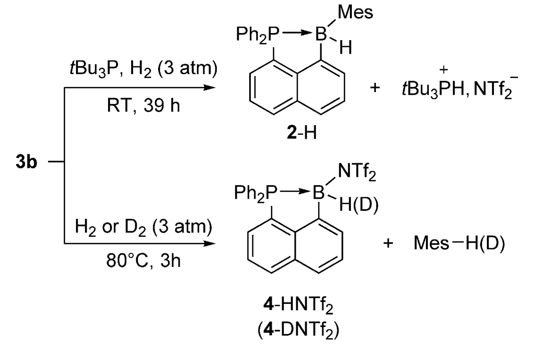


Scheme 1. Synthesis of the phosphine-stabilized borenium derivatives **3a**,**b**. NTf$_2$ = bis(trifluoromethylsulfonyl)imide. Mes = mesityl.

This can be shown spectroscopically from the high-field resonance signal ($\delta = 0.3$ ppm) in the ^{11}B NMR spectrum and crystallographically from the short P–B distance (2.05(1) Å).[10] Bromine abstraction from **2**-Br was readily achieved with either GaBr$_3$ or AgNTf$_2$ (Scheme 1; NTf$_2$ = bis(trifluoromethylsulfonyl)imide). The resulting borenium derivatives **3a**,**b** were isolated in high yields (78–99 %). The molecular structures of **3a**,**b** were unambiguously established by multinuclear NMR spectroscopy and HRMS (in both positive and negative modes). The two salts have very similar NMR spectroscopic characteristics. Most diagnostic is the resonance signal in the ^{11}B NMR spectrum which is significantly shifted to lower field compared to that of **2**-Br and appears at $\delta = 72.1$–74.2 ppm, in the typically range for tricoordinate boron centers.[11] Compounds **3a**,**b** are rare examples of phosphorus-coordinated boreniums. To our knowledge, the only related compounds are the intermolecular adducts (tBu$_2$RP–Bcat)$^+$ (Bcat = catecholboryl) prepared previously by Stephan et al. upon FLP-induced B–H activation.[6] The bonding situation in such compounds is best described by the superposition of two canonical structures, a phosphine-stabilized borenium form and a phosphonio–borane form.[6]

The reactivity of **3b** towards small molecules was then explored, starting with dihydrogen (Scheme 2).[12] An FLP-type approach was considered first. No reaction occurs between PtBu$_3$ and **3b** at room temperature, indicating that the formation of an intermolecular adduct between the electron-rich phosphine and the Lewis acidic boron center is prevented sterically. However, upon addition of H$_2$ (3 atm) the ^{31}P NMR spectrum shows the appearance of two new resonance signals, indicating the occurrence of a slow reaction (quantitative spectroscopic yield). The signal at $\delta = 56.7$ ppm has a large $^1J_{\text{P-H}}$ coupling constant (448 Hz) and corresponds to the phosphonium tBu$_3$PH$^+$ center.[13] The other ^{31}P NMR signal appears at $\delta = 9.4$ ppm and corresponds to the phosphino–hydroborane adduct **2**-H. The ^{11}B NMR signal appears in the high-field region of the spectrum at $\delta = -13.3$ ppm and in the ^{1}H NMR spectrum a signal for the H atom bound to boron appears at $\delta = 5.52$ ppm.[10] The heterolytic cleavage of H$_2$ with the **3b**/PtBu$_3$ FLP is reminiscent of that described previously from (tBu$_3$P–Bcat)$^+$ and PtBu$_3$,[14] although it proceeds under much milder conditions (herein: 3 atm, RT, 39 h, versus 4 atm, 100 °C, 24 h).[15]



Scheme 2. Heterolytic splitting of H$_2$ by the borenium **3b** with or without external base.

We were next interested in the ability of the borenium **3b** to activate H$_2$ without added base. Indeed, besides FLP, a few main group compounds have been shown to split H$_2$ at a unique reactive site.[16] Bertrand et al. pioneered the field with ambiphilic acyclic and cyclic amino carbenes,[17] Aldridge and co-workers generalized the approach to aminoboryl and aminosilyl silylenes,[18] and Piers et al. extended the field to highly electron-deficient antiaromatic boroles[2a] (see Refs. [19,20] for additional examples).

A CH$_2$Cl$_2$ solution of the borenium **3b** was pressurized with dihydrogen (3 atm). The reaction was monitored by ^{31}P NMR spectroscopy, where resonance signals showed the progressive transformation of **3b** into a new compound **4**-HNTf$_2$, with a new resonance signal appearing at $\delta = 4.7$ ppm (Scheme 2). Heating at 80 °C enabled the clean and complete conversion of **3b** to **4**-HNTf$_2$ within 3 h (62 % yield of isolated product). The ^{11}B and ^{1}H{^{11}B} NMR spectra show signals that can attributed to the tetracoordinate BH moiety in **4**-HNTf$_2$ ($\delta(^{11}\text{B}) = -6.4$ ppm, $\delta(^1\text{H}) = 4.72$ ppm). Curiously, in the ^{1}H NMR spectrum a unique set of signals for CH_3 and CH_{arom} groups ($\delta = 2.28$ and 6.81 ppm) is observed for the Mes group, suggesting the formation of Mes–H through B–C bond cleavage. Accordingly, the borenium **3b** would split H$_2$ with formal transfer of a hydride to boron and concomitant protonolysis of the B–Mes bond. This hypothesis was confirmed by reacting **3b** with D$_2$ under similar conditions. Spectroscopic analyses indicate the formation of **4**-DNTf$_2$ and Mes-D.[10] Crystals of **4**-HNTf$_2$ were analyzed by single-crystal X-ray diffraction (Figure 2).[21] The hydrogen atom at boron was unambiguously located in the difference Fourier map and the respective B–H bond length was found to be 1.07(3) Å. The P–B distance remains short (1.982(3) Å) and the triflimide NTf$_2$ is coordinate to boron (B–N = 1.602(4) Å), so that the boron center is tetracoordinate.

The mechanism of H$_2$ activation at main group centers has stimulated strong interest and various scenarios have been identified.[1,17,20b] To shed light on how the reaction between H$_2$ and **3b** proceeds, DFT calculations were performed at the B3PW91/6-31+G**(CH$_2$Cl$_2$)//B3PW91/6-31G** level of theory (Figure 3). The borenium derivative **3** (Mes at B and Ph at P) was used. The NTf$_2$ counterion was not considered (except in the last stage of the reaction, see below), but solvent effects (CH$_2$Cl$_2$) were taken into account by single-

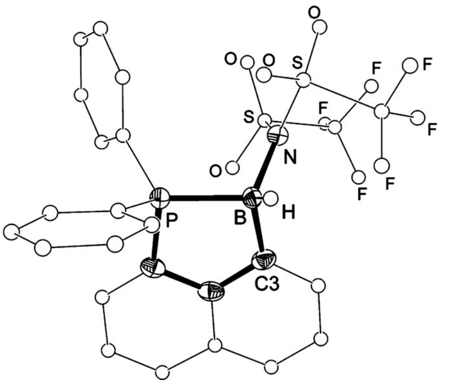


Figure 2. X-ray crystal structure of **4**-HNTf$_2$. The Ph and NTf$_2$ groups and the naphthyl spacer are simplified and the hydrogen atoms (except the one at boron) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P–B 1.982(3), B–H 1.07(3), B–N 1.602(4); N-B-H 104.4(2), H-B-C3 113.4(2), C3-B-N 118.1(2). Thermal ellipsoids are set at 50 % probability.

point calculations using the polarizable continuum model (PCM). The optimized structure of **3** revealed the presence of a strong P→B interaction (2.006 Å), in line with spectroscopic data. The reaction of H$_2$ with **3** starts by its side-on coordination to boron (B–H 1.460 and 1.511 Å). The resultant complex **3**-σ is higher in energy by 10.6 kcal mol^{-1} and the corresponding activation barrier is 17.2 kcal mol^{-1}. A few σ complexes of H$_2$ to boranes have been computationally authenticated.[2a,22] Natural bond orbital (NBO) analysis of the bonding situation in **3**-σ indicates strong σ-H$_2$ to B donation without back donation. The associated natural localized molecular orbital (NLMO) is significantly delocalized over B (23 %), resulting in noticeable distortion of the σ-H$_2$ electron density towards the B center.[10] The H–H bond is slightly elongated (0.795 Å versus 0.743 Å in free H$_2$). The next step is the splitting of H$_2$ leading to the formation of intermediate **4**-HMes, which is lower in energy than **3**-σ by 18.3 kcal mol^{-1}. One H atom (H^1) is linked to boron (B–H 1.198 Å), whereas the other (H^2) has been transferred to the C$_{ipso}$ atom of the Mes ring (C–H 1.093 Å), resulting in the formation of a Wheland-type structure. The B–C$_{Mes}$ bond is noticeably elongated (from 1.581 Å in **3**-σ to 1.836 Å in **4**-HMes). A transition state **TS1** connecting **3**-σ and **4**-HMes was located 22.3 kcal mol^{-1} in energy above that of **3** and H$_2$ (starting point). The boron center remains in the plane of the Mes ring and H$_2$ approaches perpendicularly.[23] Finally, release of MesH from **4**-HMes was found to proceed readily. The corresponding activation barrier is fairly low (approximately 4 kcal mol^{-1}). The resulting phosphorus-stabilized hydroborenium **4**-H is isoenergetic with **4**-HMes and coordination of the NTf$_2$ counterion to the sterically unhindered boron center of **4**-H drives the reaction forward (taking into account NTf$_2$, $\Delta E = -25.1$ kcal mol^{-1} was predicted for the reaction of **3b** + H$_2$ → **4**-HNTf$_2$ + MesH).[10] It is noteworthy that the phosphine moiety of **3b** does not participate directly in the reaction with H$_2$ but remains engaged in the strong P→B interaction throughout the process.[24]

From the work of Berke, Erker, and Piers, highly electrophilic boranes are known to readily react with alkynes under metal-free conditions.[25] Typically, using B(C$_6$F$_5$)$_3$ and other C$_6$F$_5$-substituted boranes, a variety of 1,1-carboboration reactions (formal insertion of vinylidene species into B–C bonds) have been discovered.[25] Clearly, borenium salts are also promising substrates for carboboration, but to our knowledge the only precedent for such a reaction is that reported very recently by Ingleson and Cade.[26] Accordingly, borenium cations deriving from 8-hydroxyquinoline (and thus stabilized intramolecularly by N→B donation) were found to react slowly with 3-hexyne at 20–60 °C by 1,2-carboboration.[27] The borenium **3b** proved very reactive towards 3-hexyne. A clean reaction occurs spontaneously upon addition of the alkyne (1 equiv) to **3b** (Scheme 3; conversion is complete within 2 h at RT). The resulting product **5** was characterized by mass spectrometry and multinuclear NMR spectroscopy. The HRMS (electrospray ionization, positive mode) shows a signal at $m/z = 522.2762$, corresponding to the molar mass of the boron cation plus one 3-hexyne molecule. The ^{31}P and ^{11}B NMR spectra for **5** ($\delta = -4.1$ and 64.9 ppm, respectively) show signals which are only slightly shifted compared with those obtained for of **3b**, consistent with the similar structure of both compounds (phosphorus-stabilized aryl versus a vinyl borenium). The ^{13}C and ^{1}H NMR spectra are more informative. Two sets of resonance signals attributable to CCH$_2$CH$_3$ groups were observed, in line with the

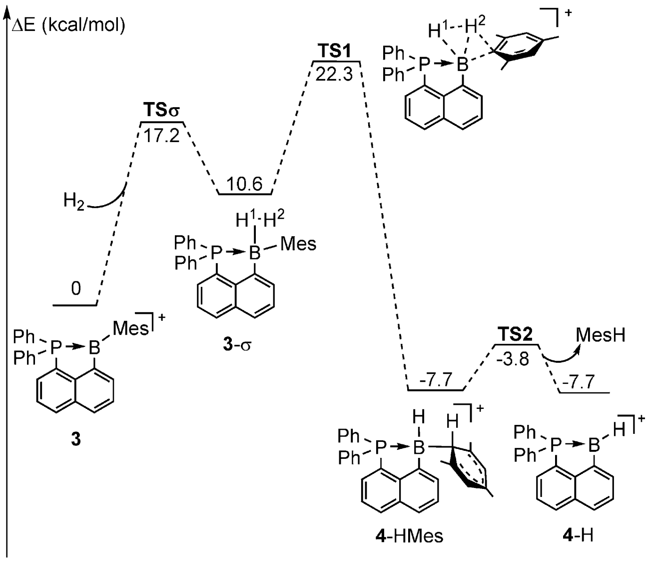
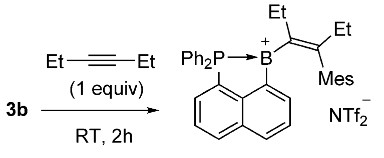


Figure 3. Energy profile calculated for the reaction of the borenium **3** with dihydrogen (electronic energy ΔE in kcal mol^{-1}).



5 (66%)

Scheme 3. 1,2-Carboboration of 3-hexyne by the borenium salt **3b** to form **5**.

desymmetrization of 3-hexyne. Complete assignment was possible thanks to ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMBC experiments, and the 1,2-*syn* arrangement of the two Et groups was deduced from a ^{1}H–^{1}H NOESY experiment.[10] Thus, the borenium **3b** undergoes rapid and clean carboboration with 3-hexyne. As for the reaction with H_2, the B–Mes bond is cleaved. In this case, it adds to the C≡C triple bond to form a vinyl borenium species. In contrast to perfluorophenyl boranes, but similarly to 8-hydroxyquinolato boreniums, 1,2-*syn* addition is observed.[26] This result demonstrates the rich reactivity of **3b** and substantiates further the unique behavior of B-aryl boreniums in carboboration reactions.

In conclusion, a new type of borenium involving a strong intramolecular P→B interaction supported by a naphthyl bridge has been synthesized. Compounds **3a**,**b** have been readily prepared by bromide abstraction with $GaBr_3$ or $AgNTf_2$. The steric demand of the mesityl group at boron prevents the coordination of P*t*Bu_3 to boron and the resulting FLP readily activates dihydrogen. Even in the absence of a base, the borenium reacts at 80 °C by heterolytic splitting of H_2 and B–Mes bond cleavage. The reactions involve side-on coordination of H_2 to boron followed by concomitant transfer of a hydride to the boron center and protonation of the Mes substituent. The phosphorus-stabilized borenium reacts spontaneously with 3-hexyne under mild conditions. In this case also the B–Mes bond is cleaved and a vinyl borenium species is formed through an uncommon *syn* 1,2-carboboration reaction.

These results substantiate further the ease with which boreniums may be structurally modified and highlight their versatile reactivity. The reactions observed with H_2 and 3-hexyne have some similarity with $B(C_6F_5)_3$ chemistry but also show significant differences. Future work in our laboratory will seek to explore further the chemistry of naphthyl-bridged P/B compounds.

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Keywords: borenium cations · density functional calculations · frustrated Lewis pairs · H_2 activation · phosphorus

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[24] As suggested by a reviewer, the reaction of **3** with H_2 may lead to a Ph_2PH^+ phosphonium/BHMes borane intermediate, but this would require the cleavage of the strong P→B interaction.

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Communications

Borenium Cations

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G. Bouhadir,*
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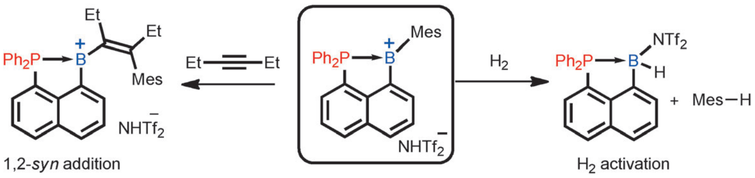
A Stable but Highly Reactive Phosphine-Coordinated Borenium: Metal-free Dihydrogen Activation and Alkyne 1,2-Carboboration



Versatile reactivity: A new type ofborenium cation is reported in which anaphthyl bridge supports a strong P→B interaction. Borenium reacts with H_2 through side-on coordination of H_2 to boron, heterolytic splitting, and concomitant cleavage of the B–Mes bond. The molecule also reacts with 3-hexyne through a *syn* 1,2-carboboration reaction. NTf_2^- = triflimide.