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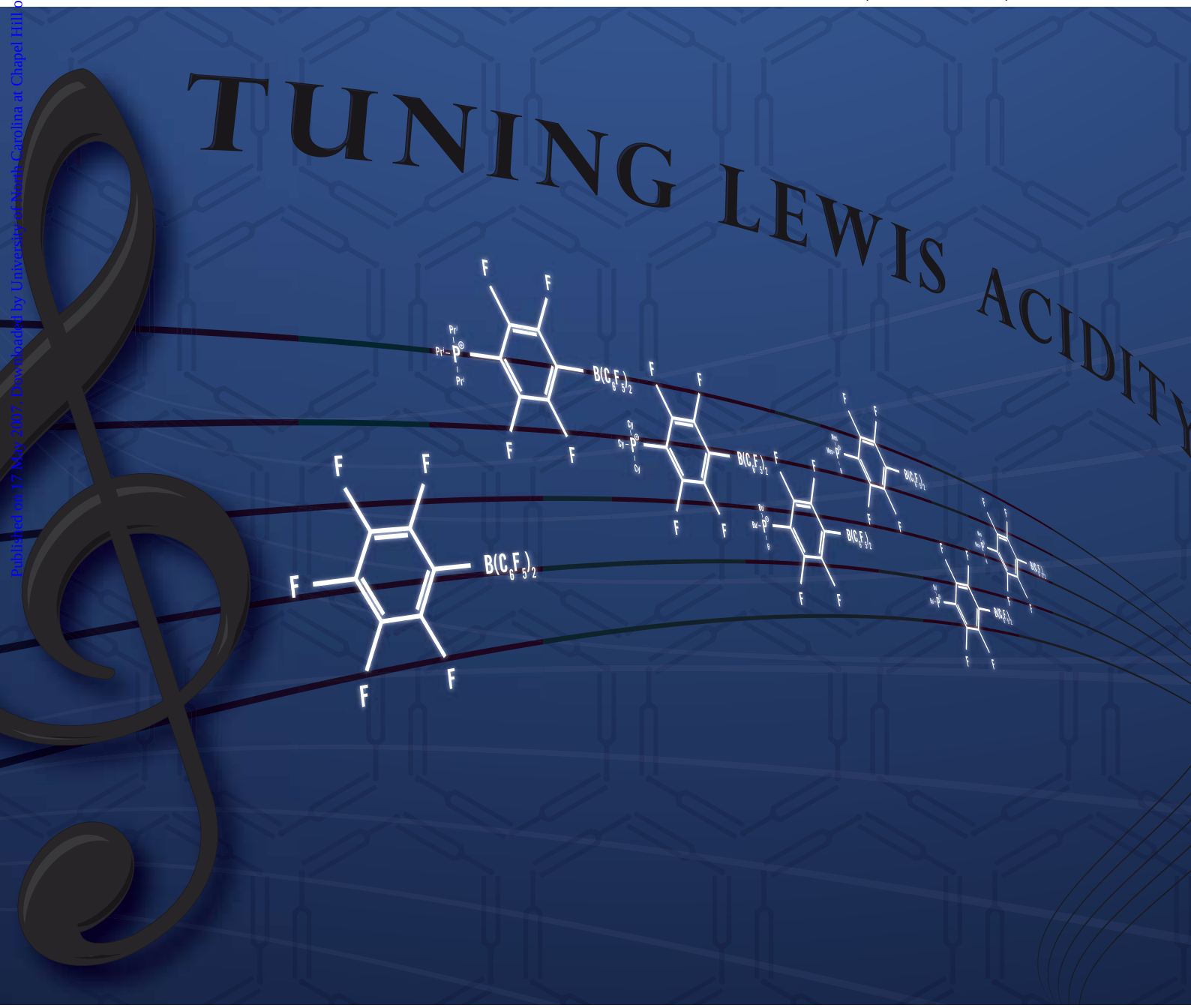

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Tuning Lewis acidity using the reactivity of "frustrated Lewis pairs": facile formation of phosphine-boranes and cationic phosphonium-boranes†

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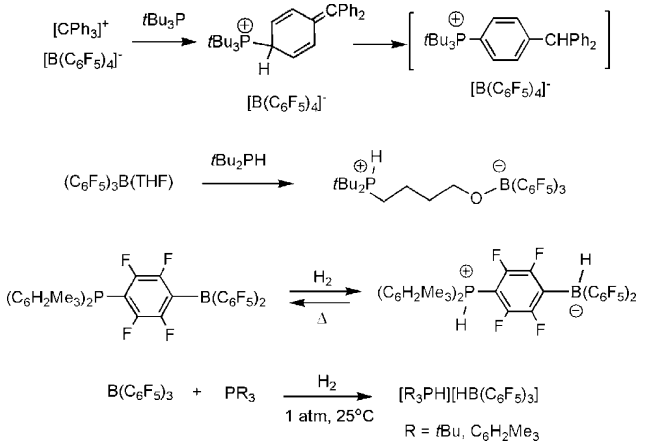
The concept of "frustrated Lewis pairs" involves donor and acceptor sites in which steric congestion precludes Lewis acid–base adduct formation. In the case of sterically demanding phosphines and boranes, this lack of self-quenching prompts nucleophilic attack at a carbon *para* to B followed by fluoride transfer affording zwitterionic phosphonium borates $[R_3P(C_6F_4)BF(C_6F_5)_2]$ and $[R_2PH(C_6F_4)BF(C_6F_5)_2]$. These can be easily transformed into the cationic phosphonium-boranes $[R_3P(C_6F_4)B(C_6F_5)_2]^+$ and $[R_2PH(C_6F_4)B(C_6F_5)_2]^+$ or into the neutral phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$. This new reactivity provides a modular route to a family of boranes in which the steric features about the Lewis acidic center remains constant and yet the variation in substitution provides a facile avenue for the tuning of the Lewis acidity. Employing the Gutmann–Beckett and Childs methods for determining Lewis acid strength, it is demonstrated that the cationic boranes are much more Lewis acidic than $B(C_6F_5)_3$, while the acidity of the phosphine-boranes is diminished.

Introduction

Lewis acids and bases play dominant roles in much of chemistry. For example, Lewis basic phosphines are ubiquitous ligands in transition metal chemistry and many forms of catalysis. On the other hand, Lewis acidic boranes are pervasive in studies of olefin polymerization[1,2] and a variety of Lewis acid catalyzed reactions in organic chemistry.[3–9] A large range of phosphines are either commercially available or readily prepared, allowing specific tuning of the steric and electronic nature of the Lewis base. The same can not be said for fluoroarylboranes. While the borane $B(C_6F_5)_3$ is very commonly used,[3,5] studies targeting structural modifications of this borane class have only begun to appear in the last few years. In particular, the groups of Marks[10–20] and Piers[21–31] have developed elegant syntheses to either elaborate the substituents on B or to access bis-borane compounds.[32] Others have developed seemingly more straightforward routes to fluoroarylborane derivatives[6,33–35] but in all cases these syntheses are not trivial. Nonetheless, such modifications of Lewis acids has been shown to dramatically impact the catalyst activity, stability and polymer properties derived from olefin polymerization.[36–45] In addition Lewis acid perturbations serve to modify reactivity in a number of catalytic organic transformations.[46,47]

In 1923, Lewis first proposed his now universally accepted molecular orbital-based rationale for acid/base reactions to describe dative donor–acceptor adducts.[48] The strong Lewis acid $B(C_6F_5)_3$ is known to form such Lewis adducts with a wide variety of Lewis bases.[49] However, we have recently observed several systems in which sterically demanding phosphine donors and Lewis acids generate what we now coin "frustrated Lewis pairs" (FLPs) in that this Lewis acid–base couple is sterically incapable of adduct formation, which opens alternate reaction pathways. An example of such FLP reactivity is provided by the reactions of $[CPh_3][B(C_6F_5)_4]$ and donors (Scheme 1). While sterically unencumbered phosphines or pyridines form classical Lewis adducts with trityl cation, reaction with bulky phosphines (PR_3, R = *i*-Pr, Cy, *t*-Bu) result in nucleophilic attack at the *para*-position of an aryl ring of the trityl cation.[50] In a related fashion mixtures of bulky phosphines with the adduct $THF–B(C_6F_5)_3$ do not undergo expected Lewis base exchange reactions but rather effect exclusive nucleophilic ring opening of the bound THF to give butoxy-tethered $R_2PH–C_4H_8O–B(C_6F_5)_3$ phosphonium-borates (Scheme 1).[51] More recently we have shown that $(C_6H_2Me_3$-2,4,6$)_2PH$ and $B(C_6F_5)_3$ generates a FLP prompting nucleophilic aromatic substitution by the phosphine at the C *para* to B with concomitant fluoride transfer to B. Subsequent removal of HF afforded a monomeric phosphine-borane which proved capable of reversible binding of H_2 (Scheme 1).[52] This unprecedented



Scheme 1 Reactivity of "frustrated Lewis pairs".

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reactivity is attributed to FLP nature of the phosphine-borane. In an analogous fashion, solutions of the FLPs derived from $B(C_6F_5)_3$ and bulky phosphines (PR_3; R = *t*-Bu, $C_6H_2Me_3$-2,4,6) have also been shown to heterolytically cleave H_2 to give the phosphonium-borates $[R_3PH][HB(C_6F_5)_3]$ (Scheme 1).[53] In this report, we exploit the reactivity of such "frustrated Lewis pairs" to access a family of *para*-substituted cationic phosphonium-boranes and neutral phosphine-boranes. The former cationic boranes are more Lewis acidic than the parent, while the acidity of the B centers in the latter phosphine-boranes is diminished. This methodology provides a facile way to remotely tune the electronic nature of the B center with minimal impact on the steric demands about B.

Experimental

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, toluene, CH_2Cl_2 and Et_2O) were purified employing a Grubbs' type column systems manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were generously donated by NOVA Chemicals Corporation. $(C_6H_2Me_3\text{-}2,4,6)_2PH$ was prepared as reported in the literature.[54]

Synthesis of $[R_3P(C_6F_4)BF(C_6F_5)_2]$ R = *i*-Pr (1), R = Cy (2), of $[R_2PH(C_6F_4)BF(C_6F_5)_2]$ R = *t*-Bu (3), $C_6H_2Me_3$-2,4,6 (4)

These compounds were prepared in a similar fashion although for species **4** refluxing in toluene was required, and thus only one preparation is detailed. A clear yellow solution of $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) and *i*-Pr_3P (0.156 g, 0.98 mmol) in toluene (20 mL) was allowed to stir for 12 h at 25 °C during which time a white precipitate formed. Pentane (10 mL) was added, the mixture filtered and dried *in vacuo* for 1 h. The product was collected as a white solid. Yield 0.620 g (94%). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2–pentane solution at 25 °C. (**1**): ^1H NMR (CD_2Cl_2): 3.23 (m, 3H, *i*-Pr), 1.47 (dd, 18H, $^3J_{H-P} = 18$ Hz, $^3J_{H-H} = 6$ Hz, *i*-Pr). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −0.89 (d, $^1J_{B-F} = 64$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 149.83 (dm, $^1J_{C-F} = 247$ Hz, C_6F_4), 148.20 (dm, $^1J_{C-F} = 230$ Hz, *o*-C_6F_5), 147.12 (dm, $^1J_{C-F} = 255$ Hz, C_6F_4), 139.34 (dm, $^1J_{C-F} = 250$ Hz, *p*-C_6F_5), 136.95 (dm, $^1J_{C-F} = 250$ Hz, *m*-C_6F_5), 89.30 (dm, $^1J_{C-P} = 70$ Hz, *p*-C_6F_4), 23.85 (d, $^1J_{C-P} = 40$ Hz, i-Pr), 17.20 (s, i-Pr). ^{19}F NMR (CD_2Cl_2): −126.84 (s, 2F, C_6F_4), −129.71 (s, 2F, C_6F_4), −134.14 (d, 4F, $^3J_{F-F} = 16$ Hz, *o*-C_6F_5), −156.11 (t, 2F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5), −165.07 (t, 4F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5), −191.37 (d, 1F, $^1J_{F-B} = 68$ Hz, B*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 53.20 (m). Anal. Calcd. for $C_{27}H_{21}BF_{15}P$: C, 48.24; H, 4.61. Found: C, 48.52; H, 4.76. (**2**): Yield 0.738 g (96%). ^1H NMR (CD_2Cl_2): 3.05 (m, 3H, Cy), 2.10–1.22 (br m, 30H, Cy). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −0.70 (d, $^1J_{B-F} = 58$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 150.40 (dm, $^1J_{C-F} = 245$ Hz, C_6F_4), 148.71 (dm, $^1J_{C-F} = 240$ Hz, *o*–C_6F_5), 147.62 (dm, $^1J_{C-F} = 255$ Hz, C_6F_4), 139.84 (dm, $^1J_{C-F} = 250$ Hz, *p*-C_6F_5), 137.40 (dm, $^1J_{C-F} = 250$ Hz, *m*-C_6F_5), 90.20 (dm, $^1J_{C-P} = 70$ Hz, *p*-C_6F_4), 33.31 (d, $^1J_{C-P} = 39$ Hz, Cy), 28.22 (d, $^2J_{C-P} = 3$ Hz, Cy), 27.40 (d, $^3J_{C-P} = 12$ Hz, Cy), 25.93 (s, Cy). ^{19}F NMR (CD_2Cl_2): −128.76 (s, 2F, C_6F_4), −132.03 (s, 2F, C_6F_4), −135.81 (d, 4F, $^3J_{F-F} = 16$ Hz, *o*-C_6F_5), −161.92 (t, 2F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5), −166.83 (t, 4F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5), −193.11 (d, 1F, $^1J_{F-B} = 72$ Hz, B*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.6 (m). Anal. Calcd. for $C_{36}H_{33}BF_{15}P$: C, 54.57; H, 4.20. Found: C, 54.22; H, 3.98. (**3**): Yield 0.552 g (78%). ^1H NMR (CD_2Cl_2): 6.32 (d, 1H, $^1J_{H-P} = 465$ Hz, P*H*), 1.58 (d, 18H, $^1J_{H-P} = 19$ Hz, *t*-Bu}. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): 0.80 (d, $^1J_{B-F} = 62$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 149.33 (dm, $^1J_{C-F} = 230$ Hz, C_6F_4), 146.65 (dm, $^1J_{C-F} = 230$ Hz, *o*-C_6F_5), 139.64 (dm, $^1J_{C-F} = 280$ Hz, *p*-C_6F_5), 137.50 (dm, $^1J_{C-F} = 260$ Hz, *m*-C_6F_5), 136.58 (dm, $^1J_{C-F} = 230$ Hz, C_6F_4), 36.92 (d, $^1J_{C-P} = 30$ Hz, *t*-Bu), 28.41 (s, *t*-Bu). ^{19}F NMR (CD_2Cl_2): −126.23 (s, 1F, C_6F_4), −127.90 (s, 1F, C_6F_4), −128.40 (s, 1F, C_6F_4), −132.52 (s, 1F, C_6F_4), −135.81 (d, 4F, $^3J_{F-F} = 23$ Hz, *o*-C_6F_5), −161.64 (t, 2F, $^3J_{F-F} = 23$ Hz, *p*-C_6F_5), −166.69 (t, 4F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5), −192.06 (bs, 1F, B*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 34.21 (m). Anal. Calcd. for $C_{26}H_{19}BF_{15}P$: C, 47.45; H, 2.91. Found: C, 47.06; H, 2.86. (**4**): Yield 1.72 g (75%). ^1H NMR (CD_2Cl_2): 8.52 (d, 1H, $^1J_{H-P} = 503$ Hz, P*H*), 7.14 (d, $^4J_{H-P} = 6$ Hz, 4H, $P(C_6H_2)_2$), 2.39 (s, 6H, C_6H_2Me-4), 2.28 (s, 12H, $C_6H_2Me_2$-2,6). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): 0.44 (d, $^1J_{B-F} = 62$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 148.36 (dm, $^1J_{C-F} = 240$ Hz, *o*-C_6F_5), 148.33 (d, $^4J_{C-P} = 2.78$ Hz, *p*-C_6H_2), 146.88 (dm, $^1J_{C-F} = 240$ Hz, *p*-C_6F_5), 144.26 (d, $^2J_{C-P} = 12$ Hz, *o*-C_6H_2), 137.25 (dm, $^1J_{C-F} = 240$ Hz, *m*-C_6F_5), 132.95 (d, $^3J_{C-P} = 12$ Hz, *m*-C_6H_2), 108.90 (d, $^1J_{C-P} = 88$ Hz, C_6H_2), 21.99 (d, $^3J_{C-P} = 9.68$ Hz, $C_6H_2Me_2$-2,6), 21.81 (s, C_6H_2Me-4). ^{19}F NMR (CD_2Cl_2): −129.02 (s, 2F, C_6F_4), −133.93 (s, 2F, C_6F_4), −135.81 (d, 4F, $^3J_{F-F} = 14$ Hz, *o*-C_6F_5), −161.75 (t, 2F, $^3J_{F-F} = 17$ Hz, *p*-C_6F_5), −166.76 (t, 4F, $^3J_{F-F} = 19.74$ Hz, *m*-C_6F_5), −192.74 (bs, 1F, B*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −37.65 (m, $^3J_{P-F} = 8$ Hz). Anal. Calcd. for $C_{36}H_{23}BF_{15}P$: C, 55.27; H, 2.96. Found: C, 54.75; H, 3.09.

Synthesis of $[R_3P(C_6F_4)BH(C_6F_5)_2]$ R = *i*-Pr (5), R = Cy (6), of $[R_2PH(C_6F_4)BH(C_6F_5)_2]$ R = *t*-Bu (7), $C_6H_2Me_3$-2,4,6 (8)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of **1** (0.400 g, 0.600 mmol) dissolved in CH_2Cl_2 (10 mL) was added $(CH_3)_2SiHCl$ (0.66 mL, 6.00 mmol) *via* syringe. The reaction was allowed to stir 12 h, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 356 mg (92%). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2–pentane solution at 25 °C. (**5**): ^1H NMR (CD_2Cl_2): 3.68 (q, 1H, $^1J_{H-B} = 90$ Hz, B*H*), 3.25 (m, 3H, *i*-Pr), 1.46 (d, 18H, $^3J_{H-P} = 20$ Hz, *i*-Pr). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −25.28 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 150.43 (dm, $^1J_{C-F} = 250$ Hz, C_6F_4), 148.25 (dm, $^1J_{C-F} = 235$ Hz, *o*-C_6F_5), 146.98 (dm, $^1J_{C-F} = 255$ Hz, C_6F_4), 139.74 (dm, $^1J_{C-F} = 250$ Hz, *p*-C_6F_5), 136.89 (dm, $^1J_{C-F} = 252$ Hz, *m*-C_6F_5), 93.67 (dm, $^1J_{C-P} = 68$ Hz, *p*-C_6F_4), 24.02 (d, $^1J_{C-P} = 44$ Hz, *i*-Pr), 17.22 (s, *i*-Pr). ^{19}F NMR (CD_2Cl_2): −127.60 (m, 2F, C_6F_4), −132.60 (m, 2F, C_6F_4), −134.18 (d, 4F, $^3J_{F-F} = 18$ Hz, *o*-C_6F_5), −164.09 (t, 2F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5), −167.66 (t, 4F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2,

121 MHz, 300 K): δ 52.57 (m). Anal. Calcd. for $C_{27}H_{22}BF_{14}P$: C, 49.57; H, 3.39. Found: C, 49.92; H, 3.44. (**6**): Yield 469 mg (95%). ^{1}H NMR (CD_2Cl_2): 3.67 (q, 1H, $^1J_{H-B} = 94$ Hz, B*H*), 2.93 (m, 3H, Cy), 2.05–1.25 (br m, 30H, Cy). ^{11}B{^{1}H} NMR (CD_2Cl_2): −25.30 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: δ 150.40 (dm, $^1J_{C-F} = 245$ Hz, C_6F_4), 148.71 (dm, $^1J_{C-F} = 240$ Hz, *o*-C_6F_5), 147.62 (dm, $^1J_{C-F} = 255$ Hz, C_6F_4), 139.84 (dm, $^1J_{C-F} = 250$ Hz, *p*-C_6F_5), 137.40 (dm, $^1J_{C-F} = 250$ Hz, *m*-C_6F_5), 90.20 (dm, $^1J_{C-P} = 70$ Hz, *p*-C_6F_4), 33.31 (d, $^1J_{C-P} = 39$ Hz, Cy), 28.22 (d, $^2J_{C-P} = 3$ Hz, Cy), 27.40 (d, $^3J_{C-P} = 12$ Hz, Cy), 25.93 (s, Cy). ^{19}F NMR (CD_2Cl_2): −127.74 (s, 2F, C_6F_4), −133.16 (s, 2F, C_6F_4), −133.98 (d, 4F, $^3J_{F-F} = 20$ Hz, *o*-C_6F_5), −164.02 (t, 2F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5), −167.50 (t, 4F, $^3J_{F-F} = 24$ Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 40.99 (m). Anal. Calcd. for $C_{36}H_{34}BF_{14}P$: C, 55.83; H, 4.43. Found: C, 56.12; H, 4.53. (**7**): Yield 160 mg (83%). ^{1}H NMR (CD_2Cl_2): 6.23 (d, 1H, $^1J_{H-P} = 462$ Hz, P*H*), 3.46 (q, 1H, $^1J_{H-B} = 82$ Hz, B*H*), 1.56 (d, 18H, $^1J_{H-P} = 19$ Hz, *t*-Bu). ^{11}B{^{1}H} NMR (CD_2Cl_2): −25.19 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 150.01 (dm, $^1J_{C-F} = 244$ Hz, C_6F_4), 148.70 (dm, $^1J_{C-F} = 237$ Hz, *o*-C_6F_5), 146.26 (dm, $^1J_{C-F} = 253$ Hz, C_6F_4), 145.35 (dm, $^1J_{C-F} = 253$ Hz, C_6F_4), 138.85 (dm, $^1J_{C-F} = 245$ Hz, *p*-C_6F_5), 137.16 (dm, $^1J_{C-F} = 247$ Hz, *m*-C_6F_5), 36.77 (d, $^1J_{C-P} = 31$ Hz, *t*-Bu), 28.37 (s, *t*-Bu). ^{19}F NMR (CD_2Cl_2): −126.93 (s, 1F, C_6F_4), −127.38 (s, 2F, C_6F_4), −133.90 (m, 1F, C_6F_4), −134.13 (d, 4F, $^3J_{F-F} = 20$ Hz, *o*-C_6F_5), −163.98 (t, 2F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5), −167.56 (t, 4F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 33.97 (m). Anal. Calcd. for $C_{26}H_{19}BF_{15}P$: C, 48.78; H, 3.15. Found: C, 48.14; H, 3.26. (**8**): Yield 375 mg (96%). ^{1}H NMR (CD_2Cl_2): 8.49 (d, 1H, $^1J_{H-P} = 502$ Hz, P*H*), 7.12 (d, $^4J_{H-P} = 6$ Hz, 4H, C_6H_2), 3.65 (q, $^1J_{H-B} = 85$ Hz, B*H*), 2.37 (s, 6H, C_6H_2Me-4), 2.26 (s, 12H, $C_6H_2Me_2$-2,6). ^{11}B{^{1}H} NMR (CD_2Cl_2): −25.16 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 149.92 (dm, $^1J_{C-F} = 240$ Hz, *o*-C_6F_5), 148.85 (dm, $^1J_{C-F} = 240$ Hz, *p*-C_6F_5), 148.28 (s, *p*-C_6H_2), 144.33 (d, $^2J_{C-P} = 11$ Hz, *o*-C_6H_2), 137.19 (dm, $^1J_{C-F} = 240$ Hz, *m*-C_6F_5), 133.14 (d, $^3J_{C-P} = 10$ Hz, *m*-C_6H_2), 109.46 (d, $^1J_{C-P} = 90$ Hz, P-C_6H_2), 22.04 (d, $^3J_{C-P} = 9$ Hz, $C_6H_2Me_2$-2,6), 21.86 (s, C_6H_2Me-*4*). ^{19}F NMR (CD_2Cl_2): −127.52 (s, 2F, C_6F_4), −134.09 (d, 4F, $^3J_{F-F} = 20$ Hz, *o*-C_6F_5), −134.95 (s, 2F, C_6F_4), −163.87 (t, 2F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5), −167.43 (t, 4F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): −37.86 (m, $^3J_{P-F} = 8$ Hz). Anal. Calcd. for $C_{36}H_{24}BF_{14}P$: C, 56.57; H, 3.16. Found: C, 55.62; H, 3.33.

Synthesis of $[R_3P(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ R = *i*-Pr (9), R = Cy (10), of $[R_2PH(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ R = *t*-Bu (11), $C_6H_2Me_3$-2,4,6 (12)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. An orange solution of $[Ph_3C][B(C_6F_5)_4]$ (0.420 g, 0.456 mmol) in CH_2Cl_2 (2 mL) was added to a slurry of **5** (0.300 g, 0.457 mmol) in CH_2Cl_2 (5 mL) to give a faint yellow solution. The reaction was allowed to stir for 30 min and the volatiles were removed *in vacuo*. Pentane (5 mL) was added and the mixture filtered and washed with toluene (2 mL) and pentane (3 × 2 mL) to give an off white solid. Yield 0.450 g (74%). (**9**): ^{1}H NMR (CD_2Cl_2): 3.27 (m, 3H, *i*-Pr), 1.49 (dd, 18H, $^3J_{H-P} = 18$ Hz, $^3J_{H-H} = 7$ Hz, *i*-Pr). ^{11}B{^{1}H} NMR (CD_2Cl_2) partial: −16.55 (s, $B(C_6F_5)_4$). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 150.20 (dm, $^1J_{C-F} = 255$ Hz, C_6F_4), 148.60 (dm, $^1J_{C-F} = 240$ Hz, C_6F_5), 147.95 (dm, $^1J_{C-F} = 250$ Hz, C_6F_5), 147.10 (dm, $^1J_{C-F} = 260$ Hz, C_6F_4), 138.52 (dm, $^1J_{C-F} = 245$ Hz, C_6F_5), 135.32 (dm, $^1J_{C-F} = 240$ Hz, C_6F_5), 134.40 (dm, $^1J_{C-F} = 245$ Hz, C_6F_5), 93.20 (dm, $^1J_{C-P} = 60$ Hz, *p*-C_6F_4), 24.05 (d, $^1J_{C-P} = 40$ Hz, *i*-Pr), 17.10 (s, *i*-Pr). ^{19}F NMR (CD_2Cl_2): −125.35 (s, 2F, C_6F_4), −129.08 (s, 2F, C_6F_4), −132.42 (br s, 4F, *o*-C_6F_5 borane), −133.55 (s, 8F, *o*-C_6F_5 borate), −146.72 (br s, 2F, *p*-C_6F_5 borane), −162.18 (br s, 4F, *m*-C_6F_5 borane), −164.20 (t, 8F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5 borate), −168.08 (t, 8F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5 borate). ^{31}P{^{1}H} NMR (CD_2Cl_2): 56.10 (m, $^3J_{P-F} = 16$ Hz). Anal. Calcd. for $C_{51}H_{21}B_2F_{34}P$: C, 45.98; H, 1.59. Found: C, 46.58; H, 1.79. (**10**): Yield 0.332 g (87%). ^{1}H NMR (CD_2Cl_2): 2.98 (m, 3H, Cy), 2.01–1.29 (br m, 30H, Cy). ^{11}B{^{1}H} NMR (CD_2Cl_2) partial: −16.97 (s, $B(C_6F_5)_4$). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 149.27 (dm, $^1J_{C-F} = 257$ Hz, C_6F_4), 148.66 (dm, $^1J_{C-F} = 240$ Hz, C_6F_5), 148.15 (dm, $^1J_{C-F} = 250$ Hz, C_6F_5), 147.00 (dm, $^1J_{C-F} = 260$ Hz, C_6F_4), 138.52 (dm, $^1J_{C-F} = 245$ Hz, C_6F_5), 136.81 (dm, $^1J_{C-F} = 240$ Hz, C_6F_5), 136.16 (dm, $^1J_{C-F} = 245$ Hz, C_6F_5), 95.50 (dm, $^1J_{C-P} = 65$ Hz, *p*-C_6F_4), 33.72 (d, $^1J_{C-P} = 36$ Hz, Cy), 28.23 (d, $^2J_{C-P} = 4$ Hz, Cy), 27.3 (d, $^3J_{C-P} = 12$ Hz, Cy), 25.72 (s, Cy). ^{19}F NMR (CD_2Cl_2): −124.33 (s, 2F, C_6F_4), −126.56 (br s, 4F, *o*-C_6F_5 borane), −126.92 (s, 2F, C_6F_4), −133.54 (s, 8F, *o*-C_6F_5 borate), −140.28 (br s, 2F, *p*-C_6F_5 borane), −160.25 (br s, 4F, *m*-C_6F_5 borane), −164.28 (t, 8F, $^3J_{F-F} = 20$ Hz, *p*-C_6F_5 borate), −168.12 (t, 8F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5 borate). ^{31}P{^{1}H} NMR (CD_2Cl_2): 45.42 (m, $^3J_{P-F} = 16$ Hz). Anal. Calcd. for $C_{60}H_{33}B_2F_{34}P$: C, 49.62; H, 2.29. Found: C, 50.24; H, 2.62. (**11**): Yield 0.110 g (97%). ^{1}H NMR (CD_2Cl_2): 6.38 (d, 1H, $^1J_{H-P} = 460$ Hz, P*H*), 1.63 (d, 18H, $^1J_{H-P} = 20$ Hz, *t*-Bu). ^{11}B{^{1}H} NMR (CD_2Cl_2) partial: −16.83 (s, $B(C_6F_5)_4$). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 147.33 (dm, $^1J_{C-F} = 235$ Hz, *o*-C_6F_5), 138.62 (dm, $^1J_{C-F} = 260$ Hz, *p*-C_6F_5), 136.82 (dm, $^1J_{C-F} = 260$ Hz, *m*-C_6F_5), 37.68 (d, $^1J_{C-P} = 28$ Hz, *t*-Bu), 28.40 (s, *t*-Bu). ^{19}F NMR (CD_2Cl_2): −121.45 (s, 1F, C_6F_4), −123.58 (s, 1F, C_6F_4), −124.39 (s, 1F, C_6F_4), −126.41 (s, 1F, C_6F_4), −126.41 (s, 4F, *o*-C_6F_5 borane), −133.42 (s, 8F, *o*-C_6F_5 borate), −139.89 (s, 2F, *p*-C_6F_5 borane), −160.14 (s, 4F, *m*-C_6F_5 borane), −164.03 (t, 8F, $^3J_{F-F} = 23$ Hz, *p*-C_6F_5 borate), −167.93 (t, 8F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5). ^{31}P NMR (CD_2Cl_2): 35.42 (m). Anal. Calcd. for $C_{50}H_{19}B_2F_{34}P$: C, 45.56; H, 1.45. Found: C, 50.24; H, 1.68. (**12**): Yield 0.168 g (89%). ^{1}H NMR (CD_2Cl_2): 8.66 (d, 1H, $^1J_{H-P} = 507.90$ Hz, P*H*), 7.14 (d, $^4J_{H-P} = 7.03$ Hz, 4H, C_6H_2), 2.42 (s, 6H, C_6H_2Me-4), 2.32 (s, 12H, $C_6H_2Me_2$-2,6). ^{11}B{^{1}H} NMR (CD_2Cl_2) partial: −16.95 (s, $B(C_6F_5)_4$). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 149.64 (dm, $^1J_{C-F} = 251$ Hz, C_6F_5), 149.60 (s, *p*-C_6H_2), 148.65 (dm, $^1J_{C-F} = 240$ Hz, C_6F_5), 147.10 (dm, $^1J_{C-F} = 250$ Hz, C_6F_5), 144.37 (d, $^2J_{C-P} = 11.7$ Hz, *o*-C_6H_2), 138.63 (dm, $^1J_{C-F} = 230$ Hz, C_6F_5), 136.78 (dm, $^1J_{C-F} = 243$ Hz, C_6F_5), 135.15 (dm, $^1J_{C-F} = 240$ Hz, C_6F_5), 133.34 (d, $^3J_{C-P} = 12.3$ Hz, *m*-C_6H_2), 107.08 (d, $^1J_{C-P} = 87$ Hz, P–C_6H_2), 22.09 (d, $^3J_{C-P} = 10$ Hz, $C_6H_2Me_2$-2,6), 21.82 (s, C_6H_2Me-4). ^{19}F NMR (CD_2Cl_2): −125.18 (s, 2F, C_6F_4), −126.85 (s, 4F, *o*-C_6F_5 borane), −128.79 (s, 2F, C_6F_4), −133.49 (s, 8F, *o*-C_6F_5 borate), −140.67 (s, 2F, *p*-C_6F_5 borane), −160.36 (s, 4F, *m*-C_6F_5 borane), −164.29 (t, 8F, $^3J_{F-F} = 23$ Hz, *p*-C_6F_5 borate), −168.13 (t, 8F, $^3J_{F-F} = 20$ Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): −37.21 (m). Anal. Calcd. for $C_{60}H_{23}B_2F_{34}P$: C, 49.96; H, 1.61. Found: C, 50.55; H, 2.21.

Synthesis of $R_2P(C_6F_4)B(C_6F_5)_2$ R = *t*-Bu (13), $C_6H_2Me_3$-2,4,6 (14)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 20 mL vial was charged with **3**

(0.099 g, 0.150 mmol), toluene (10 mL) and diethyl ether (1 mL), forming a white slurry. The mixture was cooled to −35 °C and 3.0 M MeMgBr in diethyl ether (0.060 mL, 0.180 mmol) was added *via* syringe. Immediate formation of a clear yellow solution was observed. The reaction was allowed to warm to room temperature and stirred for 12 h. All volatiles were removed *in vacuo* and the product extracted with hexanes (3 × 5 mL) and filtered through Celite. The solvent was removed *in vacuo* to give a yellow solid. Yield 54 mg (56%). (**13**): ^{1}H NMR (C_6D_6): 1.15 (d, 18H, $^{1}J_{H-P}$ = 13 Hz, *t*-Bu). ^{11}B{^{1}H} NMR (C_6D_6): No signal observed. ^{13}C{^{1}H} NMR (C_6D_6) partial: 149.85 (dm, $^{1}J_{C-F}$ = 234 Hz, C_6F_4), 148.72 (dm, $^{1}J_{C-F}$ = 252 Hz, *o*-C_6F_5), 147.63 (dm, $^{1}J_{C-F}$ = 247 Hz, *p*-C_6F_5), 144.68 (dm, $^{1}J_{C-F}$ = 220 Hz, C_6F_4), 137.86 (dm, $^{1}J_{C-F}$ = 255 Hz, *m*-C_6F_5), 33.62 (dd, $^{1}J_{C-P}$ = 27 Hz, $^{4}J_{C-F}$ = 3 Hz, *t*-Bu), 30.21 (dd, $^{1}J_{C-P}$ = 17 Hz, $^{4}J_{C-F}$ = 4 Hz, *t*-Bu). ^{19}F NMR (C_6D_6): −120.24 (s, 1F, C_6F_4), −125.19 (d, 1F, $^{3}J_{F-P}$ = 110 Hz, C_6F_4), −128.99 (s, 4F, *o*-C_6F_5), −129.68 (s, 1F, C_6F_4), −130.48 (s, 1F, C_6F_4), −142.63 (s, 2F, *p*-C_6F_5), −160.68 (s, 4F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (C_6D_6): 25.08 (dm, $^{3}J_{P-F}$ = 110 Hz). UV-Vis (hexanes): C = 3.9171 × 10^{-4} mol L^{-1}; λ_{max} = 373 nm; ε = 1667 L cm^{-1} mol^{-1}. Anal. Calcd. for $C_{26}H_{18}BF_{14}P$: C, 48.93; H, 2.84. Found: C, 48.98; H, 2.98. (**14**): Yield 78 mg (82%). ^{1}H NMR (C_6D_6): 6.67 (d, $^{4}J_{H-P}$ = 3 Hz, 4H, C_6H_2), 2.29 (s, 12H, $C_6H_2Me_2$-2,6), 2.02 (s, 6H, C_6H_2Me-4). ^{11}B{^{1}H} NMR (C_6D_6): No signal observed. ^{13}C{^{1}H} NMR (C_6D_6) partial: 148.51 (dm, $^{1}J_{C-F}$ = 250 Hz, *o*-C_6F_5), 143.36, 139.73 (*ipso*-C_6H_2), 137.65 (dm, $^{1}J_{C-F}$ = 250 Hz, *p*-C_6F_5), 134.19 (dm, $^{1}J_{C-F}$ = 250 Hz, *m*-C_6F_5), 130.67 (s, C-H, C_6H_2), 127.38 (*ipso*-C_6H_2), 23.01 (d, $^{3}J_{C-P}$ = 17 Hz, $C_6H_2Me_2$-2,6), 20.86 (s, C_6H_2Me-4). ^{19}F NMR (C_6D_6): −129.32 (br s, 4F, *o*-C_6F_5), −129.90 (br s, 2F, C_6F_4), −130.82 (br s, 2F, C_6F_4), −142.96 (br s, 2F, *p*-C_6F_5), −160.59 (br s, 4F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (C_6D_6): −41.69 (t, $^{3}J_{P-F}$ = 30 Hz). UV-Vis (hexanes): C = 1.09 × 10^{-5} mol L^{-1}; λ_{max} = 455 nm; ε = 486.8 L cm $^{-1}$ mol^{-1}. Anal. Calcd. for $C_{36}H_{22}BF_{14}P$: C, 56.72; H, 2.91. Found: C, 57.03; H, 3.52.

X-Ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer (Table 1). The data (4.5° < 2θ < 45–50.0°) were collected in a hemisphere of data in 1329 frames with 10 second exposure times. The observed extinctions were consistent with the space groups in each case. A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and SHELXTL processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.[55] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F^2, minimizing the function $\omega(F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at

Table 1 Crystallographic data[a]

	1	**2**·CH_2Cl_2	**3**	**5**	**7**
Formula	$C_{27}H_{21}BF_{15}P$	$C_{37}H_{35}BCl_2F_{15}P$	$C_{26}H_{19}BF_{15}P$	$C_{27}H_{22}BF_{14}P$	$C_{26}H_{20}BF_{14}P$
Formula weight	672.22	877.33	658.19	654.23	640.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	9.544(6)	14.235(3)	8.955(5)	9.3212(7)	9.6218(12)
b/Å	18.426(11)	25.588(5)	15.767(9)	16.4421(13)	17.225(2)
c/Å	17.134(10)	21.701(3)	19.743(11)	17.8541(14)	18.468(2)
α/°					67.652(2)
β/°	105.156(12)	101.113(5)	90.482(12)	91.0440(10)	67.652(2)
γ/°					88.612(2)
V/Å^3	2908(3)	7756(2)	2788(3)	2735.9(4)	2748.4(6)
Z	4	8	4	4	4
d_{calc}/g cm^{-1}	1.535	1.503	1.568	1.588	1.547
μ/cm^{-1}	0.208	0.309	0.215	0.214	0.211
Data collected	12247	17798	11750	25837	13680
Data $F_o^2 > 3\sigma(F_o^2)$	4120	9885	3951	4817	7884
Variables	398	979	392	391	785
R^b	0.0385	0.1082	0.0436	0.0460	0.0548
R_w^c	0.1065	0.2841	0.1008	0.1222	0.1537
GOF	0.945	1.085	0.862	1.065	1.044

[a] Data collected at 20 °C with Mo-Kα radiation (λ = 0.71069 Å). [b] $R = \sum(F_o - F_c)/\sum F_o$. [c] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]\}^{1/2}$.

1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. In the case of compound **2** a two-fold disorder of the solvate CH_2Cl_2 was employed, nonetheless the resulting *R* factor was 0.1082. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the supplementary data.†

Lewis acidity determination

Lewis acidity determination *via* the Gutmann–Beckett method used a procedure similar to that described by Britovsek *et al.*[34] Here, a NMR tube was charged with the Lewis acid and Et_3PO in a 3 : 1 ratio[57] in dry CD_2Cl_2 and the $^{31}P\{^1H\}$ NMR spectra recorded at 27 °C. For the Childs method,[56] a NMR tube was charged with the Lewis acid and crotonaldehyde in a 1 : 1 ratio in dry CD_2Cl_2 and the ^1H NMR spectra recorded at −20 °C, analogous to the original report.[57] It should be noted that attempts to use C_6D_6–CD_2Cl_2 mixtures as the solvent for Childs acidity measurements at room temperature yielded inconsistent results.

Results and discussion

The reaction of $B(C_6F_5)_3$ with sterically hindered phosphines R_3P (R = *i*-Pr, Cy) or R_2PH (R = *t*-Bu, $C_6H_2Me_3$-2,4,6) in toluene proceeds over a 12 h period at 25–110 °C. Subsequent work-up afforded the white, air and moisture stable solids $[R_3P(C_6F_4)BF(C_6F_5)_2]$ (R = *i*-Pr **1**, Cy **2**) or $[R_2PH(C_6F_4)BF(C_6F_5)_2]$ (R = *t*-Bu **3**, $C_6H_2Me_3$-2,4,6 **4**) in isolated yields ranging from 75–87% (Scheme 2). These products give rise to ^{31}P NMR signals that are consistent with quaternization at P. The room temperature ^{19}F NMR spectra for **1**, **2**, and **4** exhibited two peaks for the F atoms of the C_6F_4 fragment as well as a set of *ortho*, *meta*, and *para* signals due to two C_6F_5 rings on anionic borate centers. In the case of compound **3**, the ^{19}F NMR spectrum exhibits four distinct resonances for the bridging C_6F_4 ring due to restricted rotation about the P–C bond (*vide infra*). In addition, the ^{19}F NMR spectra shows broad resonances in the range −189 to −193 ppm attributed to a B–F linkage. The corresponding ^{11}B NMR doublets, due to B–F coupling ($^1J_{B-F}$ = 62 Hz) were observed between −0.8 and 0.8 ppm. The atom connectivites in **1–3** were unambiguously confirmed by X-ray crystallography and are consistent with the proposed zwitterionic formulations (Fig. 1). The metric parameters are unexceptional, although it is noteworthy that for compound **3**, the molecules pack in a dimeric head-to-tail fashion in the solid state accommodating P–H···F–B interactions (H···F 2.554 Å). This orientation also provides parallel yet offset π-stacking of the P and B substituted (P–C_6F_4–B) arene-rings. The formation of **1–4** stands in stark contrast to the simple Lewis acid–base adducts formed by sterically less demanding donors.[5,58] The sterically congested environment of the bulky phosphine preclude coordination to B thus generating a FLP which prompts nucleophilic attack at the electrophilic *p*-carbon of an arene ring.[59]

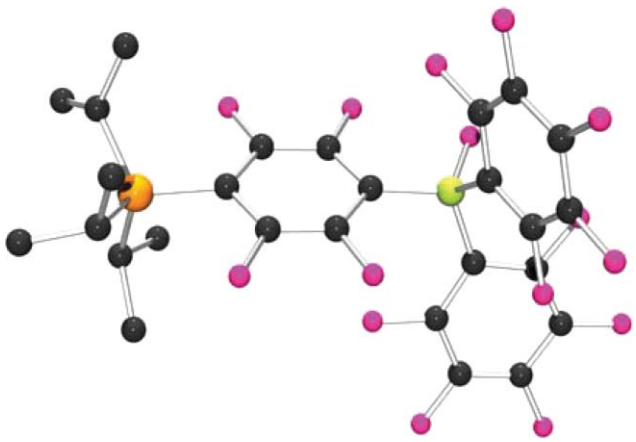
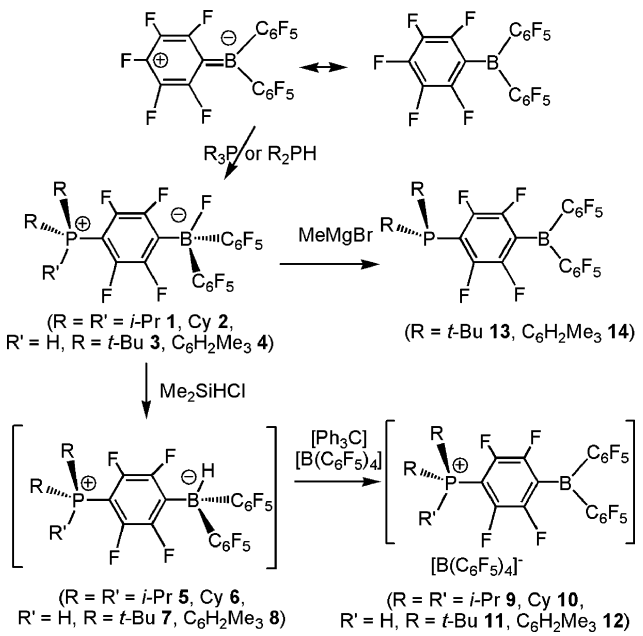


Fig. 1 POV-ray drawings of **1**. Hydrogen atoms are omitted for clarity. C: black, P: orange, F: pink, B: yellow-green.



Scheme 2 Synthetic route to **1–14**.

Compounds **1–4** rapidly react with Me_2SiHCl to effect H for F exchange at boron, generating $[R_3P(C_6F_4)BH(C_6F_5)_2]$ (R = *i*-Pr **5**, Cy **6**) and $[R_2PH(C_6F_4)BH(C_6F_5)_2]$ (R = *t*-Bu **7**, $C_6H_2Me_3$-2,4,6 **8**) (Scheme 2). The NMR spectra of **5** to **8** are similar to those of **1** to **4**. The replacement of the B–F with a B–H fragment is consistent with the resonance in the ^{11}B NMR spectrum at −25 ppm and appearance of a broad quartet in the range of 3.6 to 3.4 ppm in the ^1H NMR spectrum. The structures of compounds **5** and **7** were confirmed by X-ray crystallography (Fig. 2) and are comparable to **1–3**.

Subsequent addition of $[Ph_3C][B(C_6F_5)_4]$ to **5–8** provides direct high yield access to the cationic boranes $[(R_3P)(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ (R = *i*-Pr **9**, Cy **10**) and $[(R_2PH)(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ (R = *t*-Bu **11**, $C_6H_2Me_3$-2,4,6 **12**) (Scheme 2). While much of the NMR spectroscopy of **9–12** is similar to the corresponding precursors **1–8**, the most notable difference is the presence of a ^{11}B NMR resonance at approximately −17 ppm due to the presence of the anion $[B(C_6F_5)_4]^-$ the absence of the signal in the ^{11}B NMR spectra corresponding to a BF or BH fragment. No signals were observed for the three coordinate B-centre of the cations. In addition the ^{19}F NMR peaks of the C_6F_5 units revealed

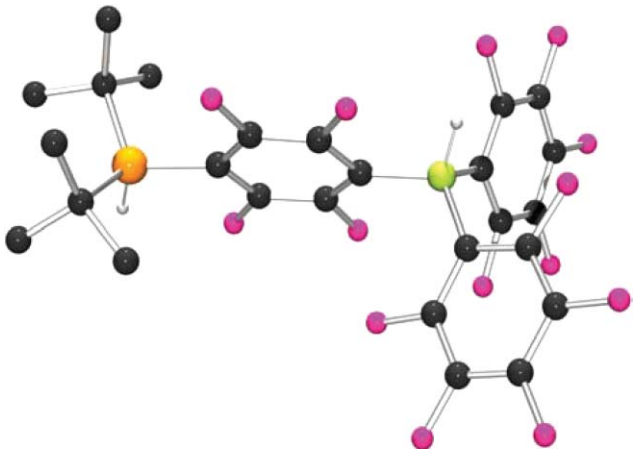


Fig. 2 POV-ray drawings of **7**. Hydrogen atoms, except for the BH and PH hydrogens, are omitted for clarity. C: black, P: orange, F: pink, B: yellow-green.

gaps between *meta* and *para* F-resonances consistent with the presence of both borane and borate fragments, establishing **9–12** as borate salts of cationic boranes. It is noteworthy that no interaction of the very weakly coordinating $[B(C_6F_5)_4]^-$ anion[60] with the corresponding cations in **9–12** was detected by NMR methods in aromatic and chloroalkane solvents. Recently, Gabbaï *et al.* have synthesized structurally related non-fluorinated cationic boranes which have been shown to be effective fluoride ion acceptors.[61]

The reaction of the phosphonium fluoroborates **3** or **4** with the Grignard reagent MeMgBr, results in the isolation of yellow and orange solids **13** and **14** in 56% and 82% yield, respectively (Scheme 2). The ^{1}H and ^{19}F NMR data confirmed the loss of HF to give the neutral species $R_2P(C_6F_4)B(C_6F_5)_2$ (R = *t*-Bu **13**, $C_6H_2Me_3$-2,4,6 **14**).[62] We have previously communicated an alternative synthesis of **14** involving the thermolysis of $[(C_6H_2Me_3\text{-}2,4,6)_2PH)(C_6F_4)BH(C_6F_5)_2]$ as well as determining its formulation *via* a crystallographic study of **14**·THF.[52] The ^{31}P NMR spectrum of **13** at 25 °C shows a signal coupled to four inequivalent F-atoms, while the ^{19}F NMR spectrum gives rise to four distinct fluorine atoms due to the C_6F_4 fragment. These observations suggest inhibited rotation about the P–C_{ArF} bond. Heating to 150 °C resulted in a broadening of the NMR signals but coalescence was not detected, consistent with a relatively high barrier to rotation. In contrast, evaluation of the parameters for a similar fluxional process was possible for **14**. The ^{31}P NMR spectrum at 25 °C revealed a resonance coupled to two equivalent F-atoms while the corresponding ^{19}F NMR spectrum showed two broad signals attributable to the C_6F_4 ring. Upon cooling to −70 °C the ^{31}P NMR signal splits into a doublet of doublets (Fig. 3) while the corresponding ^{19}F NMR signals split into doublets. These observations are consistent with coalescence of X in an ABX to A_2X spin system resulting from slowed rotation about the P–C_{ArF} bond at low temperatures. The barrier to rotation, $\Delta G^{\ddagger}$ (25 °C), was found to be 44.8(3) kJ mol^{-1} using dynamic NMR simulation software.[63] The corresponding barriers to P–C_{ArF} rotation for **4** and **12** were determined in a similar fashion to be 52.4(3) and 52.2(1) kJ mol^{-1}, respectively. The higher barriers in **4** and **12** compared to **14** are attributed to the presence of intramolecular PH···FC interactions in **4** and **12**. This view is supported by the close approach of the P–H proton to the *ortho*-F

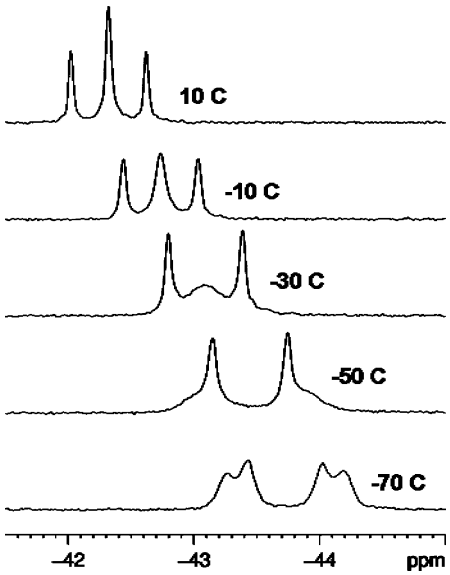
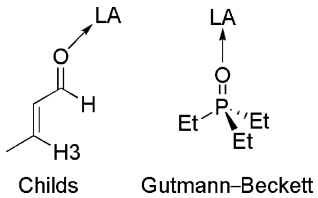


Fig. 3 Variable temperature $^{31}P\{^1H\}$ NMR spectra of **14**.

of the C_6F_4 linker (2.503 Å) noted in the crystal structure of **8**.[52] Related N–H···F–C interactions were responsible for restricted rotation in a number of amine–$B(C_6F_5)_3$ adducts.[64] It is also readily apparent that solutions of compounds **13** or **14** show no sign of aggregation *via* P donation to B. Accordingly the difference in ^{19}F NMR chemical shift between the *ortho*- and *meta*-F atoms of the C_6F_5 fragments on B are >17 ppm in each case, indicative of neutral 3-coordinate B.[25,65–69] Thus compounds **13** and **14** are also appropriately described as FLPs as the steric congestion about both the acidic and basic centers precludes traditional Lewis acid–base adduct formation.

Lewis acid strength has been shown to linearly correlate with rate of catalyzed reactions in certain cases, providing the potential to predict reactivity.[70,71] However, issues such as methodology, solvent effects and steric factors makes the construction of an absolute Lewis acidity scale problematic.[49] Nevertheless, a number of methods to assess relative Lewis acidities, including calorimetry,[16,56,72,73] reactivity[74,75] and spectroscopic investigations,[76,77] have been developed. For fluoroarylboranes, two NMR-based methods are commonly used. Gutmann's acceptor number (AN)[78,79] for scaling solvent polarity has been modified by Beckett *et al.*[70,80] and further employed by Britovsek *et al.*[34] to rank the acidity of some boron-based Lewis acids (Scheme 3). Here, the differences in the ^{31}P NMR chemical shift of $Et_3P{=}O$ *vs.* that of the Lewis acid adduct is employed to rank the relative strength of the acids.[81] A second method developed by Childs *et al.*[82] and computationally investigated by Laszlo and Teston[83] utilizes crotonaldehyde as the probe and the scale is based on the relative shift of the H3- or β-proton upon Lewis acid complexation. Notably, this site is sterically remote from the locus of complexation but electronically connected *via* unsaturation (Scheme 3). A number of groups have utilized either the Childs or Gutmann–Beckett tests to investigate the Lewis acidity of boranes and the relative scaling has been shown to predict reactivity[70,71] or shed light on mechanistic features in catalysis.[47] In addition to these methods, equilibrium constants for competition experiments have been used to directly compare the



Scheme 3 Basis of Childs and Gutmann–Beckett Lewis acidity tests.

acidity of fluoroaryl boranes[20,25,26,67] but in such cases, the nature of the coordinating atom and the sterics of the Lewis basic probe can have an unpredictable or unexpected influence on the relative rankings.[25,34,67,80]

Herein, we have employed both the Childs and Gutmann–Beckett methods to rank the Lewis acidity of the cationic phosphonium-boranes **9–12** and neutral phosphine-boranes **13** and **14** relative to the parent $B(C_6F_5)_3$. The Childs test consisted of a 1 : 1 acid : crotonaldehyde solution in CD_2Cl_2 at −20 °C while Gutmann–Beckett test was performed with a 3 : 1 acid : $Et_3P{=}O$ ratio in CD_2Cl_2 solvent. Of note is that our values obtained for $B(C_6F_5)_3$ in both tests are essentially identical to the reported literature values.[26,34,58,59,84] All cationic complexes **9–12** were found to be significantly stronger Lewis acids than $B(C_6F_5)_3$ by both methods. This is in line with the expected greater electron withdrawing effect of a cationic phosphonium group *versus* a fluorine atom. This was further verified by a competition study between the zwitterionic phosphonium hydridoborates **5–8** with $B(C_6F_5)_3$. In these cases, equimolar mixtures of **5–8** with $B(C_6F_5)_3$ in C_6D_5Br showed no evidence of hydride migration to $B(C_6F_5)_3$ even upon prolonged (16 h) heating to 110 °C. This affirms that B centers in **9–12** are markedly more Lewis acidic than that in $B(C_6F_5)_3$ (Fig. 4). Conversely, the neutral phosphine-boranes **13** and **14** exhibited reduced Lewis acidity compared to $B(C_6F_5)_3$ using both methods (Fig. 4).[57] This is consistent with donation of the P-based lone pair into the π-system diminishing the acidity of the B center. While minor variations in the relative rankings were observed, the general trends were consistent between the methods. Similar to Beckett *et al*.[70] a direct correlation between the AN values and the Childs ranking of the Lewis acids was observed for **9–14** and $B(C_6F_5)_3$. This stands in stark contrast to the series of boranes $B(C_6F_5)_n(OC_6F_5)_{3-n}$ where these tests gave conflicting trends.[34] The observed parallels between the Gutmann–Beckett and Childs methods in the present Lewis acids **9–14** is attributable to the presence of only B–C bonds, the essentially unchanged steric environment about B and the variation in Lewis acidity arising from electronic changes made remote to the B center.

In summary, a facile, modular and high yield synthetic strategy to a family of fluoroarylboranes is realized by utilizing the latent reactivity of sterically "frustrated Lewis pairs". This approach affords a simple means to tune the Lewis acidity of $B(C_6F_5)_3$ without a significant impact on the steric environment about B. Lewis acidity tests confirmed that the cationic phosphonium-boranes **9–12** are significantly more Lewis acidic than the parent borane $B(C_6F_5)_3$ while the neutral phosphine-boranes **13** and **14** are somewhat less Lewis acidic than the parent. Current efforts in our laboratory continue to probe the unique molecules accessible employing the FLP concept. Further results will be reported in due course.

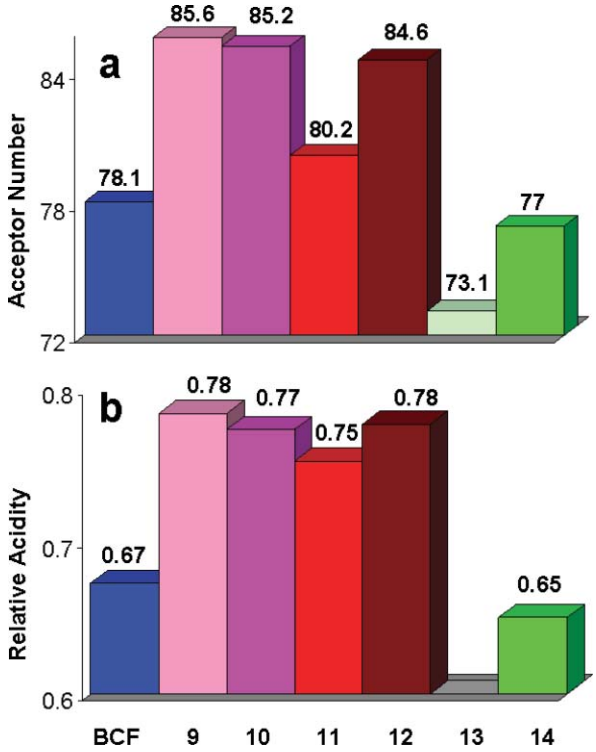


Fig. 4 (a) Plot of the Gutmann acceptor number and (b) relative acidity (to BBr_3) as determined by Childs method for $BCF(B(C_6F_5)_3)$, cationic phosphonium boranes **9–12** and phosphine-boranes **13**, **14** (NB: in (b) the relative acidity of **13** was not determined).[57]

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