B–H Activation by frustrated Lewis pairs: borenium or boryl phosphonium cation?†

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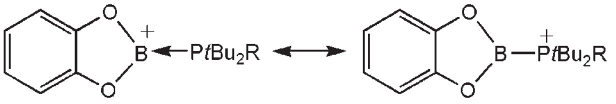
Catechol borane reacts with the frustrated Lewis pairs $t\mathrm{Bu}_2\mathrm{RP}$ (R = tBu, 2-$C_6H_4(C_6H_5)$) and $B(C_6F_5)_3$ to give the species $[(C_6H_4O_2)BPt\mathrm{Bu}_2R][HB(C_6F_5)_3]$ that can formally be described as either borenium cation or boryl-phosphonium salts; the nature of these species was probed with DFT calculations.

The concept of Lewis acidity and basicity and the formation of simple Lewis acid–base adducts[1] is a primary axiom of main group chemistry. We have recently described findings that illustrate an interesting corollary to the Lewis principle.[2] The combination of Lewis donors and acceptors in which steric demands preclude formation of simple acid–base adducts have been termed "frustrated Lewis pairs" (FLPs). As a result of the unquenched acidity and basicity, such systems have been shown to prompt non-classical and in some cases unprecedented reactivity. Employing this strategy we showed that the phosphine–borane $[(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2]$[3] react reversibly with H_2 to give the zwitterionic $[R_2PH(C_6F_4)BH(C_6F_5)_2]$.[4] This system constitutes the first metal-free system to reversibly react with H_2. Moreover, we demonstrated that the combinations of the Lewis acid $B(C_6F_5)_3$ with sterically hindered tertiary phosphines R_3P (R = tBu, $C_6H_2Me_3$) which show no evidence of adduct formation also react spontaneously with 1 atm H_2 to effect heterolytic H_2 cleavage to give the salts $[R_3PH][HB(C_6F_5)_3]$.[5,6] We have also recently furthered this work demonstrating the ability of these FLPs to act as catalysts for the hydrogenation of imines.[7] In related chemistry, the Erker group have recently shown that the alkyl-linked phosphinoborane, $[(C_6H_2Me_3)_2P(C_2H_4)B(C_6F_5)_2]$ also activates H_2 to give the zwitterionic species $[(C_6H_2Me_3)_2PH(C_2H_4)BH(C_6F_5)_2]$.[8] In addition we have shown that FLPs react with olefins to give unique alkyl-linked phosphonium borates[9] while a recent communication has probed the mechanism of this reaction.[10] In this paper, we continue our exploration of the reactivity of FLPs and report the activation of the B–H bond of catechol borane. The resulting salts can formally be considered the first to contain oxygen ligated borenium cations. Alternatively these cations can be depicted as boryl-phosphonium species. DFT calculations shed light on the description.

Reaction of the FLP, $B(C_6F_5)_3$ and $t\mathrm{Bu}_3P$, with the main group hydride $(C_6H_4O_2)BH$ was probed. Upon shaking of a reaction mixture of catecholborane with an equivalent of $t\mathrm{Bu}_3P$ and $B(C_6F_5)_3$ at −35 °C in toluene, an immiscible, colourless oil separated from solution.‡ Decantation of the toluene and washing of the oil with excess toluene followed by filtration through a short plug of Celite and solvent removal *in vacuo* afforded a clean oil. Trituration of this oil with pentane gave a white, microcrystalline solid. This product **1** exhibited $^{11}B\{^1H\}$ NMR resonances at 29.86 and −25.35 ppm. The former resonance exhibits B–P coupling of 176 Hz which is consistent with a direct B–P bond, while the latter singlet corresponds to the borate anion. The $^{31}P\{^1H\}$ NMR resonance is a quartet at 28.45 ppm. The ^{19}F NMR spectrum is comprised of resonances at −134.30, −165.10 and −167.96 ppm, consistent with the presence of a borate anion. These data support the formulation of **1** as $[(C_6H_4O_2)B(Pt\text{-}Bu_3)][HB(C_6F_5)_3]$ (Scheme 1). The analogous reaction employing $Pt\mathrm{Bu}_2(2\text{-}C_6H_4(C_6H_5))$ results in the formation of the related salt $[(C_6H_4O_2)BPt\mathrm{Bu}_2(2\text{-}C_6H_4(C_6H_5))][HB(C_6F_5)_3]$ **2** (Scheme 1) which displayed the analogous spectroscopic features, with a $^{11}B\{^1H\}$ NMR resonances at 28.75 and −25.12 ppm and $^{31}P\{^1H\}$ NMR signal at 11.11 ppm with P–B coupling of 156 Hz.



Scheme 1 Borenium and boryl-phosphonium cation formulations of **1** and **2**.

The formulation of **1** was confirmed by X-ray crystallography (Fig. 1).§ The geometry of the $[HB(C_6F_5)_3]$ anion is unexceptional. The cation is comprised of a three coordinate planar B center in which the catecholate oxygen atoms and the P of the phosphine complete the coordination sphere of B. The B–O distances were found to be 1.369(6) and 1.373(5) Å with an O–B–O chelate bite angle of 113.2(4)°. The B–P distance was found to be 1.933(5) Å, while the O–B–P angles were found to be 124.2(3) and 122.1(4)°. This B–P distance is significantly longer than that seen experimentally in the neutral three-coordinate B species of the form $R_2BPR'_2$ (1.839(8)–1.897(3) Å),[11,12] and those computed (1.769–1.919 Å) for model species $R_2BPR'_2$ (R = H, F, CF_3, R′ = H, Me, CF_3, Et, i-Pr, t-Bu)[13] but is comparable to that seen in $(TMP)BClPH(C_6H_2Me_3)$ (1.948(3) Å).[14,15] In addition, the B–P distance in **1** is longer than that seen in the cation $[(Et_3P)_2BH_2]^+$ (1.913(6) Å).[16] These observations are consistent with significant π-donation from O to B in **1**.

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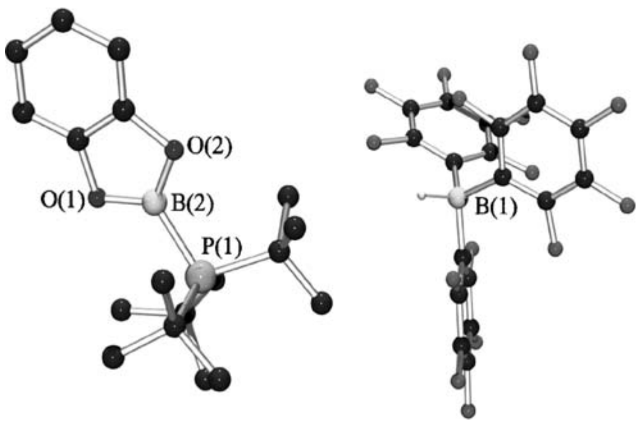


Fig. 1 POV-ray drawing of the cation and anion of **1**.

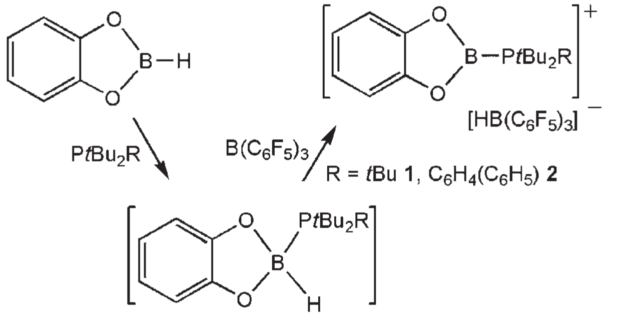
A recent and comprehensive review by Piers *et al.*[17] describes borinium, borenium and boronium cations. No B-cation isolated to date involved O-ligation, although the affinities of species such as $[B(OR)_2]^+$ for donors have been examined in the gas phase under standard EI conditions (70 eV). Indeed, De Vries and Vedejs reported that abstraction of hydride from $(L^{\bullet}BH_3)$ by trityl cation did not lead to the accumulation of borenium cation but rather B–H–B bridged species.[18] Thus, one can view the cations, **1** and **2** which are obtained via hydride abstraction, as the first isolated examples of O-ligated borenium cations. Nonetheless, an alternative and viable description of these cations is as boryl-phosphonium cations (Scheme 1).

In order to probe the better descriptor of the electronic nature of these unusual cations, the natural bond order (NBO) charges were determined at the DFT MPW1K/6-311++G(d,p) level for several model compounds (Table 1).¶ To preface this, we note that the optimized structure of $(C_6H_4O_2)B(PMe_3)^+$, entry 1, agrees quite well with that determined crystallographically for the cation of **1** (B–P = 1.929 Å; B–O = 1.350, 1.350 Å; ∠O–B–P = 122.8, 122.8°; ∠O–B–O = 114.4°). Comparison of entries 1 and 2 indicates that addition of PMe_3 to $(C_6H_4O_2)B^+$ removes a substantial amount of the positive charge from the boron (*ca.* 0.7 e^-). This holds despite the fact that the charges on the O atoms hardly change. A similar effect appears when comparing entries 3 and 4. Entry 3 is meant to simulate a "pure" cationic B atom surrounded by three peripheral atoms. This results in a charge on B that is much less than +1. Nonetheless, when PMe_3 is substituted for one of the water ligands (entry 4) the charge on B drops by 0.4 e^-. Entry 5 shows the effect of a "pure" cationic P atom. In this case, the P atom is only slightly more positively charged than the P atoms in entries 1 and 4. The methyl groups are slightly more electronegative than the P atom, increasing its charge to greater than +1. It should be noted that the predicted charge on the P-bound H atom in entry 5 is 0.032; that is, this P–H bond is essentially electroneutral. These computational data suggest that $[(C_6H_4O_2)BPMe_3]^+$ is essentially a phosphonium cation with one unusual, very slightly electron-donating $(C_6H_4O_2)B$ substituent, where the B atom is about as Lewis acidic as a proton.

Table 1 Calculated NBO charges (MPW1k/6-311++G(d,p) model) on B, O and P for model cations

Entry	Model cation	B	O	P
1	$[(C_6H_4O_2)BPMe_3]^+$	0.847	−0.650	1.181
2	$[(C_6H_4O_2)B]^+$	1.530	−0.648	
3	$[(H_2O)_3B]^+$	0.306	−0.866	
4	$[(H_2O)_2BPMe_3]^+$	−0.101	−0.814	1.112
5	$[HPMe_3]^+$			1.306

There is no doubt that $B(C_6F_5)_3$ is more Lewis acidic that $(C_6H_4O_2)BH$. However, the frustrated nature of the combination of $B(C_6F_5)_3$ and tBu_3P make the unquenched Lewis basicity available for coordination to $(C_6H_4O_2)BH$. Such adduct formation is expected to dramatically enhance the hydridic character of the B–H bond. Subsequent hydride abstraction by $B(C_6F_5)_3$ affords the salt **1**. It is also noteworthy that treatment of $(C_6H_4O_2)BH$ with PR_3 (R = Ph, *i*Pr, Cy) alone is known to effect catechol ligand redistribution, and yet this is not observed in the present reactions.[16] Seeking experimental support for the proposed mechanism, the reaction of tBu_3P and $(C_6H_4O_2)BH$ was monitored by NMR spectroscopy. At 25 °C, no evidence of adduct formation was observed by $^{31}P\{^1H\}$ NMR spectra. However, lowering the temperature to −60 °C in d_8-toluene resulted in an upfield shift in the ^{31}P $\{^1H\}$ to 23.64 ppm indicating some adduct formation, although a limiting spectrum was not observed. It is also noteworthy that phosphine adducts of the form $(C_6H_4O_2)BCl(PR_3)$ have been thoroughly studied and characterized.[19] These data suggest the formation of a weak donor–acceptor Lewis acid–base adduct consistent with the proposed mechanism (Scheme 2). This mechanism is further supported by the observation that use of phosphines $(C_6H_2Me_3)_3P$ or $(o\text{-}C_6H_4Me)_3P$ in reactions with $B(C_6F_5)_3$ or $B(C_6F_5)_3$ and $(C_6H_4O_2)BH$ failed to react presumably a result of the diminished Lewis basicity of these phosphines precluding formation of an intermediate adduct with $(C_6H_4O_2)BH$. In a similar fashion reaction of $(C_6H_4O_2)BH$, tBu_3P and BPh_3 did not yield the analog of **1**, inferring that BPh_3 is not a strong enough Lewis acid to abstract hydride from the transient adduct $(C_6H_4O_2)BH^{\bullet}PtBu_3$. However, it is also clear that a subtle balance of steric and electronic factors determine the reaction pathway. For example, the corresponding reactions of slightly less bulky phosphines PCy_3, $PiPr_3$ or tBu_2PH result only in the formation of the previously reported zwitterionic species $[R_3P(C_6F_4)BF(C_6F_5)_2]$. This observation supports the view that only unreactive FLP prompt the B–H bond activation described herein.



Scheme 2 Proposed reaction pathway to **1** and **2**.

In summary, the unquenched Lewis acidity and basicity of frustrated Lewis pairs can cooperate to effect the activation of the B–H in catechol borane, resulting in the formation of a salt incorporating the unusual cation $[(C_6H_4O_2)BPtBu_2R]^+$. Although this cation can be view as a borenium cation, DFT data suggest it is best described as a boryl-phosphonium cation. Studies continue to probe the unique abilities of FLPs to activate small molecules.

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Notes and references

‡ *Synthesis* of $[(C_6H_4O_2)B(Pt\text{-}Bu_3)][HB(C_6F_5)_3]$ **1**, $[(C_6H_4O_2)BPtBu_2(2\text{-}C_6H_4\text{-}Ph)][HB(C_6F_5)_3]$ **2**: These compounds were synthesized in a similar fashion, therefore only the procedure for **1** is described. A solution of catecholborane (208 mg, 1.7 mmol) and tBu_3P (190 mg, 0.94 mmol) in toluene (10 mL) was cooled to −35 °C at which point $B(C_6F_5)_3$ (482 mg, 0.94 mmol) was added in one portion. The reaction mixture was shaken, and dissolution of the borane was concomitant with formation of an immiscible, colourless oil. The toluene was decanted and the oil washed with toluene (10 mL) and filtered through a short plug of Celite. Solvent was removed *in vacuo* and the oil was then triturated with pentane to afford a white, microcrystalline solid, which was washed with pentane (3 × 10 mL) and dried under reduced pressure (754 mg, 96%). **1**: ^1H NMR (CD_2Cl_2): δ 1.73 (d, 27H, *t*Bu, $J_{H\text{–}P} = 15$ Hz); 3.60 (q, 1H, BH, $J_{H\text{–}B} = 87$ Hz); 7.37 (dd, 2H, $J_{H\text{–}H} = 6$ Hz, $J_{H\text{–}H} = 3$ Hz); 7.53 (dd, 2H, $J_{H\text{–}H} = 6$ Hz, $J_{H\text{–}H} = 3$ Hz). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 29.86 (d, $J_{B\text{–}P} = 176$ Hz); −25.35 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, partial): δ 30.70 (s, P*t*Bu; 40.30 (d, P*t*Bu, $J_{P\text{–}C} = 24$ Hz); 114.18 (s, *o*-$O_2C_6H_4$), 125.73 (s, *m*-$O_2C_6H_4$), 137.12 (dm, $J_{C\text{–}F} = 244$ Hz, *m*-C_6F_5), 138.53 (dm, $J_{C\text{–}F} = 242$ Hz, *p*-C_6F_5), 147.42 (s, *ipso*-$O_2C_6H_4$), 148.91 (dm, $J_{C\text{–}F} = 239$ Hz, *o*-C_6F_5).^{19}F NMR (CD_2Cl_2): δ −134.30 (d, 6F, $J_{F\text{–}F} = 21$ Hz, *o*-C_6F_5), −165.10 (t, 3F, $J_{F\text{–}F} = 20$ Hz, *p*-C_6F_5), −167.96 (t, 6F, $J_{F\text{–}F} = 18$ Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.45 (q, $J_{P\text{–}B} = 176$ Hz). C, H anal. (%) calc. for $C_{36}H_{32}B_2O_2F_{15}P$ (834.20) C: 51.83; H 3.86. Found: C: 51.66; H 4.05. **2**: Colourless microcrystalline solid (0.499 mg, 90%): ^1H NMR (CD_2Cl_2): δ 1.63 (d, 9H, *t*Bu, $J_{H\text{–}P} = 17$ Hz); 1.64 (d, 9H, *t*Bu, $J_{H\text{–}P} = 17$ Hz); 3.63 (s, br, 1H, BH); 6.65 (t, 1H, $J_{H\text{–}H} = 6$ Hz); 6.99 (t, 2H, $J_{H\text{–}H} = 6$ Hz); 7.22 (m, 6H); 7.47 (m, 1H); 7.78 (m, 2H); 8.01 (t, 1H, $J_{H\text{–}H} = 9$ Hz). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 28.75 (d, $J_{B\text{–}P} = 156$ Hz); −25.12 (s).$^{13}C\{^1H\}$ NMR (CD_2Cl_2, partial): δ 30.29.14 (s, *t*Bu; 38.82 (d, *t*Bu,, $J_{P\text{–}C} = 29$ Hz); 113.90 (s, *o*-$O_2C_6H_4$); 125.12 (s, *m*-$O_2C_6H_4$); 128.81 (s, C_{Ar}); 129.27 (s, C_{Ar}); 129.95 (s, C_{Ar}); 133.30 (s, C_{Ar}); 133.37 (s, C_{Ar}); 134.26 (s, C_{Ar}); 134.35 (s, C_{Ar}); 134.43 (s, C_{Ar}); 134.47 (s, C_{Ar}); 136.65 (dm, $J_{C\text{–}F} = 242$ Hz, *m*-C_6F_5); 138.32 (dm, br, $J_{C\text{–}F} = 241$ Hz, *p*-C_6F_5); 138.37 (s, C_{Ar}), 138.42 (s, C_{Ar}); 146.78 (s, *ipso*-$O_2C_6H_4$); 146.83 (s, *ipso*-$O_2C_6H_4$); 148.41 (dm, $J_{C\text{–}F} = 236$ Hz, *o*-C_6F_5); 149.00 (d, $J_{P\text{–}C} = 56$ Hz, *ipso*-PC_6H_4Ph).^{19}F NMR (CD_2Cl_2): δ −134.06 (s, 6F, *o*-C_6F_5), −165.00 (s, 3F, *p*-C_6F_5), −167.79 (s, 6F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 11.11 (q, $J_{P\text{–}B} = 156$ Hz). C, H anal. (%) calc. for $C_{44}H_{32}B_2O_2F_{15}P$ (930.31) C: 56.81; H 3.47. Found: C: 56.52; H 3.60.

¶ *Computational methods*: All calculations were performed with the GAUSSIAN (G98) code.[20] Monocations were fully optimized without constraints at the HF level using the 6-31+G(d) basis set. Examination of the optimized structures by analytical frequency analysis at this level demonstrated them to be minima (no imaginary frequencies). The structures were reoptimized using the MPW1K/6-311++G(d,p) DFT model, generated using the mPWPW91 model[21] and IOp keywords.[22] Relative energies were corrected using scaled[23] zero point energies (ZPEs) from the frequency analysis. Natural Bond Order (NBO) calculations were performed using a upgraded version of the NBO subroutine in the Gaussian98 program,[24,25] using the MPW1K/6-311++G(d,p)-optimized structures and wavefunctions. Optimized Cartesian coordinates for the monocations investigated are available as Supporting Information.

§ X-Ray quality crystals were grown from slow cooling (−35 °C) of a saturated solution in chlorobenzene. $T = -150$ °C, monoclinic, space group $P2_1/n$, $a = 13.738(3)$, $b = 14.126(3)$, $c = 18.960(4)$ Å, $\beta = 99.44(3)°$, $V = 3629.6(12)$ Å^3, $Z = 4$, unique data: 6385, parameters: 509, $R = 0.0569$, $R_w = 0.1126$, GOF = 1.000; CCDC 688387.

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