

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

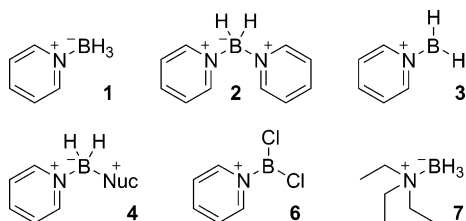
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Summary: Borenium ions do not accumulate under the conditions of hydride abstraction from Lewis base borane complexes ($L\cdot BH_3$) using trityl cation because subsequent rapid reaction with $L\cdot BH_3$ occurs to form $B-H-B$ bonds. The hydride-bridged 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 hydroboration,⁷ and hydrodefluorination chemistry triggered by interaction with weakly nucleophilic n or π electrons, as in **4**.⁸

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(1) (a) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430. For reviews see: (b) Lambert, J. B.; Zhao, Y.; Zhang, S. M. *J. Phys. Org. Chem.* **2001**, *14*, 370. (c) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325. (d) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. For leading references to recent work see: (e) Panisch, R.; Bolte, M.; Müller, T. *J. Am. Chem. Soc.* **2006**, *128*, 9676. (f) Cheng, T.-Y.; Szalda, D. J.; Zhang, J.; Bullock, R. M. *Inorg. Chem.* **2006**, *45*, 4712.

(2) For reviews of cationic boron compounds see: (a) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016. (b) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399.

(3) Benjamin, L. E.; Carvalho, D. A.; Stafiej, S. F.; Takacs, E. A. *Inorg. Chem.* **1970**, *9*, 1844.

(4) Ryschkewitsch, G. E.; Miller, V. R. *J. Am. Chem. Soc.* **1973**, *95*, 2836.

(5) Despite formal charge assignment in **3** to nitrogen, computational studies of this cation show significant positive charge character at the boron atom, supporting its electrophilic character and its description as a borenium ion: Schneider, W. F.; Narula, C. K.; Nöth, H.; Bursten, B. E. *Inorg. Chem.* **1991**, *30*, 3919.

The 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 ¹¹B NMR spectrum of **1** activated by $Ph_3C^+B(C_6F_5)_4^-$ (TrTPFPB, **5**)¹⁰ in CD_2Cl_2 (room temperature) 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** or to the solvent adduct (**4**, Nuc = CD_2Cl_2). We have assigned this signal as $PyBCl_2^+$ (**6**) on the basis of ¹¹B 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 room temperature, 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 $-78^\circ C$ in CD_2Cl_2 . This procedure gave little decomposition, and the best spectra were acquired from activation of $Et_3N\cdot BH_3$ (**7**). Samples were warmed to $-20^\circ C$ for ¹H and ¹¹B NMR analysis, conditions that minimize line broadening, especially for the ¹¹B signals.¹² Surprisingly, a 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 $\delta(^1H)$ -2.6 ppm that was integrated for 1H relative to Ph_3CH . By ¹¹B NMR, signals were observed for $^-B(C_6F_5)_4$ (sharp singlet at -17 ppm) and for a new broad peak at -3 ppm. Warming the sample to room temperature 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

(6) For leading references see: (a) Varela, J. A.; Peña, D.; Goldfuss, B.; Denisenko, D.; Kulhanek, J.; Polborn, K.; Knochel, P. *Chem. Eur. J.* **2004**, *10*, 4252. (b) Zhou, Q. J.; Worm, K.; Dolle, R. E. *J. Org. Chem.* **2004**, *69*, 5147.

(7) Clay, J. M.; Vedejs, E. *J. Am. Chem. Soc.* **2005**, *127*, 5766.

(8) For leading references see: (a) Vela, J.; Smith, J. M.; Yu, Y.; Ketterer, N. A.; Flaschenriem, C. J.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2005**, *127*, 7857. (b) Scott, V. J.; Çelenligil-Çetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852.

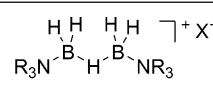
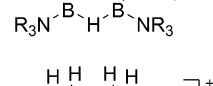
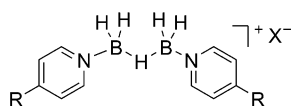
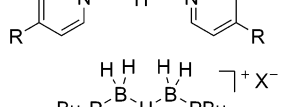
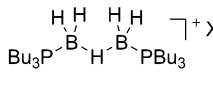
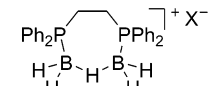
(9) This highly electrophilic species may exist as the solvent-coordinated cation (**4**, Nuc = solvent), which would technically be a boronium ion. To avoid confusion, this distinction in nomenclature and structure is left unspecified, and **4** will be considered equivalent to the free borenium ion **3**.

(10) (a) Vedejs, E.; Nguyen, T.; Powell, D. R.; Schrimpf, M. R. *Chem. Commun.* **1996**, 2721. (b) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

(11) The ¹¹B NMR signal for 4-Me-C₅H₄N⁺·BCl₂⁺·Al₂Cl₇⁻ is reported at +47 ppm by: Ryschkewitsch, G. E.; Wiggins, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1790. See the Supporting Information for quenching studies.

(12) Beall, H.; Bushweller, C. H.; Dewkett, W. J.; Grace, M. *J. Am. Chem. Soc.* **1970**, *92*, 3484.

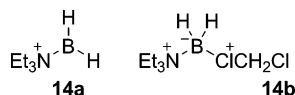
Table 1. ^1H and ^{11}B NMR Data for Activated Borane Complexes^a

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

^a In CD₂Cl₂ at -20 °C. In all cases X⁻ = TPFPB. ^b Bridging hydride signal, in ppm. ^c Contaminated with **2** and unidentified pyridinium impurities.

with **10**. In each example, conversion to a dominant product having a high-field ^1H NMR signal (δ 0.5 to -3.7 ppm) was observed.

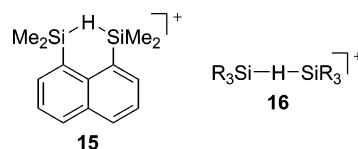
The above data are consistent with the initial formation of transient borenium ion intermediates that undergo rapid capture by the B-H bond of unreacted substrate to form the symmetrical cations **8–13**. The key event leading to **8** corresponds to overlap between a nucleophilic B-H σ orbital of **7** with the empty p -orbital of [Et₃N·BH₂]⁺ (**14a**) or the equivalent displacement of dichloromethane (DCM) from the solvent adduct [Et₃N·BH₂·Cl₂·CD₂]⁺ (**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 those for B-H-B bonds of neutral structures, including diborane,¹⁴ as well as the B₂H₇⁻ 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**.

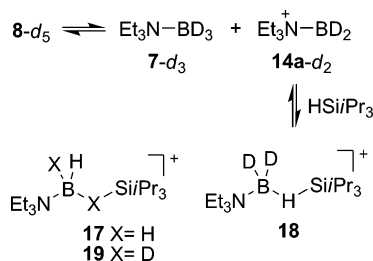
In the absence of nucleophiles, excess TrTPFPB (beyond 50 mol %) did not react with the hydride-bridged products **8–13** and did not produce signals that could be assigned to borenium ions.¹⁷ This is in contrast to the reaction of singly hydride

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 L·BH₃, and the chemical shifts were not affected by the presence of unreacted L·BH₃. 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 the unsymmetrical structure **17** was obtained.



However, when **8-d₅** was generated from **7-d₃** followed by exposure to *i*Pr₃SiH at room temperature 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, in contrast to our findings at room temperature. A reductive quench (Bu₄NBH₄) of the solution obtained from activation of **7** with TrTPFPB (CH₂Cl₂, 1 h, room temperature) 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

(13) (a) Merle, N.; Koicok-Köhn, G.; Mahon, M. F.; Frost, C. G.; Ruggerio, G. D.; Weller, A. S.; Willis, M. C. *Dalton Trans.* **2004**, 3883. (b) Shimoi, M.; Nagai, S.; Ichikawa, M.; Kawano, Y.; Kato, K.; Uruichi, M.; Ogino, H. *J. Am. Chem. Soc.* **1999**, *121*, 11704. (c) Parry, R. W.; Kodama, G. *Coord. Chem. Rev.* **1993**, *128*, 245. (d) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(14) Kern, C. W.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 275.

(15) (a) Hertz, R. K.; Johnson, H. D., II; Shore, S. G. *Inorg. Chem.* **1973**, *12*, 1875. (b) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420.

(16) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978.

(17) Treatment of DMAP·BH₃ with 1 equiv of TrTPFPB led to a new ^{11}B NMR signal at +20 ppm (doublet). The structure responsible for this signal remains unclear, but the chemical shift is not consistent with a borenium ion.

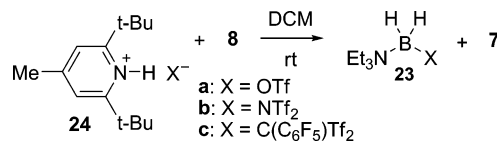
(18) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

(19) A cationic species with a Mo-H-Mo bond was reported to be unreactive toward excess trityl cation: Voges, M. H.; Bullock, R. M. *Dalton Trans.* **2002**, 759.

(20) Hoffmann, S. P.; Kato, T.; Tham, F. S.; Reed, C. A. *Chem. Commun.* **2006**, 767.

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**) and 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 and [−]NTf₂ 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 **8**:**23c**) upon addition of **24c** or on treatment of **7** with 0.5 equiv of the strong, bulky carbon



acid HC(C₆F₅)Tf₂ (**22c**)^{25,26} at room temperature. In this case, unreacted **7** competes with the weakly nucleophilic anion [−]C(C₆F₅)Tf₂ 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·BH₃) due to subsequent rapid reaction with L·BH₃ 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 *i*PrSiH suggests that borenium ions such as **14a** may resemble silylium cations in terms of electrophilicity. Considering the solvent-assisted decomposition of Ph₃CH 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

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Supporting Information Available: Text and figures giving experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

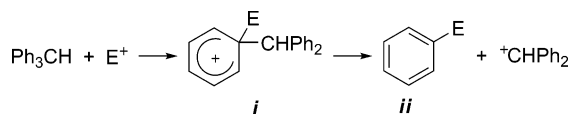
OM070228W

(25) Ishihara, K.; Hasegawa, A.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 4077.

(26) Et₃NH⁺ was a major product from the reaction of **7** + **22c** and a minor product from **8** + **24c** if the salt was dried prior to use; see the Supporting Information.

(27) (a) Okuda, J.; Musikabhumma, K.; Sinnema, P.-J. *Isr. J. Chem.* **2002**, *42*, 383. (b) Song, X.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1998**, *17*, 1004.

(21) Electrophilic substitution with E⁺ = CD₂Cl⁺ affords *i*. After fragmentation to PhCD₂Cl (*ii*; E = CD₂Cl) and Ph₂CH⁺, reductive quenching by hydride capture forms toluene-*d*₂ (observed by GC/MS) and Ph₂CH₂. When the reaction solvent was switched to benzene or toluene, slow formation of Ph₂CH₂ was still observed, indicating the involvement of other sources of E⁺ in these solvents. To test the possibility that **8** or **14** can act as E⁺, **7** was treated with TrTPFPB in the electron-rich arene *p*-xylene as solvent. Oxidative workup after 20 h at room temperature gave the expected 2,5-dimethylphenol, albeit in <5% yield. This experiment raises the possibility that formation of *i* with E = BH₂·NEt₃ may also contribute to C–C bond cleavage. For an example of the reaction of chloromethyl cation with hexamethylbenzene, see: Davlieva, M. G.; Lindeman, S. V.; Neretin, I. S.; Kochi, J. K. *J. Org. Chem.* **2005**, *70*, 4013.



(22) For the reaction of diarylcarbenium fluoroborates with amine boranes, see: Funke, M.-A.; Mayr, H. *Chem. Eur. J.* **1997**, *3*, 1214.

(23) Formation of Et₃N·BF₃ is evidence that **8** or **14** can extract fluoride from [−]BF₄.

(24) Heitsch, C. W. *Inorg. Chem.* **1965**, *4*, 1019.