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Frustrated Lewis Pairs

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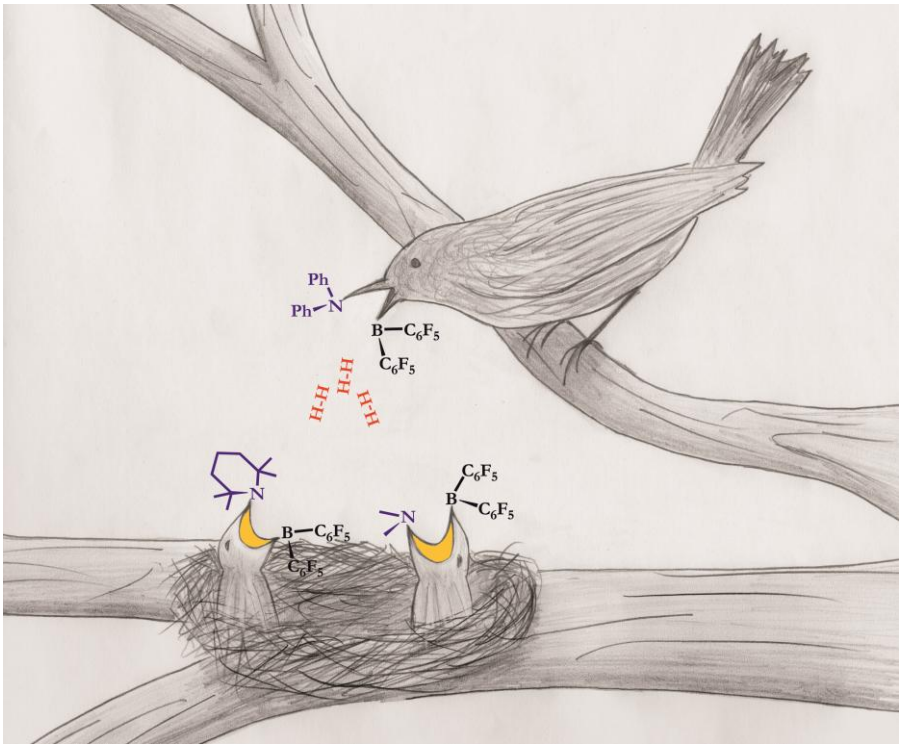

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PAPER

Heterolytic activation of hydrogen using frustrated Lewis pairs containing tris(2,2′,2″-perfluorobiphenyl)borane†

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The extremely sterically hindered borane tris(2,2′,2″-perfluorobiphenyl)borane (PBB) has been structurally characterised. In combination with bulky nitrogen bases, it forms the 'frustrated Lewis pairs' (FLPs) PBB/2,2,6,6-tetramethylpiperidine (TMP) (**1**), PBB/1,4-diazobicyclo[2.2.2]-octane (DABCO) (**2**) and PBB/2,6-lutidine (lut) (**3**). These novel, unquenched acid–base pairs have been shown to effect facile room temperature heterolytic cleavage of dihydrogen to form the ammonium borate salts [2,2,6,6-$Me_4C_5H_6NH_2$][$HB(C_{12}F_9)_3$] (**4**) and [$N(C_2H_4)_3NH$][$HB(C_{12}F_9)_3$] (**5**), and lutidinium borate [2,6-$Me_2C_5H_3NH$][$HB(C_{12}F_9)_3$] (**6**). Although these reactions are equilibria, the reverse reaction and release of hydrogen gas was not apparent at temperatures up to 120 °C. The relative Lewis acidity of PBB has been determined using the Gutmann–Beckett method.

Introduction

In 2006, Welch and Stephan published the first example of a metal-free system that reversibly and cleanly cleaves hydrogen.[1] The zwitterionic phosphonium hydridoborate salt R_2PH-(*p*-C_6F_4)-BHR'_2 [R = 2,4,6-$C_6Me_3H_2$, R′ = C_6F_5] loses hydrogen upon heating at 150 °C, and reacts with H_2 gas at room temperature to regenerate the zwitterion. Prior to this exciting discovery, there are few examples of non-metal mediated activation of hydrogen,[2–5] with the only non-metal *p*-block mediated heterolytic splitting under ambient conditions involving metalloid germanium compounds.[6]

Subsequently, combinations of $B(C_6F_5)_3$ with phosphines,[7–11] bulky amines,[12–14] pyridines,[15–17] imines,[12,18] carbonyls,[19] carbenes,[20–24] and phosphinoalkylboranes[8] have all been used to successfully cleave dihydrogen. This is attributed to their ability to form 'frustrated Lewis pairs' (FLPs), where bulky substituents on an electron pair acceptor and donor preclude the formation of a dative bond by preventing close approach of their respective acidic and basic centres.[9] FLPs have been shown to activate an important and significant range of small molecules, with additions to carbonyls,[25] CO_2,[26–32] N_2O,[33] and unsaturated systems,[10,25,30,34–39] the ring opening of heterocycles,[16,24,40–43] and cleavage of disulfide bonds being reported.[44] One of their most attractive features is their ability to effect catalytic hydrogenation of unsaturated substrates under mild conditions.[12,18,45–48] Where equilibria exist between Lewis adducts and their FLPs, or can be accessed through thermal dissociation of an adduct,[14] both classical and frustrated reactivity can be exploited.[1,15,16,49]

Although there has been extensive variation in the acidic and basic partners, most investigations into the nature of the Lewis acid involve changing C_6F_5 groups of tris(pentafluorophenyl)-borane, $B(C_6F_5)_3$, for substituents with different steric and electronic requirements.[38,45,49–52] Tris(2,2′,2″-perfluorobiphenyl)-borane (PBB) increases the steric bulk on the borane compared to $B(C_6F_5)_3$, while maintaining an electronegativity at the *ortho*-position which is comparable to a fluorine substituent.[54]

PBB is a cocatalyst or activator in Ziegler Natta homogeneous olefin polymerisation, exhibiting higher activities than its $B(C_6F_5)_3$ analogue and yielding more desirable polymers with higher molecular weights and narrow polydispersities.[51,52] Herein, we report the molecular structure of PBB and report its use for the first time in forming frustrated Lewis pairs with a series of nitrogen bases. We document the ability of these systems to effect the heterolytic activation of dihydrogen and their subsequent reactivity with carbon dioxide.

Results and discussion

PBB was synthesised from bromopentafluorobenzene according to the procedure developed by Marks and co-workers.[56] Colourless single crystals suitable for X-ray crystal structural analysis were obtained by slow cooling of a concentrated hot hexane solution to 20 °C. PBB crystallises in pairs of non-identical molecules, and the crystal structure shows the propeller conformation about a trigonal planar boron atom expected for *ortho*-substituted triaryl boranes (Fig. 1).[57] B–C bond lengths and angles between the reference plane containing the BC_3 fragments and the mean plane of the attached C_6F_4 rings are expressed in

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† Electronic supplementary information (ESI) available: ORTEP drawing and significant bond lengths for other PBB molecule in unit cell. CCDC 866505. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30334e

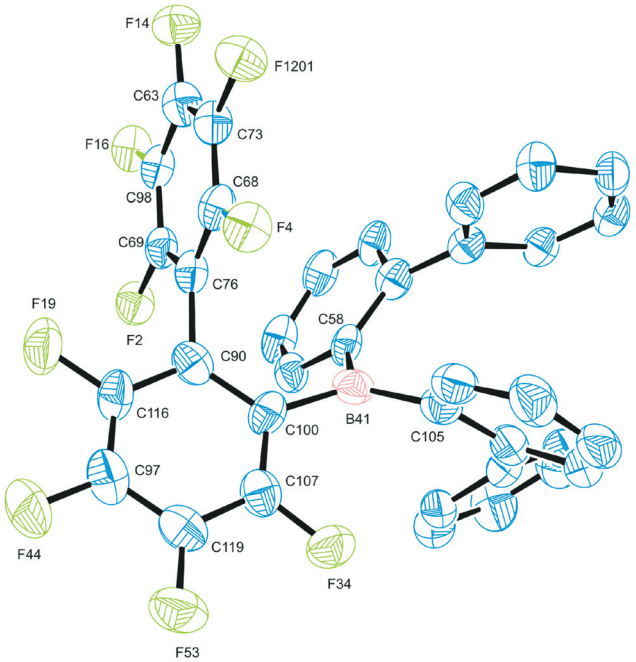
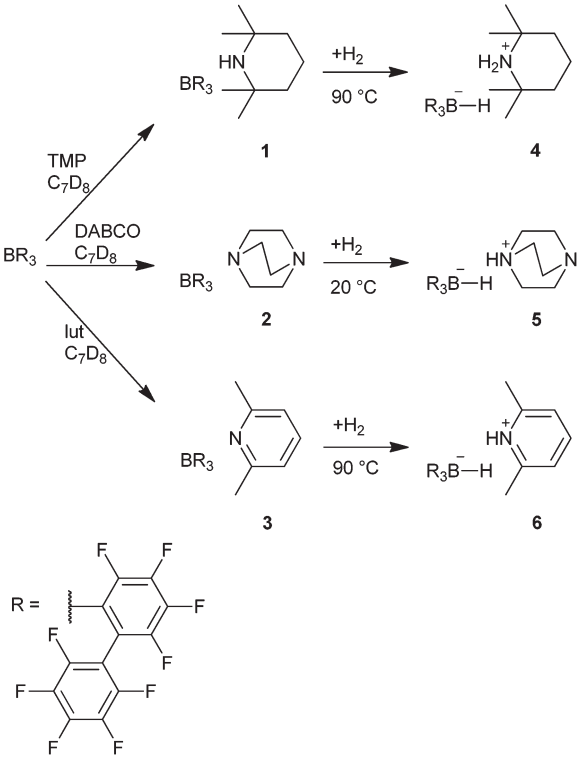


Fig. 1 Molecular structure drawing of $B(C_{12}F_9)_3$, PBB, showing 50% thermal ellipsoids for one of the two crystallographically unique molecules. Fluorine atoms on two $C_{12}F_9$ groups have been omitted for clarity.[53] Selected bond lengths for displayed molecule: B(41)–C(58) 1.57(1); B(41)–C(100) 1.59(1); B(41)–C(105) 1.583(9) Å. Angle between mean planes $B(41)C_3$–C(58) 42.7(3)°; $B(41)C_3$–C(100) 41.6(3)°; $B(41)C_3$–C(105) 48.9(4)°.



Scheme 1 Reactions of tris(2,2′,2″-perfluorobiphenyl)borane with nitrogen bases and dihydrogen.

Fig. 1. The B–C bond lengths ranging from 1.56(1) to 1.59(1) Å are comparable to the B–C distances of 1.573(4) and 1.580(4) Å seen in $BMes_3$ (Mes = 2,4,6-$C_6H_2Me_3$),[57] and to the analogous B–C bond length of 1.57(2) Å in bis(pentafluorophenyl)-(2-perfluorobiphenyl)borane, BPB, $(C_6F_5)_2BC_6F_4(o\text{-}C_6F_5)$.[58] The angles of rotation out of the reference plane containing the BC_3 fragment, ranging from 41.6(3)° to 48.9(4)°, are smaller than the analogous 49.1° or 51° angles in $BMes_3$, suggesting more favourable pπ-donation from fluorine substituents into the p-orbital of boron.[57]

The reactions of PBB with an equimolar amount of each of the nitrogen bases 2,2,6,6-tetramethylpiperidine (TMP), 1,4-diazobicyclo[2.2.2]octane (DABCO) and 2,6-lutidine (lut) in toluene were monitored by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy. No adduct formation was apparent in all three cases, with resonances characteristic of the separate starting materials consistent with formation of the new, coloured 'frustrated Lewis pairs' PBB/TMP (**1**), PBB/DABCO (**2**) and PBB/lut (**3**) (Scheme 1). Introduction of hydrogen (1 atm) to the NMR samples of each of these systems resulted in immediate reaction (as observed by ^{19}F NMR) at room temperature. The ^{19}F NMR spectra of the anions suggest immediate formation of a tetrahedral borohydride anion, $[HPBB]^-$, with nine new ^{19}F resonances accompanying the dominant seven of unreacted PBB. The spectroscopic signatures of the borohydride species exhibit similar features to those seen for $[MePBB]^-$,[55,56] and from this we can infer formation of the ammonium borate salts $[2,2,6,6\text{-}Me_4C_5H_6NH_2][HB(C_{12}F_9)_3]$, (**4**), and $[N(C_2H_4)_3NH][HB(C_{12}F_9)_3]$ (**5**), and lutidinium borate $[2,6\text{-}Me_2C_5H_3NH][HB(C_{12}F_9)_3]$ (**6**) respectively. No coupling is observed between fluorine and boron nuclei in the ^{1}H NMR spectra, while fast exchange of H^+ between nitrogen species in solution prevented NH signals being observed in the salts (expected around 4.32,[13] 10.20,[59] and 12.01 ppm[16] for **4**, **5** and **6** respectively).

To maximise the yields of **4** and **6** required heating of the sealed reactions at 90 °C for 72 h. The maximum spectroscopic yields of **4** and **6** were 28% and 29% respectively, determined by ^{19}F integration relative to residual starting material. Strong BH doublets were observed by ^{11}B NMR spectroscopy at −18.41 ppm (**4**) and −18.42 ppm (**6**). These borohydride shifts are more positive than the analogous shifts in $[HB(C_6F_5)_3]^-$ at −24.13 ppm and −24.7 ppm, and more similar to the −18.8 ppm value observed for the borohydride $[PhC_2H_4BH(C_6F_5)_2]^-$.[51] The parent borane of this latter borohydride is found to be a stronger Lewis acid than $B(C_6F_5)_3$,[51] suggesting PBB becomes more Lewis acidic upon *ortho*-substitution of a fluorine for C_6F_5.

In the reaction between **2** and H_2, the borohydride salt formed after 48 h stirring at 20 °C has the same spectroscopic features as products of the reactions of **1** and **3** with hydrogen. Upon cooling to −20 °C, **5** precipitated as a white solid, an analytically pure sample can be isolated by decanting the supernatant, and washing with pentane. The five ^{19}F NMR resonances from the C_6F_5 rings each divide in a 1 : 1 ratio, indicating restricted C–C rotation between perfluorinated rings and resulting in inequivalent $C_{12}F_9$ environments. Following isolation and characterisation, **5** was redissolved in toluene and again placed under a hydrogen atmosphere and heated to 90 °C. The ^{19}F NMR spectra after 24 hours indicated complete loss of the initial salt

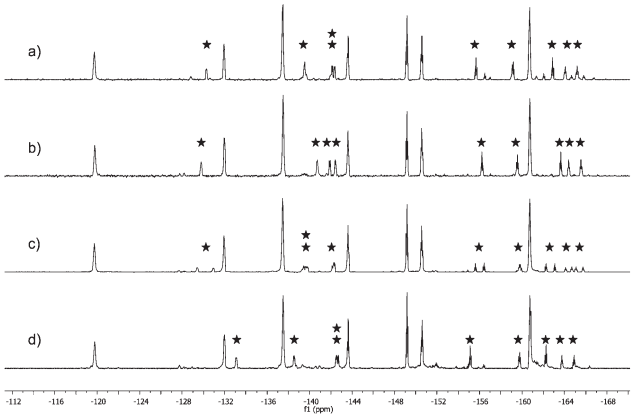
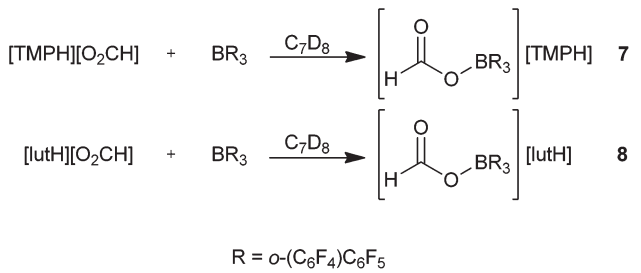


Fig. 2 ^{19}F NMR spectra showing formation of $[HPBB]^-$ resonances (★) of (a) **4** after heating at 90 °C for 24 h, (b) **6** after heating at 90 °C for 24 h, (c) **5** after 24 h at 20 °C, and (d) **5** after heating at 90 °C for 3 days. Unlabelled resonances correspond to unreacted PBB.



Scheme 2 Reaction scheme showing the formation of the boroformate salts [TMPH][HCO_2PBB], (**7**) and [lutH][HCO_2PBB], (**8**).

[DABCOH][HPBB] (**5**), and the growth of nine new resonances (Fig. 2d). A shift of the borohydride doublet from −18.58 ppm to −22.92 ppm ($^1J_{BH}$ = 94.3 Hz) suggests the boron nucleus in the new species is less strongly deshielded and further identification and characterisation of this product is underway.

Unlike mixtures of $B(C_6F_5)_3$ and TMP, which cleave H_2 quantitatively at 20 °C,[13] FLP **1** requires heating and does not go to completion. This corroborates work by Soós *et al.* where it was found TMP in combination with the modified borane $(C_6F_5)_2$BMes yields only one sixth of the hydrogen-cleaved product compared to its DABCO analogue.[59]

The adduct of lut–$B(C_6F_5)_3$ exists in equilibrium with the dissociated acid–base pair at room temperature,[16] yet despite this, still undergoes reaction with H_2 at room temperature in 87% yield. The increased bulkiness of **3** on the other hand causes it to exist purely in the unquenched state, and again requires heating to effect a reaction with dihydrogen.

The CO_2 insertion reactivity of the salts **4** and **6** was subsequently investigated. As a comparison, the anticipated product formates [TMPH][HCO_2PBB], (**7**), and [lutH][HCO_2PBB], (**8**), were independently synthesised by adding 1 : 1 solutions of TMP–formic acid or lut–formic acid in toluene to PBB (Scheme 2) and were characterised by NMR spectroscopy. However, preliminary investigations into the reactivity of **1**, **3**, **4** and **6** with carbon dioxide shows only degradation of the borohydride signals in the ^{19}F NMR spectrum, with no binding of CO_2 to the FLP, nor insertion into the B–H bond being clearly apparent. These results contrast to the $B(C_6F_5)_3$ analogues of **4** and **6** which successfully reduce carbon dioxide *via* insertion into the B–H bond,[56,57] and to the unquenched acid–base systems $B(C_6F_5)_3/P^tBu_3$ and $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ which can activate CO_2 directly, forming new B–O and P–C bonds.[26,28]

The formates **7** and **8** were heated under an atmosphere of CO_2, and the reappearance of the borohydride doublet was observed *via* ^{11}B NMR spectroscopy at 145 °C, indicating relatively facile decarboxylation, and supporting the failure of the reverse insertion reaction. Dehydrogenation to the FLP was not observed however.

As the PBB *ortho*-C_6F_5 groups render the boron centre less sterically accessible than in $B(C_6F_5)_3$, we therefore carried out NMR studies to determine how this affects the Lewis acidity of the borane. The Lewis acidity of boranes is commonly determined *via* two NMR methods. Using the Gutmann–Beckett method, which has been adapted to solutions of boranes by Britovsek *et al.*,[62–66] the difference in $^{31}P\{^1H\}$ chemical shift between uncoordinated Et_3PO (50.41 ppm) and the Et_3PO → Lewis acid adduct (80.68 ppm) is measured, giving a $\Delta\delta$ = 30.27 ppm and an Acceptor Number (AN) for PBB of 87.90.‡[65] This indicates PBB is a stronger Lewis acid than $B(C_6F_5)_3$ (AN 79.8).[61,62] The same trend was observed by Marks *et al.* using Child's method, where deshielding of proton H_3 in *trans*-crotonaldehyde occurs upon coordination to a Lewis acid.[67–69] Hence it is postulated that the *o*-C_6F_5 substituent has a greater inductively withdrawing effect through the sigma framework than an *o*-F, causing boron to be more deshielded in PBB anions compared to $B(C_6F_5)_3$.

Experimental

General data

Air and moisture sensitive reactions were performed on a dual-manifold vacuum/N_2 line using standard Schlenk techniques, or in a N_2 filled MBraun Unilab glovebox. Hexane, pentane and toluene were dried using a Braun SPS-800 solvent purification system. Et_2O was dried at reflux over Na/benzophenone and distilled under N_2. Dry solvents were stored under N_2 over K mirrors in oven dried ampoules with a Rotaflo cap. H_2 gas (>99.95% dry) from Sigma Aldrich and CO_2 gas (99.99%) from ARGO International Ltd were passed directly into a dual manifold Schlenk line. Deuterated NMR solvents were purchased from Goss Scientific, dried and freeze–pump–thaw degassed (×3) over the appropriate drying agent: C_7D_8 (99.6% D)(K), CD_2Cl_2 (99.8% D)(activated 3 Å molecular sieves). All other organic reagents were purified by conventional methods unless otherwise stated. BCl_3 (1.0 M in hexanes), ^{n}BuLi (1.6 M in hexanes), 2,2,6,6-tetramethylpiperidine (>99%), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Sigma Aldrich, and 2,6-lutidine (>98%) from Alfa Aesar. Bases were dried as follows: TMP and lutidine were freeze–pump–thaw degassed (×3) and stored over 3 Å molecular sieves in the glove

‡ AN = $[\Delta\delta]/[\delta(Et_3PO \rightarrow SbCl_5) - \delta(Et_3PO$ in hexane$)] \times 100$; $\Delta\delta = \delta(Et_3PO \rightarrow$ LA in $CD_2Cl_2) - \delta(Et_3PO$ uncoordinated in hexane); 3 : 1 excess of LA to Et_3PO.

box. DABCO was sublimed under vacuum. ^{1}H, ^{19}F, ^{31}P and ^{11}B NMR measurements were recorded on 300 MHz Varian VX-Works spectrometers. ^{1}H shifts are referenced internally to residual proteo-solvent, relative to TMS ($\delta = 0$); ^{19}F, ^{31}P and ^{11}B shifts were referenced externally to $CFCl_3$, 85% H_3PO_4 ($\delta = 0$) and $BF_3{\cdot}OEt_2$ respectively. *J* values are given in Hz.

X-ray data collection, reduction, solution and refinement

A typical crystal was mounted on MiTeGen MicroMounts using perfluoropolyether oil and cooled rapidly to 150 K in a stream of N_2 using an Oxford Cryosystems CryoStream unit.[70] Data were collected with an Enraf-Nonius KappaCCD diffractometer, using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Raw frame data were reduced using the DENZO-SMN package.[71] Intensity data were corrected using multi-scan method with SCALEPACK (within DENZO-SMN). The structure was solved using direct methods with SIR92[72] and refined using full-matrix least squares refinement on all F^2 data using the CRYSTALS program suite.[73,74] The structure was found to be a non-merhodal twin due to a 180 degree rotation about the *a*-axis.[75] In general distances and angles were calculated using the full variance–covariance matrix; dihedral angles were calculated using PLATON.[76]

Synthesis of tris(2,2′,2″-perfluorobiphenyl)borane (PBB).[55] $B(C_{12}F_9)_3$ PBB was synthesised according to a literature procedure and single crystals were grown by slow cooling of a hot hexane solution to 20 °C.

Crystal structure determination of PBB

Crystal data. $C_{36}F_{27}B$, triclinic ($P\bar{1}$), $a = 10.4698(3)$, $b = 16.4472(5)$, $c = 20.0203(6)$ Å, $\alpha = 77.4208(15)$, $\beta = 90.0050(15)$, $\gamma = 80.2753(16)°$, $V = 3313.93(17)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $\mu = 0.219$ mm^{-1}, $D_{calc} = 1.916$ Mg m^{-3}, 14 572 independent reflections [R(int) = 0.049]; $R_1 = 0.0868$, w$R_2 = 0.2264$ [$I > 2\sigma(I)$]. CCDC 866505.

Synthesis of (2,2,6,6-Me$_4$C$_5$H$_6$N)B(C$_{12}$F$_9$)$_3$, 1, [N(C$_2$H$_4$)$_3$N]-B(C$_{12}$F$_9$)$_3$, 2, and (2,6-Me$_2$C$_5$H$_3$NH)B(C$_{12}$F$_9$)$_3$, 3. These compounds were synthesised in a similar manner and thus only one preparation is described. $B(C_{12}F_9)_3$ (37.8 mg, 0.040 mmol) and TMP (5.6 mg, 0.040 mmol) were dissolved in 0.7 ml d_8-toluene in a vial to give a yellow (**1** and **3**) or peach-orange (**2**) solution which was transferred to a Young's tap NMR tube.

1. ^{11}B{^{1}H} NMR (96 MHz, C_7D_8) δ ppm 70.0 (s, br); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 1.54 (2 H, m, CH_2), 1.23 (4 H, t, $^{3}J_{HH} = 6.0$, CH_2), 1.03 (12 H, s, CH_3); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −119.59 (3 F, s, br), −131.82 (3 F, s, br), −137.32 (6 F, s, br), −143.49 (3 F, td, $^{3}J_{FF} = 20.9$, $^{4}J_{FF} = 9.3$), −149.02 (3 F, t, $^{3}J_{FF} = 21.3$), −150.42 (3 F, td, $^{3}J_{FF} = 21.2$, $^{4}J_{FF} = 6.5$), −160.57 (6 F, t, $^{3}J_{FF} = 17.1$).

2. ^{11}B{^{1}H} NMR (96 MHz, C_7D_8) δ ppm 70.0 (s, br); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 2.39 (12 H, s); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −119.63 (3 F, s, br), −131.82 (3 F, s, br), −137.37 (6 F, s, br), −143.44 (3 F, td, $^{3}J_{FF} = 20.7$, $^{4}J_{FF} = 9.5$), −149.00 (3 F, t, $^{3}J_{FF} = 21.6$), −150.41 (3 F, td, $^{3}J_{FF} = 21.55$, $^{4}J_{FF} = 6.0$), −160.57 (6 F, t, $^{3}J_{FF} = 17.2$).

3. ^{11}B{^{1}H} NMR (96 MHz, C_7D_8) δ ppm 67.0 (br, s); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 7.01 (1 H, t, $^{3}J_{HH} = 7.7$, CH), 6.56 (2 H, d, $^{3}J_{HH} = 7.7$, CH), 2.39 (6 H, s, CH_3); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −119.84 (3F, s, br), −132.05 (3 F, s, br), −137.57 (6 F, s, br), −143.73 (3 F, td, $^{3}J_{FF} = 20.7$, $^{4}J_{FF} = 9.5$), −149.25 (3 F, t, $^{3}J_{FF} = 21.3$), −150.66 (3 F, td, $^{3}J_{FF} = 21.3$, $^{4}J_{FF} = 6.5$), −160.82 (6 F, t, $^{3}J_{FF} = 17.2$).

NMR scale synthesis of [2,2,6,6-Me$_4$C$_5$H$_6$NH$_2$][HB(C$_{12}$F$_9$)$_3$] 4, [N(C$_2$H$_4$)$_3$NH][HB(C$_{12}$F$_9$)$_3$] 5, and [2,6-Me$_2$C$_5$H$_3$NH][HB-(C$_{12}$F$_9$)$_3$] 6. These compounds were synthesised in a similar manner and thus only one preparation is described. A Young's tap NMR tube containing the FLP **1** (0.040 mmol) in 0.7 ml d_8-toluene was freeze–thaw–degassed (×3) and backfilled with H_2 (1 atm). The sealed reaction was heated to 90 °C for 3 days.

4. ^{11}B NMR (96 MHz, C_7D_8) δ ppm −18.41 (d, $^{1}J_{BH} = 82.2$); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 3.31 (1 H, s, br, BH), 1.39 (2 H, quin, $^{3}J_{HH} = 5.4$, CH_2), 1.12 (4 H, t, $^{3}J_{HH} = 5.4$, CH_2), 0.89 (12 H, s, CH_3); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −130.12 (3 F, s, br), −139.38 (3 F, dd, $^{3}J_{FF} = 20.7$, $^{4}J_{FF} = 13.0$), −141.98 (3 F, d, $^{3}J_{FF} = 21.6$), −142.22 (3 F, d, $^{3}J_{FF} = 22.4$), −155.51 (3 F, t, $^{3}J_{FF} = 21.1$), −159.01 (3 F, t, $^{3}J_{FF} = 22.4$), −162.72 (3 F, t, $^{3}J_{FF} = 21.1$), −163.91 (3 F, t, $^{3}J_{FF} = 21.1$), −165.03 (3 F, td, $^{3}J_{FF} = 21.0$, $^{4}J_{FF} = 6.9$).

5. ^{11}B NMR (96 MHz, C_7D_8) δ ppm −18.58 (d, $^{1}J_{BH} = 86.3$); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 13.07 (1 H, s, br, NH), 2.27 (12H, s, br, CH_2); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −138.43 (3 F, dd, $^{3}J_{FF} = 21.6$, $^{4}J_{FF} = 12.5$), −142.44 (3 F, d, $^{3}J_{FF} = 22.0$), −142.65 (3 F, dd, $^{3}J_{FF} = 23.0$, $^{4}J_{FF} = 7.0$), −155.05 (3 F, t, $^{3}J_{FF} = 21.0$), −159.71 (3 F, t, $^{3}J_{FF} = 22.6$), −162.15 (3 F, t, $^{3}J_{FF} = 21.0$), −163.68 (3 F, tt, $^{3}J_{FF} = 21.7$, $^{4}J_{FF} = 6.5$), −164.80 (3 F, td, $^{3}J_{FF} = 21.6$, $^{4}J_{FF} = 7.8$).

6. ^{11}B NMR (96 MHz, C_7D_8) δ ppm −18.42 (d, $^{1}J_{BH} = 84.3$); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 7.05 (1 H, t, $^{3}J_{HH} = 7.6$, CH), 6.53 (2 H, d, $^{3}J_{HH} = 7.6$, CH), 3.53 (1 H, s, br, BH), 2.16 (6 H, s, CH_3); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −129.62 (3 F, s, br), −140.55 (3 F, dd, $^{3}J_{FF} = 20.7$, $^{4}J_{FF} = 12.1$), −141.75 (3 F, d, $^{3}J_{FF} = 23.3$), −142.27 (3 F, d, $^{3}J_{FF} = 22.4$), −156.07 (3 F, t, $^{3}J_{FF} = 21.1$), −159.40 (3 F, t, $^{3}J_{FF} = 22.0$), −163.48 (3 F, t, $^{3}J_{FF} = 21.1$), −164.23 (3 F, t, $^{3}J_{FF} = 21.1$), −165.39 (3 F, t, $^{3}J_{FF} = 22.0$).

Scaled-up attempted synthesis of 4 and 6, and bulk synthesis of 5. Solutions of **1**, **2** and **3** (0.314 mmol) in 3 ml toluene were each freeze–thaw–degassed three times in a Rotaflo ampoule, and backfilled with 1 atm hydrogen. The sealed reactions were stirred at room temperature for 15 hours yielding pink (**4**), amber (**5**) and pale yellow (**6**) solutions respectively. **5** was isolated as a white powder by decanting the toluene and washing with −20 °C pentane. Yield 62 mg, 18%. Anal. Calcd for $C_{42}H_{14}BF_{27}N$: C, 47.1; H, 1.3; N, 2.6. Found: C, 47.0; H, 1.2; N, 2.6.

Synthesis of [2,2,6,6-Me$_4$C$_5$H$_6$NH$_2$][HCO$_2$B(C$_{12}$F$_9$)$_3$] 7, and [2,6-Me$_2$C$_5$H$_3$NH][HCO$_2$B(C$_{12}$F$_9$)$_3$] 8. Formic acid (0.2 ml, 5.19 mmol) was added dropwise to a stirring solution of 2,6-lutidine (0.6 ml, 5.19 mmol) in Et_2O (20 ml). The solvent was removed *in vacuo* to leave a white powder ([TMPH][O_2CH]) or colourless oil ([lutH][O_2CH]). This formate salt (0.0314 mmol) was dissolved in d_8-toluene (0.7 ml) and added to PBB (30 mg, 0.0314 mmol).

7. ^{11}B NMR (96 MHz, C_7D_8) δ ppm −0.8 (s, br); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 8.05 (1 H, s, br, O_2CH), 5.92 (2 H, br, NH), 0.97 (2 H, s, CH_2), 0.88 (4 H, t, br, CH_2), 0.68 (12 H, br, CH_3); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −124.13 (3 F, s, br), −136.05 (3 F, dd, $^3J_{FF}$ = 23.2, $^5J_{FF}$ = 10.2), −136.11 (3 F, s, br), −137.06 (3 F, s, br), −155.01 (3 F, s, br), −156.12 (3 F, t, $^3J_{FF}$ = 20.3), −158.27 (3 F, t, $^3J_{FF}$ = 19.5), −164.38 (3 F, s), −164.60 (3 F, s).

8. ^{11}B NMR (96 MHz, C_7D_8) δ ppm 0.18 (br, s); ^{1}H NMR (300 MHz, C_7D_8) δ ppm 12.53 (1 H, br, NH), 8.08 (1 H, s, O_2CH), 6.82 (1 H, t, $^3J_{HH}$ = 7.9), 6.17 (2 H, d, $^3J_{HH}$ = 7.9), 2.03 (12 H, s, CH_3); ^{19}F NMR (282 MHz, C_7D_8) δ ppm −123.79 (3 F, s, br), −136.32 (3 F, dd, $^3J_{FF}$ = 23.6, $^5J_{FF}$ = 10.4), −136.44 (3 F, s, br), −136.95 (3 F, s, br), −155.48 (3 F, t, $^3J_{FF}$ = 21.0), 156.04 (3 F, t, $^3J_{FF}$ = 20.9), −158.42 (3 F, t, $^3J_{FF}$ = 21.3), −164.51 (3 F, br), −164.74 (3 F, t, br, $^3J_{FF}$ = 20.0).

Lewis acidity determination. Gutmann–Beckett method:[60,61] An NMR tube is charged with PBB and Et_3PO in a 3 : 1 molar ratio in dry CD_2Cl_2 with a sealed capillary insert of uncoordinated Et_3PO in CD_2Cl_2 and the ^{31}P NMR spectrum was recorded at 20 °C. $^{31}P\{^1H\}$ NMR Et_3PO reference δ = 50.4 ppm; $(Et_3PO)B(C_6F_5)_3$ reference adduct δ = 77.0 ppm; reference shift $\Delta\delta$ = 26.6 ppm. $(Et_3PO)B(C_{12}F_9)_3$ adduct δ = 80.7 ppm, shift $\Delta\delta$ = 30.27.‡

Childs method:[67] To an NMR tube charged with PBB in 0.6 ml dry CD_2Cl_2, *trans*-crotonaldehyde (5 mg, 0.0059 ml, 0.07 mmol) in 0.2 ml CD_2Cl_2 was added *via* vacuum transfer to the frozen sample, and the temperature of the reaction maintained below −20 °C. The ^{1}H NMR spectrum was recorded at −20 °C and the difference in shift of the vinylic proton H_3 measured: $\delta(H_3$ uncoordinated) 6.88 ppm; $\delta(H_3$ coordinated) 7.86 ppm; $\Delta\delta$ = 0.98 ppm.

Conclusion

Three novel FLP systems capable of affecting metal-free hydrogen-splitting have been prepared using the bulky borane PBB in combination with the nitrogen bases TMP, 2,6-lutidine and DABCO. The vastly increased bulk of PBB compared to $B(C_6F_5)_3$ reduces the reactivity of its analogous frustrated Lewis pairs significantly. We continue to investigate activation of small molecules by these unquenched donor–acceptor adducts and intend to report matters in due course.

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