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Electrophilic Activation of Lewis Base Complexes of Borane with Trityl Tetrakis(pentafluorophenyl)borate

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Borenium ions do not accumulate under the conditions of hydride abstraction from Lewis base-borane complexes ($L \cdot BH_3$) using trityl cation because subsequent rapid reaction with $L \cdot BH_3$ occurs to form B–H–B bonds. The hydride bridged cations are sufficiently stabilized to resist abstraction of the remaining hydride by excess trityl cation; however, reversible cleavage of the 3c2e bond does take place to release borenium ion equivalents, as evidenced by interaction with weak nucleophiles.

Trityl cation has been used extensively as a potent hydride acceptor to generate reactive cationic species from neutral hydride donors.¹ In an early example, Benjamin et al. reported the reaction of $Ph_3C^+ BF_4^-$ with pyridine borane (**1**) in the presence of pyridine to give $Py_2BH_2^+$ (**2**, a four-coordinate boron cation, bis(pyridine)boronium according to the conventional nomenclature),² as well as Ph_3CH .³ A three-coordinate boron cation, the (pyridine)borenium ion **3**, was later proposed as an intermediate,⁴ but no attempts to detect **3** or other primary borenium ions have been reported. Little is known regarding such species, although the trivalent boron cation should be highly electrophilic at boron,⁵ perhaps sufficiently so for applications in borylation,⁶ hydroboration⁷ and hydrodefluorination chemistry triggered by interaction with weakly nucleophilic n or π electrons, as in **4**.⁸

Borenium ion **3** is isoelectronic with benzyl cation, and should benefit from significant π delocalization. We therefore attempted to observe **3**⁹ using NMR methods. While the ^{11}B NMR spectrum of **1** activated by $Ph_3C^+ B(C_6F_5)_4^-$ (TrTPFPB, **5**)¹⁰ in CD_2Cl_2 (rt) has a major peak (among several) at δ 44 ppm, well within the range where trisubstituted borenium ions have been reported,⁴ the signal is not coupled to protons and cannot be due to **3** nor to the solvent adduct (**4**, Nuc = CD_2Cl_2). We have assigned this signal as $PyBCl_2^+$ (**6**) based on ^{11}B chemical shift comparisons and a pyridine quench to form the known $Py_2BCl_2^+$.¹¹ None of the expected Ph_3CH singlet was found in the 1H NMR spectrum after 1 h at rt, apparently due to decomposition, although shorter reaction times did afford Ph_3CH .

Cleaner reactions were observed between **5** and amine boranes (1:1 molar ratio) at $-78\text{ }^{\circ}\text{C}$ in CD_2Cl_2 . This procedure gave little decomposition, and the best spectra were acquired from activation of $\text{Et}_3\text{N}\cdot\text{BH}_3$ (**7**). Samples were allowed to warm to $-20\text{ }^{\circ}\text{C}$ for ^1H and ^{11}B NMR analysis, conditions that minimize line broadening especially for the ^{11}B signals.¹²

Surprisingly, ^1H NMR assay indicated complete conversion of **7** but only ca. 50% conversion of trityl cation, as evidenced by a 1:1 ratio of Ph_3CH to unreacted Ph_3C^+ . A highly shielded peak appeared at $\delta\text{ }^1\text{H} = -2.6\text{ ppm}$ that integrated for 1H relative to Ph_3CH . By ^{11}B NMR, signals were observed for $\text{B}(\text{C}_6\text{F}_5)_4$ (sharp singlet at -17 ppm) and for a new broad peak at -3 ppm . Warming the sample to rt resolved coupling to two protons for this peak, but did not result in greater conversion of trityl cation prior to quenching with methanol, and did not produce signals in the trivalent boron region. Qualitatively similar results were obtained when **1**, **7** or other Lewis base borane complexes were treated with 50 mol% TrTPFPB (Table 1), although **1** still produced **2** and other contaminants along with **10**. In each example, conversion to a dominant product having a high field ^1H NMR signal ($\delta\text{ }^1\text{H}$ 0.5 to -3.7 ppm) was observed.

The above data are consistent with the initial formation of transient borenium ion intermediates that undergo rapid capture by the B–H bond of unreacted substrate to form symmetrical cations **8–13**. The key event leading to **8** corresponds to overlap between a nucleophilic B–H σ orbital of **7** with the empty p -orbital of $[\text{Et}_3\text{N}\cdot\text{BH}_2]^+$ (**14a**), or the equivalent displacement of dichloromethane (DCM) from the solvent adduct $[\text{Et}_3\text{N}\cdot\text{BH}_2\cdot\text{Cl}_2\text{CD}_2]^+$ (**14b**). Coordination of B–H bonds into electrophilic centers to form 3-center, 2-electron (3c2e) bonds is well established,¹³ but cationic species with the B–H–B structural motif have not been reported previously. The upfield ^1H NMR signals for **8–13** are in the range of B–H–B bonds of neutral structures including diborane¹⁴ as well as the B_2H_7^- anion^{15a} and cyclic derivatives.^{15b} The hydride-bridged structure **8** is also consistent with the -3 ppm ^{11}B NMR chemical shift.¹⁵,¹⁶ The “dimeric” structure of **8** explains the stoichiometry, with 50 mol% of the TrTPFPB required for reaction with **7**.

In the absence of nucleophiles, excess TrTPFPB (beyond 50 mol%) did not react with the hydridebridged products **8–13** and did not produce signals that could be assigned to borenium ions.¹⁷ This is in contrast to the reaction of singly hydride-bridged cationic M–H–M species^{1d,18} with trityl cation, a process which typically results in full conversion to the M^+ cation (M = transition metal).¹⁹ The Si–H–Si 3c2e bond of **15** also undergoes further activation upon treatment with TrTPFPB.^{1e,20} The only reported case of intermolecular stabilization of a silylium cation with an external Si–H bond (**16**) requires a large excess of silane, suggesting an equilibrium between **16** and solvent- and anion-coordinated species.²⁰ In contrast, **8–13** were formed in the absence of excess borane complex $\text{L}\cdot\text{BH}_3$, and the chemical shifts were not affected by the presence of unreacted $\text{L}\cdot\text{BH}_3$. However, the highly electrophilic cations **8–13** could not be isolated, and were only observed in solution.

Given the structural and electronic analogies to silylium cation chemistry,¹ we were interested to learn whether **8** might interact with *i*Pr₃SiH as a potential 3c2e hydride donor. No NMR evidence for an unsymmetrical structure **17** was obtained. However, when **8**-d₅ was generated from **7**-d₃ followed by exposure to *i*Pr₃SiH at rt in CD₂Cl₂ (1 h), H/D exchange was observed in **8** as well as *i*Pr₃SiH by ¹H NMR, ²H NMR, and MS assay. According to these results, **8**-d₅ dissociates reversibly to release a small amount of the borenium ion **14**-d₂. Reversible formation of a 3c2e bond with *i*Pr₃SiH leads to **18**, and equilibration with **19** provides the pathway for H/D exchange. The symmetrical cation **8** therefore functions as a source of the highly electrophilic borenium species **14**. We regard these data as the strongest evidence so far that monosubstituted borenium ions such as **14a** (or the equivalent DCM adduct **14b**) are viable intermediates.

With a clear picture of the activated species, the unexpected decomposition of Ph₃CH was studied more closely. Prior literature implicitly assumes that Ph₃CH is inert to the potent electrophiles produced by hydride abstraction using TrTPFPB, contrary to our findings at rt. A reductive quench (Bu₄NBH₄) of the solution obtained from activation of **7** with TrTPFPB (CH₂Cl₂, 1 h, rt) gave Ph₂CH₂ as the major byproduct, along with a complex mixture of hydrocarbons. Analysis by GC/MS revealed benzene, toluene, MeC₆H₄CH₂Ph (**20**), and MeC₆H₄CHPh₂ (**21**). The use of CD₂Cl₂ as solvent increased the masses of toluene, **20**, and **21** by 2 amu, indicating solvent incorporation. This likely occurs from **14b**-d₂ by Cl-C heterolysis, Friedel-Crafts alkylation of Ph₃CH at an *ipso*-carbon, fragmentation to Ph₂CH(+), and reductive trapping by hydride to give Ph₂CH₂.²¹ Similar events involving DCM explain the formation of PyBCl₂⁺ (**5**) from **1** via **10** and the solvent adduct **4** (Nuc = CH₂Cl₂).

We attribute the reactivity of **8** with the weak nucleophiles Ph₃CH and DCM as well as *i*Pr₃SiH to the presence of a small amount of borenium ion **14** in equilibrium with **8**. To gain further insight, the compatibility of **8** with various counterions was explored. No B-H-B bonded structures were detected when **7** was reacted with excess TrBF₄,^{2,22} although Ph₃CH (>95%) was formed along with Et₃N•BF₃.^{23,24} Furthermore, treatment of **7** with the strong acids HOTf (**22a**) or HNTf₂ (**22b**) as hydride acceptors formed tetravalent adducts **23a,b** as dominant products. Preformed **8** with X = TPFPB also gave **23a,b** (as well as **7**) when the

corresponding ^-OTf or $^-NTf_2$ salts **24a,b** were added, thereby confirming cleavage of the B–H–B bond by these anions. On the other hand, **8** was only partly converted to **23c** (ca. 1:1.1 **7**:**23c**) upon addition of **24c**, or when **7** was treated with 0.5 equiv of the strong, bulky carbon acid $HC(C_6F_5)Tf_2$ (**22c**)^{25,26} at rt. In this case, unreacted **7** competes with the weakly nucleophilic anion $^-C(C_6F_5)Tf_2$ for coordination into the unoccupied orbital of borenium ion **14a**.²⁶

To summarize, borenium ions do not accumulate under the conditions of hydride abstraction from Lewis base-borane complexes ($L \cdot BH_3$) due to subsequent rapid reaction with $L \cdot BH_3$ to form B–H–B bonds. However, reversible cleavage of the 3c2e bond releases borenium ion equivalents, as evidenced by the interaction with weak nucleophiles. Hydride bridged cations such as **8** are sufficiently stabilized to resist abstraction of the remaining hydride by excess trityl cation. The isotopic exchange between **8-d₅** and $HSiEt_3$ suggests that borenium ions such as **14a** may resemble silylium cations in terms of electrophilicity. Considering the solvent-assisted decomposition of Ph_3CH reported here, the use of TrTPFPB for generation of other reactive electrophiles may warrant closer scrutiny, especially in cases where decomposition of cationic products has been noted.²⁷

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Table 1¹H and ¹¹B NMR Data for Activated Borane Complexes^a

		$\delta^1\text{H}^b$	$\delta^{11}\text{B}$
8: R = Et 9: R = Me	-2.6 -1.9	-3 0
10: R = H ^c 11: R = NMe ₂	0.5 0.1	-2 -1
12	-3.7	-27
13	-2.2	-27

^aIn CD₂Cl₂ at -20 °C. In all cases X⁻ = TFPBPB.^bBridging hydride signal, ppm.^cContaminated with **2** and unidentified pyridinium impurities.