Reactions of phosphines with electron deficient boranes†

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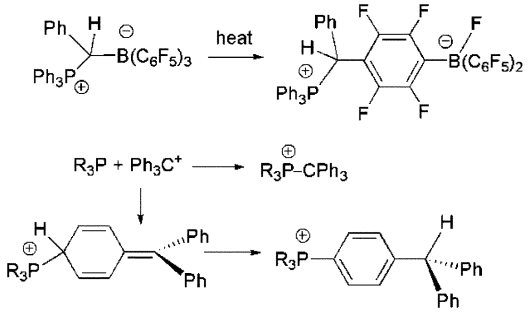
Received 20th August 2008, Accepted 7th November 2008
First published as an Advance Article on the web 19th January 2009
DOI: 10.1039/b814486a

A series of classical $B(C_6F_5)_3$-phosphine adducts are shown to be reactive molecules. Reaction of $(THF)B(C_6F_5)_3$ with phosphines are shown to effect ring-opening of THF affording the zwitterionic phosphonium-borate species of the form $R_2PH(C_4H_8O)B(C_6F_5)_3$ and $R_3P(C_4H_8O)B(C_6F_5)_3$. Alternatively, treatment of $(THF)B(C_6F_5)_3$ with a lithium phosphide (R_2PLi, R = *t*Bu, Ph Mes) affords species of the form $[Li(THF)_x][R_2P(C_4H_8O)B(C_6F_5)_3]$. Additionally, double THF ring-opening is also demonstrated to give species of the form $[Li(THF)_x][R_2P(C_4H_8OB(C_6F_5)_3)_2]$. In addition a series of classical borane-phosphine adducts are also shown to undergo thermal rearrangement reactions to give the zwitterionic products of aromatic substitution $R_2PH(C_6F_4)BF(C_6F_5)_2$ and $R_3P(C_6F_4)BF(C_6F_5)_2$. The mechanism of these substitutions is considered. A series of crystallographic studies of phosphine-borane adducts, THF ring-opened zwitterions and *para*-attack zwitterionic phosphonium borates are reported and discussed.

Introduction

Lewis acidic reagents play important roles in a variety of stoichiometric and catalytic reactions. In the case of polymerization catalysis, Lewis acid reagents such as the triorganoborane $B(C_6F_5)_3$ or the carbocation analog $[Ph_3C]^+$ (trityl) are powerful co-catalysts as these species are used to generate catalytically active cationic early metal alkyl complexes as a result of the vacant 2p-orbitals on boron and carbon, respectively.[1–3] Amines, pyridines and phosphines have been shown to form simple Lewis acid–base adducts with $B(C_6F_5)_3$[4–6] and trityl cation.[7–15] In the case of trityl cation, recent work in our research group has shown that sterically demanding phosphines are too large to interact with the central carbon of the carbocation and instead effect nucleophilic aromatic substitution at a position *para* to the central carbon.[16] While such chemistry was both unexpected and unique, the resulting cylcohexadienyl and benzylhydryl-phenyl species are robust (Scheme 1). Similarly, the unusual rearrangement of the ylide-borane adduct $(Ph_3PCHPh)B(C_6F_5)_3$ to give the zwitterion *p*-$(Ph_3PCHPh)(C_6F_4)BF(C_6F_5)_2$ has been reported by Erker and co-workers (Scheme 1).[17] These reactions demonstrate the non-conventional reactivity of simple Lewis acid–base adducts. We have previously communicated that sterically bulky phosphines react with $(THF)B(C_6F_5)_3$ to effect the ring-opening of THF affording the zwitterions $R_3P(C_4H_8O)B(C_6F_5)_3$.[18] Similarly, bulky phosphines were shown to undergo *para*-attack of the C_6F_5 aryl ring of $B(C_6F_5)_3$ to give zwitterionic phosphonium borates of the form $R_3P(C_6F_4)BF(C_6F_5)_2$.[19] Related zwitterions of the form *p*-$R_2EH(C_6F_4)B(C_6F_5)_3$[20] and *p*-$R_2EH(C_6H_4)B(C_6F_5)_3$[21] (E = N, P) have been claimed in the patent literature as polymerization catalyst activators; however, they were synthesized *via* traditional Grignard routes. In this full report of this chemistry, we broaden and explore the range of phosphines that exhibit both THF ring-opening and *para*-aromatic substitution of a phosphine for fluoride on a C_6F_5 ring on $B(C_6F_5)_3$ and other related electron deficient boranes.



Scheme 1 Non-conventional reactivity of the Lewis acids $B(C_6F_5)_3$ and Ph_3C^+.

Experimental

General data

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, hexanes, toluene, and CH_2Cl_2) were purified employing a Grubbs' type column system manufactured by Innovative Technology and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 h prior to use. Uninhibited THF was purchased from EMD and distilled from sodium/benzophenone. Deuterated solvents were dried over Na/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br). All common organic reagents were purified

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† CCDC reference numbers 698991–699003. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b814486a

by conventional methods unless otherwise noted. ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectra are recorded on a Bruker Avance-300 spectrometer at 300 K unless otherwise noted. ^{1}H 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 spectra are referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. ^{7}Li NMR spectra are referenced to LiCl in D_2O. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. DEPT and 2-D ^{1}H/^{13}C correlation experiments were completed for assignment of the carbon atoms. Combustion analyses were performed in-house employing a Perkin Elmer CHN Analyzer. $B(C_6F_5)_3$ was generously donated by NOVA Chemicals Corporation. All phosphines were purchased from Aldrich or Strem and used as received unless otherwise noted. Mes_2PH[22] and *t*Bu(Mes)PH[23] were prepared as reported in the literature. Paratone-N oil was purchased from Hampton Research. $(Cy_2PH)B(C_6F_5)_3$ **3**,[24] $(Ph_2PH)B(C_6F_5)_3$ **6**,[24] $(Me_3P)B(C_6F_5)_3$ **8**,[25–27] $(Ph_3P)B(C_6F_5)_3$ **11**,[28,29] $tBu_2PH(C_6F_4)BF(C_6F_5)_2$ **24**, $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ **26**, $iPr_3P(C_6F_4)BF(C_6F_5)_2$ **30**, $Cy_3P(C_6F_4)BF(C_6F_5)_2$ **32**,[30] and $PhB(C_6F_5)_2$ **36**[31] were prepared by published methods.

Synthesis of $(CyPH_2)B(C_6F_5)_3$ 1, $((C_5H_9)_2PH)B(C_6F_5)_3$ 2, $(Cy_2PH)B(C_6F_5)_3$ 3, $(Et_2PH)B(C_6F_5)_3$ 4, $(Et_3P)B(C_6F_5)_3$ 9, $(n\text{-}Bu_3P)B(C_6F_5)_3$ 10

These compounds were prepared in a similar fashion and thus only one preparation is detailed. To a clear solution of $B(C_6F_5)_3$ (0.100 g, 0.20 mmol) in toluene (5 mL) was added $(C_5H_9)_2PH$ (0.034 g, 0.20 mmol). The reaction was allowed to stir for 1 h at 25 °C. The solvent was removed *in vacuo* to give the product **2** as a white solid.

1. Yield 0.230 g (93%). ^{1}H NMR (C_6D_5Br): 4.65 (d, 2H, $^{1}J_{HP}$ = 393 Hz, P*H*$_2$), 1.68 (br s, 1H, PCy), 1.43–1.36 (br m, 5H, PCy), 0.95–0.84 (br m, 5H, PCy). ^{11}B{^{1}H} NMR (C_6D_5Br): −17.5 (br). ^{13}C{^{1}H} NMR (C_6D_5Br) partial: 147.9 (dm, $^{1}J_{CF}$ = 242 Hz, *C*F), 140.3 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 137.1 (dm, $^{1}J_{CF}$ = 246 Hz, *C*F), 114.8 (quat), 31.4 (d, $^{3}J_{CP}$ = 6 Hz, PCy), 27.7 (d, $^{1}J_{CP}$ = 33 Hz PCy), 26.1 (d, $^{2}J_{CP}$ = 12 Hz PCy), 24.8 (s, PCy). ^{19}F NMR (C_6D_5Br): −130.5 (s, 6F, *o*-C_6F_5), −155.3 (t, 3F, $^{3}J_{FF}$ = 21 Hz, *p*-C_6F_5), −162.3 (m, 6F, $^{3}J_{FF}$ = 20 Hz *m*-C_6F_5). ^{31}P NMR (C_6D_5Br): −30.0 (br t, $^{1}J_{PH}$ = 392 Hz).

2. Yield 95%. Crystals suitable for X-ray diffraction were grown *via* slow diffusion of pentane into a CH_2Cl_2/toluene solution at 25 °C. ^{1}H NMR (CD_2Cl_2): 5.60 (d, 1H, $^{1}J_{HP}$ = 408 Hz, P*H*), 2.16 (m, 2H, P(C_5H_9)), 1.95 (m, 2H, P(C_5H_9)), 1.69–1.35 (br m, 14H, P(C_5H_9)). ^{11}B{^{1}H} NMR (CD_2Cl_2): −15.9 (d, $^{1}J_{BP}$ = 80 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 148.7 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 140.5 (dm, $^{1}J_{CF}$ = 254 Hz, *C*F), 138.0 (dm, $^{1}J_{CF}$ = 254 Hz, *C*F), 117.4 (br s, quat), 32.5 (s, P(C_5H_9)$_2$), 30.3 (br m, P(C_5H_9)$_2$), 29.8 (s, P(C_5H_9)$_2$), 26.2 (d, $^{2}J_{CP}$ = 8 Hz, P(C_5H_9)$_2$), 25.7 (d, $^{2}J_{CP}$ = 8 Hz, P(C_5H_9)$_2$). ^{19}F NMR (CD_2Cl_2): −129.7 (s, 6F, *o*-C_6F_5), −157.9 (t, 3F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), −164.1 (m, 6F, $^{3}J_{FF}$ = 20 Hz *m*-C_6F_5). ^{31}P NMR (CD_2Cl_2): 11.2 (dq, $^{1}J_{PH}$ = 402 Hz, $^{1}J_{PB}$ = 80 Hz). Anal. calcd. for $C_{28}H_{19}BF_{15}P$: C, 49.30; H, 2.81. Found: C, 49.20; H, 2.75.

3. Yield 135 mg (97%). ^{1}H NMR (C_6D_5Br): 1.77 (m, 2H, C*H*$_2$), 1.34 (m, 2H, C*H*$_2$), 1.63 (m, 2H, C*H*$_2$), 0.75 (t, 3H, $^{3}J_{HH}$ = 7 Hz, Me). ^{11}B{^{1}H} NMR (C_6D_5Br): −13.5 (bs). ^{13}C{^{1}H} NMR (C_6D_5Br): 148.3 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 139.5 (dm, $^{1}J_{CF}$ = 252 Hz, *C*F), 136.91 (dm, $^{1}J_{CF}$ = 254 Hz, *C*F), 115.93 (br, quat), 25.3 (d, $^{3}J_{CP}$ = 5 Hz, *C*H$_2$), 23.9 (d, $^{2}J_{CP}$ = 11 Hz, *C*H$_2$), 20.1 (d, $^{1}J_{CP}$ = 30 Hz, *C*H$_2$), 12.8 (s, Me). ^{19}F NMR (C_6D_5Br): −129.3 (d, 6F, $^{3}J_{FF}$ = 20 Hz, *o*-C_6F_5), −156.0 (t, 3F, $^{3}J_{FF}$ = 23 Hz, *p*-C_6F_5), −163.0 (m, 6F, $^{3}J_{FF}$ = 24 Hz, *m*-C_6F_5). ^{31}P {^{1}H} NMR (C_6D_5Br): −0.6 (bs). Anal. calcd. for $C_{30}H_{27}BF_{15}P$: C, 50.44; H, 3.81. Found: C, 50.24; H, 3.75.

4. Yield 94%. Crystals suitable for X-ray diffraction were grown *via* slow evaporation of a concentrated bromobenzene solution at 25 °C. ^{1}H NMR (C_6D_5Br): 4.42 (dm, 1H, $^{1}J_{HP}$ = 410 Hz, P*H*), 0.90 (dm, 4H, $^{2}J_{HP}$ = 132 Hz, C*H*$_2$), 0.45 (dt, 6H, $^{3}J_{HP}$ = 16 Hz, $^{3}J_{HH}$ = 18 Hz Me). ^{11}B{^{1}H} NMR (C_6D_5Br): −16.2 (d, $^{1}J_{BP}$ = 95 Hz). ^{13}C{^{1}H} NMR (C_6D_5Br) partial: 148.3 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 140.1 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 137.1 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 115.8 (br s, quat), 11.91 (d, $^{1}J_{CP}$ = 36 Hz, *C*H$_2$), 10.9 (d, $^{2}J_{CP}$ = 8 Hz, Me). ^{19}F NMR (C_6D_5Br): −130.4 (s, 6F, *o*-C_6F_5), −155.6 (t, 3F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), −162.9 (m, 6F, $^{3}J_{FF}$ = 20 Hz *m*-C_6F_5). ^{31}P NMR (C_6D_5Br): 5.7 (dq, $^{1}J_{PH}$ = 412 Hz, $^{1}J_{PB}$ = 92 Hz). Anal. calcd. for $C_{22}H_{11}BF_{15}P$: C, 43.98; H, 1.84. Found: C, 44.20; H, 2.05.

9. Yield 86%. Crystals suitable for X-ray diffraction were grown *via* slow evaporation of a concentrated THF solution at 25 °C. ^{1}H NMR (THF-d_8): 1.94–1.88 (br m, 6H, C*H*$_2$), 1.24–1.14 (m, 9H, Me). ^{11}B{^{1}H} NMR (THF-d_8): −13.4 (d, $^{1}J_{BP}$ = 75 Hz). ^{13}C{^{1}H} NMR (THF-d_8): 149.2 (dm, $^{1}J_{CF}$ = 239 Hz, *C*F), 140.92 (dm, $^{1}J_{CF}$ = 249 Hz, *C*F), 138.4 (dm, $^{1}J_{CF}$ = 254 Hz, *C*F), 117.6 (br s, quat), 14.6 (d, $^{1}J_{CP}$ = 35 Hz, *C*H$_2$), 8.6 (d, $^{2}J_{CP}$ = 8 Hz, Me). ^{19}F NMR (THF-d_8): −130.2 (d, 6F, $^{3}J_{FF}$ = 22 Hz, *o*-C_6F_5), −158.7 (m, 3F, $^{3}J_{FF}$ = 22 Hz, *p*-C_6F_5), −165.3 (m, 6F, $^{3}J_{FF}$ = 22 Hz, *m*-C_6F_5). ^{31}P {^{1}H} NMR (THF-d_8): 5.6 (dm, $^{1}J_{PB}$ = 80 Hz). Anal. calcd. for $C_{24}H_{15}BF_{15}P$: C, 45.75; H, 2.40. Found: C, 46.20; H, 2.55%.

10. Yield 97%. ^{1}H NMR (C_6D_5Br): 1.77 (m, 2H, C*H*$_2$), 1.34 (m, 2H, C*H*$_2$), 1.63 (m, 2H, C*H*$_2$), 0.75 (t, 3H, $^{3}J_{HH}$ = 7 Hz, Me). ^{11}B{^{1}H} NMR (C_6D_5Br): −13.5 (br). ^{13}C{^{1}H} NMR (C_6D_5Br): 148.3 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 139.5 (dm, $^{1}J_{CF}$ = 252 Hz, *C*F), 136.9 (dm, $^{1}J_{CF}$ = 254 Hz, *C*F), 115.9 (br s, quat), 25.3 (d, $^{3}J_{CP}$ = 5 Hz, *C*H$_2$), 23.9 (d, $^{2}J_{CP}$ = 11 Hz, *C*H$_2$), 20.1 (d, $^{1}J_{CP}$ = 30 Hz, *C*H$_2$), 12.0 (s, Me). ^{19}F NMR (C_6D_5Br): −129.3 (d, 6F, $^{3}J_{FF}$ = 20 Hz, *o*-C_6F_5), −156.0 (t, 3F, $^{3}J_{FF}$ = 23 Hz, *p*-C_6F_5), −163.0 (m, 6F, $^{3}J_{FF}$ = 24 Hz, *m*-C_6F_5). ^{31}P {^{1}H} NMR (C_6D_5Br): −0.58 (bs). Anal. calcd. for $C_{30}H_{27}BF_{15}P$: C, 50.44; H, 3.81. Found: C, 50.24; H, 3.75.

Generation of $(tBu_2PH)B(C_6F_5)_3$ 5

An NMR tube was charged with $B(C_6F_5)_3$ (0.050 g, 0.098 mmol) and CD_2Cl_2 (0.75 mL). The NMR tube was capped with a rubber septum, wrapped with parafilm, and cooled to −78 °C in a dry ice/acetone bath. Using a syringe, tBu_2PH (18 μL, 0.097 mmol) was added to the NMR tube. The NMR tube was then inserted into an NMR spectrometer pre-cooled to −60 °C. Crystals could only be isolated at low temperature as this species proved to be thermally unstable. ^{1}H NMR (CD_2Cl_2, 213 K): 5.58 (d, 1H, $^{1}J_{HP}$ = 397 Hz, P*H*), 1.19 (d, 18H, $^{1}J_{HP}$ = 14 Hz, P*t*Bu}. ^{11}B{^{1}H} NMR (CD_2Cl_2, 213 K): −12.8 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2, 213 K)

partial: 148.2 (dm, $^1J_{CF} = 250$ Hz, *C*F), 147.2 (dm, $^1J_{CF} = 245$ Hz, *C*F), 139.4 (dm, $^1J_{CF} = 245$ Hz, *C*F), 139.0 (dm, $^1J_{CF} = 250$ Hz, *C*F), 138.9 (dm, $^1J_{CF} = 245$ Hz, *C*F), 118.5 (quat), 114.9 (quat), 36.8 (d, $^1J_{CP} = 22$ Hz, P*t*Bu), 30.3 (s, P*t*Bu). ^{19}F NMR (CD_2Cl_2, 213 K): −126.4 (m, 2F, *o*-C_6F_5), −128.7 (d, 2F, $^3J_{FF} = 26$ Hz, *o*-C_6F_5), −131.3 (m, 2F, *o*-C_6F_5), −156.4 (m, 1F, $^3J_{FF} = 22$ Hz, *p*-C_6F_5), −158.8 (t, 2F, $^3J_{FF} = 24$ Hz, *p*-C_6F_5), −163.7 (m, 2F, $^3J_{FF} = 26$ Hz, *m*-C_6F_5), −164.1 (m, 2F, *m*-C_6F_5), −164.7 (m, 2F, *m*-C_6F_5). ^{31}P NMR (CD_2Cl_2, 213 K): 17.4 (d, $^1J_{PH} = 394$ Hz, P*H*).

Synthesis of $(Mes_2PH)B(C_6F_5)_3$ 7

A clear yellow solution of $B(C_6F_5)_3$ (1.50 g, 2.93 mmol) and dimesityl phosphine (0.800 g, 2.96 mmol) in toluene (10 mL) was prepared. The reaction was cooled to −35 °C and allowed to stir for 12 h during which time the solution turned red and a white precipitate formed. Pentane (10 mL) was added and the mixture filtered. The resulting red filtrate was evaporated to dryness to give the product as a pink solid. Yield 0.475 g (20%). ^{1}H NMR (CD_2Cl_2): 6.88 (s, 4H, P(C_6H_2)$_2$), 6.64 (bs, 1H, P*H*), 2.26 (s, 6H, P(C_6H_2Me-4)$_2$), 2.15 (s, 12H, P(C_6H_2Me-2,6)$_2$). ^{11}B{^{1}H} NMR (CD_2Cl_2): 23.6 (bs). ^{13}C{^{1}H} NMR (CD_2Cl_2, partial): 148.9 (dm, $^1J_{CF} = 245$ Hz, *C*F), 143.0 (dm, $^1J_{CF} = 250$ Hz, *C*F), 142.9 (d, $^2J_{CP} = 9$ Hz, *o*-C_6H_2), 140.9 (s, *p*-C_6H_2), 138.1 (dm, $^1J_{CF} = 250$ Hz, *C*F), 130.3 (d, $^3J_{CP} = 5$ Hz, *m*-C_6H_2), 120.7 (d, $^1J_{CP} = 80$ Hz, P-C_6H_2), 23.1 (d, $^3J_{CP} = 17$ Hz, C_6H_2Me-2,6), 21.2 (s, C_6H_2Me-4). ^{19}F NMR (CD_2Cl_2): −128.0 (s, 6F, *o*-C_6F_5), −151.5 (s, 3F, *p*-C_6F_5), −163.0 (s, 6F, *m*-C_6F_5). ^{31}P {^{1}H} NMR (CD_2Cl_2): −67.7 (br). Anal. calcd. for $C_{36}H_{23}BF_{15}P$: C, 55.27; H, 2.96. Found: C, 55.34; H, 3.24.

Synthesis of $tBu_2PH(C_4H_8O)B(C_6F_5)_3$ 12, $Mes_2PH(C_4H_8O)B(C_6F_5)_3$ 13, $Cy_3P(C_4H_8O)B(C_6F_5)_3$ 15

These compounds were prepared in a similar fashion and thus only one preparation is detailed. To a faint yellow solution of $B(C_6F_5)_3$ (0.350 g, 0.684 mmol) in THF (4 mL) was added tBu_2PH (0.100 g, 0.684 mmol) *via* syringe and the reaction mixture was left to stir for 72 h at 25 °C. All volatiles were removed *in vacuo* and the resulting white solid was dried under vacuum for 12 h.

12. Yield 0.404 g (81%). Crystals suitable for X-ray diffraction were grown from a layered THF/C_6D_6/pentane solution at 25 °C. ^{1}H NMR (THF-d_8): 5.60 (dt, 1H, $^1J_{HP} = 453$ Hz, $^3J_{HH} = 4$ Hz, P*H*), 3.24 (t, 2H, $^3J_{HH} = 5$ Hz, CH_2O), 2.64 (m, 2H, PCH_2), 1.99 (m, 2H, PCH_2CH_2), 1.67 (m, 2H, CH_2CH_2O), 1.45 (d, 18H, $^3J_{HP} = 16$ Hz, *t*Bu). ^{11}B NMR (C_6D_6): −2.9. ^{13}C{^{1}H} NMR (C_6D_6): 149.2 (dm, $^1J_{CF} = 230$ Hz, *C*F), 139.3 (dm, $^1J_{CF} = 244$ Hz, *C*F), 137.4 (dm, $^1J_{CF} = 237$ Hz, *C*F), 125.7 (quat, C_6F_5), 64.4 (s, *C*H$_2$O), 33.6 (d, $^1J_{CP} = 35.9$ Hz, quat, P*t*Bu), 32.79 (d, $^3J_{CP} = 11$ Hz, *C*H$_2$CH$_2$O), 27.1 (s, *t*Bu), 26.93 (m, PCH$_2$*C*H$_2$), 15.0 (d, $^1J_{CP} = 39$ Hz, P*C*H$_2$CH$_2$). ^{19}F NMR (C_6D_6): −133.9 (d, $^3J_{FF} = 23$ Hz, 6F, *o*-C_6F_5), −164.78 (t, $^3J_{FF} = 11$ Hz, 3F, *p*-C_6F_5), −168.02 (t, $^3J_{FF} = 20$ Hz, 6F, *m*-C_6F_5). ^{31}P NMR (C_6D_6): 50.9 ($^1J_{HP} = 453$ Hz). Anal. calcd. for $C_{30}H_{27}BF_{15}OP$: C, 49.34; H, 3.73. Found: C, 48.85; H, 3.58.

13. Yield 0.497 g (79%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in C_6D_6 at 25 °C. ^{1}H NMR (C_6D_6): 7.33 (dt, 1H, $^1J_{HP} = 531$ Hz, $^3J_{HH} = 7$ Hz, P*H*), 6.40 (d, $^4J_{HP} = 4$ Hz, 4H, P(C_6H_2)), 3.48 (m, 2H, CH_2O), 2.85 (m, 2H, PCH_2CH$_2$), 1.90 (s, 6H, P(C_6H_2Me-4)$_2$), 1.87 (s, 12H, P(C_6H_2Me-2,6)$_2$), 1.62 (m, 2H, CH_2CH$_2$O), 1.23 (m, 2H, PCH$_2$CH_2). ^{11}B NMR (C_6D_6): −2.8. ^{13}C{^{1}H} NMR (C_6D_6): 149.0 (dm, $^1J_{CF} = 246$ Hz, *C*F), 146.1 (s, *p*-C_6H_2), 143.36 (d, $^2J_{CP} = 11$ Hz, *o*-C_6H_2), 139.28 (dm, $^1J_{CF} = 252$ Hz, *C*F), 137.5 (dm, $^1J_{CF} = 257$ Hz, *C*F), 132.2 (d, $^2J_{CP} = 11$ Hz, *m*-C_6H_2), 125.0 (quat, C_6F_5), 112.1 (d, $^1J_{CP} = 80$ Hz, quat, C_6H_2), 65.6 (s, *C*H$_2$O), 30.9 (s, PCH$_2$*C*H$_2$), 24.9 (d, $^1J_{CP} = 58$ Hz, P*C*H$_2$CH$_2$), 24.0 (s, *C*H$_2$CH$_2$O), 21.8 (d, $^3J_{CP} = 8$ Hz, C_6H_2Me-2,6), 21.1 (s, C_6H_2Me-4). ^{19}F NMR (C_6D_6): −133.9 (d, $^3J_{FF} = 23$ Hz, 6F, *o*-C_6F_5), −162.2 (s, 3F, *p*-C_6F_5), −165.9 (s, 6F, *m*-C_6F_5). ^{31}P {^{1}H} NMR (C_6D_6): −12.0. Anal. calcd. for $C_{40}H_{31}BF_{15}OP$: C, 56.23; H, 3.66. Found: C, 56.48; H, 3.83.

15. Yield 302 mg (98%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in CH_2Cl_2/toluene layered with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): 3.21 (m, 2H, CH_2O), 2.46–2.40 (br m, 2H, PCH_2), 2.23–2.15 (m, 3H, Cy), 1.89–1.80 (br m, 12H, Cy), 1.72–1.66 (m, 2H, PCH$_2$CH_2), 1.65 (m, 2H, CH_2CH$_2$O), 1.50–1.41 (br m, 6H, Cy), 1.36–1.26 (br m, 12H, Cy). ^{11}B{^{1}H} NMR (CD_2Cl_2): −2.1. ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 148.6 (dm, $^1J_{CF} = 240$ Hz, *C*F), 138.8 (dm, $^1J_{CF} = 250$ Hz, *C*F), 137.0 (dm, $^1J_{CF} = 245$ Hz, *C*F), 125.9 (br s, quat), 63.8 (s, CH$_2$*C*H$_2$O), 32.8 (d, $^3J_{CP} = 17$ Hz, *C*H$_2$CH$_2$O), 30.5 (d, $^1J_{CP} = 42$ Hz, Cy), 27.5 (s, Cy), 27.2 (d, $^3J_{CP} = 11$ Hz, Cy), 25.9 (s, Cy). 21.9 (s, PCH$_2$*C*H$_2$), 16.2 (d, $^1J_{CP} = 44$ Hz, P*C*H$_2$CH$_2$). ^{19}F NMR (CD_2Cl_2): −134.5 (d, 6F, $^3J_{FF} = 23$ Hz, *o*-C_6F_5), −163.8 (t, 3F, $^3J_{FF} = 23$ Hz, *p*-C_6F_5), −167.4 (t, 6F, $^3J_{FF} = 20$ Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 32.1. Anal. calcd. for $C_{40}H_{41}BF_{15}OP$: C, 55.57; H, 4.78. Found: C, 56.10; H, 4.98. Mp: 200–205 °C.

Synthesis of $Et_3P(C_4H_8O)B(C_6F_5)_3$ 14

$(Et_3P)B(C_6F_5)_3$ (0.100 g, 0.16 mmol) was dissolved in THF (10 mL) and transferred to a 50 mL reaction bomb. The solution was heated to 80 °C for 5 h. Upon cooling all volatiles were removed *in vacuo* to give the ring-opened product as a white solid. Yield 90 mg (81%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in CH_2Cl_2/toluene layered with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): 3.23 (m, 2H, CH$_2$CH_2O), 2.59–2.49 (br m, 2H, PCH_2CH$_2$), 2.11–1.99 (dq, 6H, $^3J_{HP} = 12$ Hz, $^3J_{HH} = 8$ Hz, CH_2), 1.83 (m, 2H, PCH$_2$CH_2), 1.66 (m, 2H, CH_2CH$_2$O), 1.32–1.23 (dt, 9H, $^3J_{HP} = 18$ Hz, $^3J_{HH} = 8$ Hz, Me). ^{11}B{^{1}H} NMR (CD_2Cl_2): −2.9. ^{13}C{^{1}H} NMR (CD_2Cl_2): 148.5 (dm, $^1J_{CF} = 240$ Hz, *C*F), 138.7 (dm, $^1J_{CF} = 246$ Hz, *C*F), 137.2 (dm, $^1J_{CF} = 250$ Hz, *C*F), 124.9 (br s, quat), 63.1 (s, CH$_2$*C*H$_2$O), 31.9 (d, $^3J_{CP} = 14$ Hz, *C*H$_2$CH$_2$O), 20.2 (d, $^2J_{CP} = 7$ Hz, PCH$_2$*C*H$_2$), 17.8 (d, $^1J_{CP} = 47$ Hz, P*C*H$_2$CH$_2$), 12.3 (d, $^1J_{CP} = 50$ Hz, *C*H$_2$), 5.7 (s, *Me*). ^{19}F NMR (CD_2Cl_2): −134.8 (d, 6F, $^3J_{FF} = 20$ Hz, *o*-C_6F_5), −163.5 (m, 3F, $^3J_{FF} = 20$ Hz, *p*-C_6F_5), −167.3 (m, 6F, $^3J_{FF} = 20$ Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 38.7. Anal. calcd. for $C_{28}H_{23}BF_{15}OP$: C, 47.89; H, 3.30. Found: C, 48.11; H, 3.52. Mp: 165–170 °C.

Generation of $[Li(THF)_2][tBu_2P(C_4H_8O)B(C_6F_5)_3]$ 16

Method A. The species **12** (0.207 g, 0.283 mmol) was dissolved in THF (5 mL) and cooled to −35 °C. To this reaction mixture was added *t*BuLi in hexanes (0.18 mL, 0.301 mmol) *via* syringe. The mixture became pale yellow and then colorless and was allowed to warm to room temperature over 30 min, during which time the solution again became pale yellow. The reaction was stirred for a

further 2 h. All volatiles were removed *in vacuo* and the resulting white solid was dried under vacuum for 12 h. Yield 0.180 g (73%).

Method B. LiP*t*Bu$_2$ (0.100 g, 0.657 mmol) was dissolved in THF (4 mL) and cooled to −78 °C in a dry ice/acetone bath. A solution of B(C$_6$F$_5$)$_3$ (0.340 g, 0.664 mmol) in THF (2 mL) was then added to the phosphide *via* syringe over the course of 15 min. The yellow solution was warmed to room temperature over the course of 6 h and then further stirred at room temperature overnight. All volatiles were removed *in vacuo* to give a white sticky solid. The residue was triturated with hexanes (10 mL), the solvent decanted and the residual solvent removed *in vacuo* three times. The resulting off-white solid was dried under vacuum overnight. Yield 0.350 g (65%).^{1}H NMR (THF-d$_8$): 4.02 (m, 2H, CH$_2$C*H*$_2$O), 3.60 (s, 8H, THF), 2.18 (m, 2H, PC*H*$_2$CH$_2$), 1.84 (m, 2H, C*H*$_2$CH$_2$O), 1.90 (s, 8H, THF), 1.75 (m, 2H, PCH$_2$C*H*$_2$), 1.46 (d, 18H, $^3J_{HP}$ = 11 Hz, *t*Bu). ^{1}H NMR (C$_6$D$_6$): 3.55 (s, 8H, THF), 3.45 (m, 2H, CH$_2$C*H*$_2$O), 1.75 (s, 8H, THF), 1.40 (m, 2H, PC*H*$_2$CH$_2$), 1.29 (m, 2H, C*H*$_2$CH$_2$O), 1.08 (m, 2H, PCH$_2$C*H*$_2$), 0.96 (d, 18H, $^3J_{HP}$ = 11 Hz, *t*Bu). ^{11}B NMR (THF-d$_8$): −2.9. ^{13}C{^{1}H} NMR (THF-d$_8$): 149.3 (dm, $^1J_{CF}$ = 235 Hz, *C*F), 139.2 (dm, $^1J_{CF}$ = 242 Hz, *C*F), 137.2 (dm, $^1J_{CF}$ = 244 Hz, *C*F), 126.61 (quat, P*C*$_6$F$_5$), 64.5 (s, CH$_2$*C*H$_2$O), 35.4 (d, $^1J_{CP}$ = 30 Hz, quat, *t*Bu), 31.8 (d, $^3J_{CP}$ = 20 Hz, *C*H$_2$CH$_2$O), 30.42 (d, $^2J_{CP}$ = 9 Hz, *t*Bu), 28.31 (d, $^1J_{CP}$ = 26 Hz, P*C*H$_2$CH$_2$), 22.38 (d, $^2J_{CP}$ = 20 Hz PCH$_2$*C*H$_2$). ^{19}F NMR (THF-d$_8$): −136.7 (m, 6F, *o*-C$_6$*F*$_5$), −159.6 (t, $^3J_{PF}$ = 20 Hz, 3F, *p*-C$_6$*F*$_5$), −164.1 (s, 6F, *m*-C$_6$*F*$_5$). ^{31}P NMR (THF-d$_8$): 27.4. Anal. calcd. for C$_{40}$H$_{42}$BF$_{15}$O$_3$PLi: C, 53.12; H, 4.68. Found: C, 53.00; H, 4.83.

Generation of [Li][*t*Bu$_2$P(C$_4$H$_8$O)B(C$_6$F$_5$)$_3$] 17

The species **12** (0.200 g, 0.274 mmol) was slurried in toluene (8 mL) and cooled to −35 °C. To this mixture was added *t*BuLi in hexanes (0.16 mL, 0.274 mmol) *via* syringe. The reaction was allowed to warm to 25 °C over 30 min, at which time all solids dissolved. The reaction was stirred for a further 2 h. All volatiles were removed *in vacuo* and the resulting solid was dried under vacuum for 12 h, giving the product as an off-white solid. Yield 0.180 g (89%). ^{1}H NMR (toluene-d$_8$): δ 3.18 (br s, 2H, CH$_2$C*H*$_2$O), 1.35 (m, 2H, PC*H*$_2$CH$_2$), 1.30 (m, 2H, PCH$_2$CH$_2$C*H*$_2$CH$_2$O), 0.95 (m, 2H, PCH$_2$C*H*$_2$), 0.88 (d, 18H, $^3J_{HP}$ = 11.60 Hz, *t*Bu). ^{11}B NMR (toluene-d$_8$): −2.9. ^{13}C{^{1}H} NMR (toluene-d$_8$): 148.9 (dm, $^1J_{CF}$ = 235 Hz, C*F*), 140.11 (dm, $^1J_{CF}$ = 250 Hz, C*F*), 137.98 (dm, $^1J_{CF}$ = 238 Hz, C*F*), 126.0 (quat, C*F*), 64.1 (s, CH$_2$*C*H$_2$O), 31.7 (d, $^1J_{CP}$ = 32 Hz, quat, *t*Bu), 30.9 (d, $^3J_{CP}$ = 7 Hz, *C*H$_2$CH$_2$O), 29.5 (d, $^2J_{CP}$ = 10 Hz, *t*Bu), 22.7 (d, $^1J_{CP}$ = 17 Hz, P*C*H$_2$CH$_2$), 19.6 (s, PCH$_2$*C*H$_2$). ^{19}F NMR (toluene-d$_8$): −139.2 (s, 6F, *o*-C$_6$*F*$_5$), −158.3 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-C$_6$*F*$_5$), −163.3 (t, $^3J_{FF}$ = 20 Hz, 6F, *m*-C$_6$*F*$_5$). ^{7}Li NMR (toluene-d$_8$): 1.3–0.5 (dm, J_{LiP} = 75 Hz). ^{31}P NMR (toluene-d$_8$): 26.7 (q, J_{PLi} = 75 Hz).

Synthesis of [Li(THF)$_2$][Ph$_2$P(C$_4$H$_8$O)B(C$_6$F$_5$)$_3$] 18, [Li(THF)$_2$][Mes$_2$P(C$_4$H$_8$O)B(C$_6$F$_5$)$_3$] 19

These compounds were prepared in a similar fashion and thus one preparation is detailed. To a faint yellow solution of B(C$_6$F$_5$)$_3$ (0.200 g, 0.391 mmol) in toluene (2 mL) was added THF (0.16 mL, 1.97 mmol). LiPPh$_2$ (0.075 g, 0.390 mmol) in toluene (2 mL) and THF (0.16 mL, 1.97 mmol) was added and the reaction mixture was left to stir for 24 h at 25 °C. All volatiles were removed *in vacuo* and the resulting cream-colored solid was washed with Et$_2$O (2 mL) and pentane (2 mL) and then dried under vacuum for 24 h.

18. Yield 0.188 g (62%). ^{1}H NMR (C$_6$D$_6$): 7.28 (m, 4H, PPh$_2$), 7.05 (m, 6H, PPh$_2$), 3.38 (t, $^3J_{HH}$ = 7 Hz, 2H, CH$_2$C*H*$_2$O), 3.25 (m, 8H, THF), 1.85 (t, $^3J_{HH}$ = 7 Hz, 2H, PC*H*$_2$CH$_2$), 1.42 (m, 2H, C*H*$_2$CH$_2$O), 1.26 (m, 2H, PCH$_2$C*H*$_2$), 1.19 (s, 8H, THF). ^{11}B NMR (C$_6$D$_6$): −2.7. ^{13}C{^{1}H} NMR (C$_6$D$_6$) partial: 148.7 (dm, $^1J_{CF}$ = 232 Hz, *C*F), 139.59 (dm, $^1J_{CF}$ = 237 Hz, *C*F), 137.22 (dm, $^1J_{CF}$ = 249 Hz, *C*F), 133.41, 132.75, 131.57, 128.81 (quat, *C*$_6$H$_5$), 68.37 (s, THF), 65.13 (s, CH$_2$*C*H$_2$O), 31.96 (d, $^3J_{CP}$ = 10 Hz, *C*H$_2$CH$_2$O), 27.59 (d, $^1J_{CP}$ = 10 Hz, P*C*H$_2$CH$_2$), 25.15 (s, THF), 22.56 (d, $^2J_{CP}$ = 15 Hz, PCH$_2$*C*H$_2$). ^{19}F NMR (C$_6$D$_6$): −137.5 (d, $^3J_{FF}$ = 14 Hz, 6F, *o*-C$_6$*F*$_5$), −159.1 (t, $^3J_{FF}$ = −20 Hz, 3F, *p*-C$_6$*F*$_5$), −164.2 (t, $^3J_{FF}$ = 20 Hz, 6F, *m*-C$_6$*F*$_5$). ^{31}P NMR (C$_6$D$_6$): −18.9. Anal. calcd. for C$_{42}$H$_{32}$BF$_{15}$LiO$_3$P: C, 54.81; H, 3.72. Found: C, 54.77; H, 4.01.

19. Yield 0.844 g (80%). Crystals suitable for X-ray diffraction were grown from a layered CH$_2$Cl$_2$/pentane solution at 25 °C. ^{1}H NMR (CD$_2$Cl$_2$): 6.75 (s, 4H, C$_6$*H*$_2$), 3.72 (s, 8H, THF), 3.22 (m, 2H, CH$_2$C*H*$_2$O), 2.33 (m, 2H, PC*H*$_2$CH$_2$), 2.20 (s, 18H, *Me*), 1.85 (s, 8H, THF), 1.49 (m, 2H, C*H*$_2$CH$_2$O), 1.14 (m, 2H, PCH$_2$C*H*$_2$). ^{11}B NMR (CD$_2$Cl$_2$): −3.1. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 148.4 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 142.2 (d, $^2J_{CP}$ = 13 Hz, *o*-*C*$_6$H$_2$), 139.7 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 138.1 (s, *p*-*C*$_6$H$_2$), 137.3 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 130.4 (s, *m*-*C*$_6$H$_2$), 122.5, 118.0 (quat, *C*$_6$F$_5$, *C*$_6$H$_2$), 68.9 (s, THF), 65.6 (s, CH$_2$*C*H$_2$O), 33.4 (d, $^2J_{CP}$ = 14 Hz, PCH$_2$*C*H$_2$), 28.2 (d, $^1J_{CP}$ = 14 Hz, P*C*H$_2$CH$_2$), 25.9 (s, THF), 23.9 (s, *C*H$_2$CH$_2$O), 23.2 (d, $^3J_{CP}$ = 14 Hz, C$_6$H$_2$*Me*-2,6), 21.0 (s, C$_6$H$_2$*Me*-4). ^{19}F NMR (CD$_2$Cl$_2$): −137.6 (d, $^3J_{FF}$ = 20 Hz, 6F, *o*-C$_6$*F*$_5$), −161.0 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-C$_6$*F*$_5$), −165.6 (t, $^3J_{FF}$ = 20 Hz, 6F, *m*-C$_6$*F*$_5$). ^{31}P NMR (CD$_2$Cl$_2$): −21.4. Anal. calcd. for C$_{48}$H$_{46}$BF$_{15}$LiO$_3$P: C, 57.39; H, 4.62. Found: C, 57.57; H, 5.25.

Synthesis of [Li][*t*Bu$_2$P(C$_4$H$_8$OB(C$_6$F$_5$)$_3$)$_2$] 20

To a faint yellow solution of B(C$_6$F$_5$)$_3$ (0.673 g, 1.314 mmol) in THF (2 mL) was added LiP*t*Bu$_2$ (0.100 g, 0.657 mmol) in THF (4 mL) and the reaction mixture was left to stir for 12 h at 25 °C. All volatiles were removed *in vacuo* and the resulting white solid was dried under vacuum for 24 h. Yield 0.776 g (89%). Crystals suitable for X-ray diffraction were grown from a layered THF/pentane solution at 25 °C. ^{1}H NMR (THF-d$_8$): 3.22 (t, 4H, $^3J_{HH}$ = 5 Hz, CH$_2$C*H*$_2$O), 2.51 (m, 4H, PC*H*$_2$CH$_2$CH$_2$CH$_2$O), 1.92 (m, 4H, PCH$_2$C*H*$_2$), 1.65 (m, 4H, C*H*$_2$CH$_2$O), 1.35 (d, 18H, $^3J_{HP}$ = 14 Hz, *t*Bu). ^{11}B NMR (THF-d$_8$): −2.9. ^{13}C{^{1}H} NMR (THF-d$_8$): 149.2 (dm, $^1J_{CF}$ = 246 Hz, *C*F), 139.2 (dm, $^1J_{CF}$ = 244 Hz, *C*F), 137.5 (dm, $^1J_{CF}$ = 245 Hz, *C*F), 126.22 (quat, *C*$_6$F$_5$), 64.5 (s, CH$_2$*C*H$_2$O), 35.3 (d, $^1J_{CP}$ = 38 Hz, quat, P*t*Bu), 33.4 (d, $^3J_{CP}$ = 12 Hz, *C*H$_2$CH$_2$O), 27.5 (s, *t*Bu), 26.6 (m, PCH$_2$*C*H$_2$), 17.8 (d, $^1J_{CP}$ = 40 Hz, P*C*H$_2$CH$_2$). ^{19}F NMR (THF-d$_8$): −133.9 (d, $^3J_{FF}$ = 23 Hz, 12F, *o*-C$_6$*F*$_5$), −165.2 (t, $^3J_{FF}$ = 11 Hz, 6F, *p*-C$_6$*F*$_5$), −168.2 (t, $^3J_{FF}$ = 20 Hz, 12F, *m*-C$_6$*F*$_5$). ^{31}P NMR (THF-d$_8$): 45.3. Anal. calcd. for C$_{52}$H$_{34}$B$_2$F$_{30}$LiO$_2$P: C, 47.30; H, 2.60. Found: C, 47.58; H, 2.89.

Synthesis of [Li(THF)$_4$][Mes$_2$P(C$_4$H$_8$OB(C$_6$F$_5$)$_3$)$_2$] 21

To a faint yellow solution of B(C$_6$F$_5$)$_3$ (0.200 g, 0.391 mmol) in THF (5 mL) was added dropwise an orange solution of LiPMes$_2$ (0.054 g, 0.195 mmol) in THF (5 mL). The reaction mixture immediately went colorless followed by a gradual color change to red. The reaction mixture was allowed to stir for 12 h, at which time all volatiles were remove *in vacuo*. Pentane (5 mL) was added and the reaction stirred for 10 min. All volatiles were removed *in vacuo* and the residue dried under vacuum for 24 h yielding the product as a tan solid. Yield 0.844 g (80%). ^{1}H NMR (CD$_2$Cl$_2$): 6.99 (d, $^4J_{HP}$ = 4 Hz, 4H, C$_6H_2$), 3.69 (s, 16H, THF), 3.15 (m, 4H, CH$_2$CH_2O), 2.75 (m, 4H, PCH_2CH$_2$), 2.32 (s, 6H, C$_6$H$_2$*Me*-4), 2.17 (s, 12H, C$_6$H$_2$*Me*-2,6), 1.85 (s, 16H, THF), 1.48 (m, 4H, CH_2CH$_2$O), 1.36 (m, 4H, PCH$_2$CH_2). ^{11}B NMR (CD$_2$Cl$_2$): –3.0. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 148.4 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 145.8 (s, *p*-C$_6$H$_2$), 142.2 (d, $^2J_{CP}$ = 10 Hz, *o*-C$_6$H$_2$), 139.3 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 137.3 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 133.5 (d, $^3J_{CP}$ = 10 Hz, *m*-C$_6$H$_2$), 123.4 (quat, *C*$_6$F$_5$), 117.1 (d, $^1J_{CP}$ = 88 Hz, quat, *C*$_6$H$_2$), 68.7 (s, THF), 64.8 (s, CH$_2$*C*H$_2$O), 32.3 (d, $^2J_{CP}$ = 13 Hz, PCH$_2$*C*H$_2$), 27.2 (d, $^1J_{CP}$ = 44 Hz, P*C*H$_2$CH$_2$), 25.9 (s, THF), 23.5 (d, $^3J_{CP}$ = 14 Hz, C$_6$H$_2$*Me*-2,6), 21.2 (s, C$_6$H$_2$*Me*-4), 21.0 (s, *C*H$_2$CH$_2$O). ^{19}F NMR (CD$_2$Cl$_2$): –136.1 (s, 12F, *o*-C$_6F_5$), –161.8 (s, 6F, *p*-C$_6F_5$), –166.0 (m, 12F, *m*-C$_6F_5$). ^{31}P NMR (CD$_2$Cl$_2$): 30.9. Anal. calcd. for C$_{78}$H$_{70}$B$_2$F$_{30}$LiO$_6$P: C, 54.06; H, 4.07. Found: C, 53.58; H, 3.89.

Synthesis of (C$_5$H$_9$)$_2$PH(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 22, Cy$_2$PH(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 23, (*t*Bu)(Ph)PH(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 27, (*t*Bu)(Mes)PH(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 28, *n*Bu$_3$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 31, Ph$_3$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 33, (*p*-FC$_6$H$_4$)$_3$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 34, (*o*-C$_6$H$_4$OMe)$_3$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ 35

These compounds were prepared in a similar fashion and thus one preparation is detailed. Minor modifications are indicated. To a clear yellow solution of B(C$_6$F$_5$)$_3$ (0.556 g, 1.09 mmol) in toluene (20 mL) was added (C$_5$H$_9$)$_2$PH (0.199 g, 1.18 mmol) in toluene (5 mL) *via* syringe. The reaction was heated to 130 °C in a sealed glass bomb with a Teflon cap for 24 h. During such time the reaction turned yellow in color and a white precipitate formed. Pentane (40 mL) was added and the mixture filtered, washed with pentane (3 × 10 mL), and dried *in vacuo* for 1 h. The product was collected as a white solid. Yield 0.560 g (76%). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/benzene/pentane solution at 25 °C.

22. ^{1}H NMR (THF-d$_8$): 7.24 (d, 1H, $^1J_{HP}$ = 508 Hz, P*H*), 3.11 (m, 2H, P(C$_5$H$_9$)), 2.25 (m, 2H, P(C$_5$H$_9$)), 2.07 (m, 2H, P(C$_5$H$_9$)), 1.86–1.68 (br m, 12H, P(C$_5$H$_9$)). ^{11}B{^{1}H} NMR (THF-d$_8$): –0.1 (d, $^1J_{BF}$ = 54 Hz). ^{13}C{^{1}H} NMR (THF-d$_8$) partial: 148.8 (dm, $^1J_{CF}$ = 255 Hz, *C*F), 148.1 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 146.3 (dm, $^1J_{CF}$ = 255 Hz, *C*F), 138.9 (dm, $^1J_{CF}$ = 252 Hz, *C*F), 136.6 (dm, $^1J_{CF}$ = 252 Hz, *C*F), 123.3 (br m, quat), 92.1 (m, $^1J_{CP}$ = 70 Hz, quat), 30.6 (d, $^1J_{CP}$ = 45 Hz, P(C$_5$H$_9$)$_2$), 29.9 (s, P(C$_5$H$_9$)$_2$), 29.7 (s, P(C$_5$H$_9$)$_2$), 27.2 (d, $^3J_{CP}$ = 12 Hz, P(C$_5$H$_9$)$_2$), 26.4 (d, $^3J_{CP}$ = 12 Hz, P(C$_5$H$_9$)$_2$). ^{19}F NMR (THF-d$_8$): –129.8 (s, 2F, C$_6F_4$), –133.5 (s, 2F, C$_6F_4$), –135.3 (m, 4F, *o*-C$_6F_5$), –163.4 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C$_6F_5$), –167.9 (t, 4F, $^3J_{FF}$ = 20 Hz, *m*-C$_6F_5$), –193.3 (br m, 1F, B*F*). ^{31}P{^{1}H} NMR (THF-d$_8$): 12.7 (m). Anal. calcd. for C$_{28}$H$_{19}$BF$_{15}$P: C, 49.30; H, 2.81. Found: C, 48.76; H, 2.93.

23. Yield 0.510 g (73%). ^{1}H NMR (CD$_2$Cl$_2$): 6.50 (d, 1H, $^1J_{HP}$ = 480 Hz, P*H*), 3.80 (m, 2H, PCy$_2$), 2.09–1.27 (br m, 20H, PCy$_2$). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): –0.2 (br). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) partial: 149.3 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 148.37 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 146.3 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 139.4 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 137.2 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 129.1, 122.7, 87.1 (quat), 33.3 (d, $^1J_{CP}$ = 41 Hz, PCy$_2$), 28.3 (s, PCy$_2$), 27.2 (s, PCy$_2$), 26.4 (s, PCy$_2$), 26.2 (d, $^3J_{CP}$ = 15 Hz, PCy$_2$), 25.2 (s, PCy$_2$). ^{19}F NMR (CD$_2$Cl$_2$): –129.2 (s, 2F, C$_6F_4$), –131.9 (s, 2F, C$_6F_4$), –135.8 (d, 4F, $^3J_{FF}$ = 19 Hz, *o*-C$_6F_5$), –161.6 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C$_6F_5$), –166.6 (t, 4F, $^3J_{FF}$ = 20 Hz, *m*-C$_6F_5$), –191.5 (br, 1F, B*F*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 11.5 (m). Anal. calcd. for C$_{30}$H$_{23}$BF$_{15}$P: C, 50.73; H, 3.26. Found: C, 50.65; H, 3.22.

27. Heated to reflux in toluene for 24 h. Yield 0.510 g (77%). ^{1}H NMR (CD$_2$Cl$_2$): 7.98–7.89 (m, 3H, P(C$_6H_5$)), 7.76–7.69 (m, 2H, P(C$_6H_5$)), 7.39 (d, 1H, $^1J_{HP}$ = 487 Hz, P*H*), 1.54 (d, 9H, $^1J_{HP}$ = 21 Hz, P*t*Bu). ^{11}B NMR (CD$_2$Cl$_2$): 0.4 (d, $^1J_{BF}$ = 63 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) partial: 149.9 (dm, $^1J_{CF}$ = 246 Hz, *C*$_6$F$_4$), 147.9 (dm, $^1J_{CF}$ = 240 Hz, *C*$_6$F$_5$), 145.5 (dm, $^1J_{CF}$ = 250 Hz, *C*$_6$F$_5$), 140.0 (dm, $^1J_{CF}$ = 240 Hz, *C*$_6$F$_4$), 137.0 (dm, $^1J_{CF}$ = 246 Hz, *C*$_6$F$_5$), 136.9 (s, *Ph*), 134.4 (d, $^3J_{CP}$ = 11 Hz, *Ph*), 131.3 (d, $^2J_{CP}$ = 12 Hz, *Ph*), 112.41 (d, $^1J_{CP}$ = 82 Hz, PPh), 35.0 (d, $^1J_{CP}$ = 40 Hz, P*t*Bu), 26.0 (s, *t*Bu). ^{19}F NMR (CD$_2$Cl$_2$): –128.7 (s, 2F, C$_6F_4$), –130.3 (m, 2F, C$_6F_4$), –135.8 (m, 4F, *o*-C$_6F_5$), –161.5 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C$_6F_5$), –166.6 (t, 4F, $^3J_{FF}$ = 22 Hz, *m*-C$_6F_5$), –191.4 (br s, 1F, B*F*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 14.7 (m). Anal. calcd. for C$_{28}$H$_{15}$BF$_{15}$P: C, 49.59; H, 2.23. Found: C, 49.50; H, 2.33.

28. Heated to reflux in toluene for 24 h. Yield 0.450 g (64%). Crystals suitable for X-ray diffraction were grown *via* slow diffusion of pentane into a CH$_2$Cl$_2$/toluene solution of the product at 25 °C (open to air in wet solvents). ^{1}H NMR (THF-d$_8$): 8.21 (d, 1H, $^1J_{HP}$ = 505 Hz, P*H*), 7.17 (d, $^4J_{HP}$ = 7 Hz, 2H, P(C$_6H_2$)), 2.47 (br s, 6H, P(C$_6$H$_2$*Me*-2,6)), 2.32 (s, 3H, P(C$_6$H$_2$*Me*-4)), 1.61 (d, 9H, $^3J_{HP}$ = 21 Hz, P*t*Bu). ^{11}B NMR (THF-d$_8$): 0.4 (d, $^1J_{BF}$ = 59 Hz). ^{13}C{^{1}H} NMR (THF-d$_8$) partial: 149.9 (dm, $^1J_{CF}$ = 230 Hz, *C*F), 149.0 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 148.1 (s, *p*-C$_6$H$_2$), 146.6 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 145.1 (d, $^2J_{CP}$ = 11 Hz, *o*-C$_6$H$_2$), 139.8 (dm, $^1J_{CF}$ = 245 Hz, *C*F), 137.3 (dm, $^1J_{CF}$ = 275 Hz, *C*F), 132.6 (d, $^3J_{CP}$ = 10 Hz, *m*-C$_6$H$_2$), 110.6 (d, $^1J_{CP}$ = 77 Hz, P-C$_6$H$_2$), 37.8 (d, $^1J_{CP}$ = 40 Hz, P*t*Bu), 26.4 (s, *t*Bu), 22.7 (d, $^3J_{CP}$ = 7 Hz, C$_6$H$_2$*Me*-2,6), 21.0 (s, C$_6$H$_2$*Me*-4). ^{19}F NMR (THF-d$_8$): –123.0 (br s, 4F, C$_6F_4$), –135.2 (m, 4F, *o*-C$_6F_5$), –163.4 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C$_6F_5$), –167.8 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C$_6F_5$), –193.2 (br s, 1F, B*F*). ^{31}P{^{1}H} NMR (THF-d$_8$): –2.9 (m). Anal. calcd. for C$_{31}$H$_{21}$BF$_{15}$P: C, 51.69; H, 2.94. Found: C, 51.36; H, 3.20.

31. Heated at 125 °C for 2 days. Yield 205 mg (74%). Crystals suitable for X-ray diffraction were grown *via* slow diffusion of pentane into a CH$_2$Cl$_2$/toluene solution at 25 °C. ^{1}H NMR (C$_6$D$_5$Br): 2.22 (m, 6H, CH_2), 1.25 (m, 12H, CH_2CH_2), 0.74 (m, 9H, Me). ^{11}B{^{1}H} NMR (C$_6$D$_5$Br): –0.8 (bs). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br) partial: 149.2 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 148.2 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 146.5 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 139.2 (dm, $^1J_{CF}$ = 245 Hz, *C*F), 137.0 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 92.4 (dt, $^1J_{CP}$ = 78 Hz, $^2J_{CF}$ = 20 Hz, quat), 23.6 (br m, *C*H$_2$CH$_2$), 20.0 (d, $^1J_{CP}$ = 50 Hz, *C*H$_2$), 13.0 (s, Me). ^{19}F NMR (C$_6$D$_5$Br): –129.2 (s, 2F, C$_6F_4$), –133.5 (m, 2F, C$_6F_4$), –135.1 (m, 4F, *o*-C$_6F_5$), –160.5 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C$_6F_5$), –166.0 (m, 4F, *m*-C$_6F_5$), –190.3

(br s, 1F, B*F*). ^{31}P {^{1}H} NMR (C_6D_5Br): 33.1 (br). Anal. calcd. for $C_{30}H_{27}BF_{15}P$: C, 50.44; H, 3.81. Found: C, 50.24; H, 3.63.

33. Heated at 125 °C for 2 days. Yield 110 mg (73%). Crystals suitable for X-ray diffraction were grown *via* slow evaporation of a concentrated bromobenzene solution at 25 °C. ^{1}H NMR (C_6D_5Br): 7.44–7.14 (m, 3H, Ph), 7.28–7.23 (m, 12H, Ph). ^{11}B{^{1}H} NMR (C_6D_5Br): –0.3 (br s). ^{13}C{^{1}H} NMR (C_6D_5Br) partial: 149.5 (dm, $^{1}J_{CF}$ = 245 Hz, *C*F), 148.5 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 146.4 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 139.3 (dm, $^{1}J_{CF}$ = 245 Hz, *C*F), 136.5 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 135.5 (d, $^{4}J_{CP}$ = 3 Hz, Ph), 133.5 (d, $^{3}J_{CP}$ = 11 Hz, Ph), 130.2 (d, $^{2}J_{CP}$ = 14 Hz, Ph), 117.0 (d, $^{1}J_{CP}$ = 92 Hz, quat Ph). ^{19}F NMR (C_6D_5Br): –127.9 (m, 2F, C_6F_4), –128.0 (m, 2F, C_6F_4), –133.6 (m, 4F, *o*-C_6F_5), –160.7 (t, 2F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), –165.5 (m, 4F, *m*-C_6F_5), –193.0 (br s, 1F, B*F*). ^{31}P{^{1}H} NMR (C_6D_5Br): 15.1. Anal. calcd. for $C_{36}H_{15}BF_{15}P$: C, 55.84; H, 1.95. Found: 55.65; H, 1.87.

34. Heated at 125 °C for 12 h. Yield 122 mg (75%). Crystals suitable for X-ray diffraction were grown *via* slow evaporation of a concentrated bromobenzene solution at 25 °C. ^{1}H NMR (C_6D_5Br): 7.25–7.15 (ddd, 6H, $^{3}J_{HF}$ = 13 Hz, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HP}$ = 5 Hz, Ph), 6.85–6.78 (ddd, 6H, $^{3}J_{HP}$ = 8 Hz, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HF}$ = 3 Hz, Ph). ^{11}B{^{1}H} NMR (C_6D_5Br): –0.2 (br s). ^{13}C{^{1}H} NMR (C_6D_5Br) partial: 167.3 (d, $^{1}J_{CF}$ = 260 Hz, *C*F), 149.9 (dm, $^{1}J_{CF}$ = 245 Hz, *C*F), 148.7 (dm, $^{1}J_{CF}$ = 235 Hz, *C*F), 139.9 (dm, $^{1}J_{CF}$ = 246 Hz, *C*F), 137.1 (dm, $^{1}J_{CF}$ = 247 Hz, *C*F), 137.0 (dd, $^{2}J_{CP}$ = 13 Hz, $^{3}J_{CF}$ = 11 Hz, Ph), 118.6 (dd, $^{2}J_{CF}$ = 16 Hz, $^{3}J_{CP}$ = 13 Hz, Ph), 113.04 (d, $^{1}J_{CP}$ = 97 Hz, quat Ph). ^{19}F NMR (C_6D_5Br): –97.8 (s, 3F, *F*-C_6H_4), –128.1 (m, 4F, C_6F_4), –134.9 (m, 4F, *o*-C_6F_5), –160.4 (t, 2F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), –165.4 (m, 4F, *m*-C_6F_5), –192.3 (br s, 1F, B*F*). ^{31}P {^{1}H} NMR (C_6D_5Br): 14.1 (s). Anal. calcd. for $C_{36}H_{12}BF_{18}P$: C, 52.21; H, 1.46. Found: C, 53.05; H, 2.10.

35. Heated to reflux in toluene for 6 h. Yield 400 mg (76%). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. ^{1}H NMR (CD_2Cl_2): 7.77–7.72 (m, 3H, Ph), 7.50–7.45 (m, 3H, Ph), 7.19–7.09 (m, 3H, Ph), 7.06–7.01 (m, 3H, Ph), 3.52 (br s, 9H, OMe). ^{11}B{^{1}H} NMR (CD_2Cl_2): –0.5 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 162.1 (quat *Ph*OMe), 149.4 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 148.5 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 148.9 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 139.5 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 137.8 (Ph), 135.8 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 135.1 (d, $^{3}J_{CP}$ = 11 Hz, Ph), 122.39 (d, $^{2}J_{CP}$ = 16 Hz, Ph), 113.2 (d, $^{3}J_{CP}$ = 5 Hz, Ph), 106.4 (d, $^{1}J_{CP}$ = 106 Hz, quat Ph), 56.4 (s, O*Me*). ^{19}F NMR (CD_2Cl_2): –127.9 (br, 1F, C_6F_4), –131.4 (br s, 2F, C_6F_4), –136.0 (m, 5F, C_6F_4, *o*-C_6F_5), –162.2 (t, 2F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), –165.5 (m, 4F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5), –192.8 (br m, 1F, B*F*). ^{31}P {^{1}H} NMR (CD_2Cl_2): 10.9. Anal. calcd. for $C_{39}H_{21}O_3BF_{15}P$: C, 54.91; H, 2.45. Found: C, 54.85; H, 2.10. Preliminary X-ray: triclinic $P\bar{1}$, a = 12.041 Å, b = 12.245 Å, c = 14.757 Å, α = 99.370°, β = 111.626°, γ = 90.521°.

Generation of $Ph_2PH(C_6F_4)BF(C_6F_5)_2$ 25

In a re-sealable J.Young NMR tube the adduct Ph_2PH-$B(C_6F_5)_3$ (0.050 mg, 0.072 mmol) was dissolved in C_6D_5Br (0.75 mL) and heated to 140 °C for 24 h. Near quantitative product formation was observed by NMR. NMR resonances for the major product are reported. Other minor products were observed (>15%) and were unidentified. ^{1}H NMR (CD_2Cl_2): 7.9–7.4 (m, 10H, Ph), 7.5 (d, 1H, P*H*). ^{11}B{^{1}H} NMR (CD_2Cl_2): –1.0 (br s). ^{19}F NMR (CD_2Cl_2): –129.3 (m, 2F, C_6F_4), –132.5 (m, 2F, C_6F_4), –135.8 (m, 4F, *o*-C_6F_5), –160.7 (m, 2F, *p*-C_6F_5), –166.1 (m, 4F, *m*-C_6F_5), –194.8 (br s, 1F, B*F*). ^{31}P {^{1}H} NMR (CD_2Cl_2): 6.5.

Generation of $Et_3P(C_6F_4)BF(C_6F_5)_2$ 29

In a re-sealable J.Young NMR tube $(Et_3P)B(C_6F_5)_3$ (0.050 mg, 0.056 mmol) was dissolved in C_6D_5Br (0.75 mL) and heated to 120 °C for 24 h. Quantitative product formation was observed by NMR spectroscopy although this species was not isolated in analytically pure form. ^{1}H NMR (C_6D_5Br): 2.04–1.93 (m, 6H, $^{2}J_{HP}$ = 20 Hz, $^{3}J_{HH}$ = 7 Hz, C*H*$_2$), 0.85–0.76 (dt, 9H, $^{3}J_{HP}$ = 21 Hz, $^{3}J_{HH}$ = 7 Hz, Me). ^{11}B{^{1}H} NMR (C_6D_5Br): 0.5 (br). ^{13}C{^{1}H} NMR (C_6D_5Br) partial: 149.7 (dm, $^{1}J_{CF}$ = 248 Hz, *C*F), 148.21 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 146.3 (dm, $^{1}J_{CF}$ = 255 Hz, *C*F), 139.3 (dm, $^{1}J_{CF}$ = 248 Hz, *C*F), 137.0 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 91.0 (dt, $^{1}J_{CP}$ = 80 Hz, $^{2}J_{CF}$ = 18 Hz, quat), 13.7 (d, $^{1}J_{CP}$ = 48 Hz, *C*H$_2$), 5.3 (d, $^{2}J_{CP}$ = 5 Hz, Me). ^{19}F NMR (C_6D_5Br): –129.8 (m, 2F, C_6F_4), –134.0 (m, 2F, C_6F_4), –135.8 (m, 6F, $^{3}J_{FF}$ = 20 Hz, *o*-C_6F_5), –161.1 (m, 3F, $^{3}J_{FF}$ = 21 Hz, *p*-C_6F_5), –166.2 (m, 6F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5), –192.2 (br s, 1F, B*F*). ^{31}P {^{1}H} NMR (C_6D_5Br): 39.1.

Synthesis of $Cy_3P(C_6F_4)BF(C_6F_5)$(Ph) 37

A clear yellow solution of **36** (0.100 g, 0.237 mmol) and Cy_3P (0.067 g, 0.240 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 and the mixture filtered and dried *in vacuo* for 1 h. The product was collected as a white solid. Yield 0.110 g (80%). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. ^{1}H NMR (CD_2Cl_2): 7.40 (d, 2H, $^{3}J_{HH}$ = 7 Hz, Ph), 7.16 (d, 2H, $^{3}J_{HH}$ = 7 Hz, Ph), 7.10 (m, 1H, $^{3}J_{HH}$ = 7 Hz, Ph), 2.92 (m, 3H, $^{3}J_{HH}$ = 12 Hz, PCy), 1.95–1.27 (br m, 30H, PCy). ^{11}B{^{1}H} NMR (CD_2Cl_2): 2.2 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 145.0 (dm, $^{1}J_{CF}$ = 250 Hz, *C*F), 148.5 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 147.6 (dm, $^{1}J_{CF}$ = 255 Hz, *C*F), 139.2 (dm, $^{1}J_{CF}$ = 240 Hz, *C*F), 137.6 (dm, $^{1}J_{CF}$ = 245 Hz, *C*F), 131.98 (s, Ph), 127.17 (s, Ph), 125.41 (s, Ph), 88.73 (dm, $^{1}J_{CP}$ = 70 Hz, PC_6F_4), 33.2 (d, $^{1}J_{CP}$ = 40 Hz, PCy_3), 28.0 (s, PCy_3), 27.5 (d, $^{3}J_{CP}$ = 14 Hz, PCy_3), 25.9 (s, PCy_3). ^{19}F NMR (CD_2Cl_2): –126.9 (m, 2F, C_6F_4), –132.1 (m, 2F, C_6F_4), –133.6 (d, 2F, $^{3}J_{FF}$ = 16 Hz, *o*-C_6F_5), –162.9 (t, 1F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), –166.8 (t, 2F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5), –193.4 (br s, B*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2): 41.2. Anal. calcd. for $C_{36}H_{38}BF_{10}P$: C, 54.91; H, 2.45. Found: C, 54.55; H, 2.45.

X-Ray data collection, reduction, solution and refinement

Single crystals were mounted in thin-walled capillaries either under an atmosphere of dry N_2 in a glove box and flame sealed or coated in paratone-N oil. The data were collected using the SMART software package[32] on a Siemens SMART System CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A hemisphere of data was collected in 1448 frames with 10 second exposure times unless otherwise noted. Data reduction was performed using the SAINT software package[33] and an absorption correction applied using SADABS.[34]

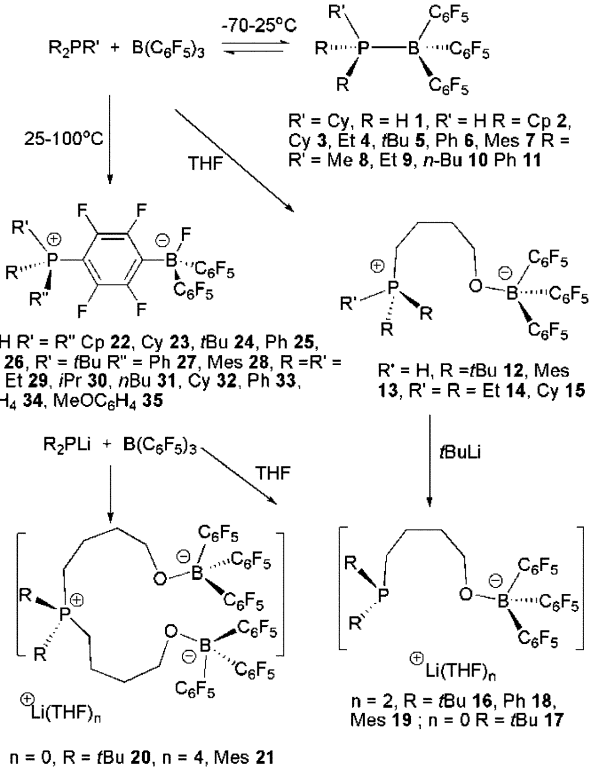
The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[35] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Phosphorus-bound hydrogen atoms were located in the electron difference map and their positions refined isotropically. In the case of compound **5**, constraints were imposed on the disordered toluene solvate. Disordered CH_2Cl_2 solvent molecules were removed using the 'squeeze' command in PLATON for compounds **28** and **34**. In the case of compound **37** the disordered CH_2Cl_2 was modelled.

Crystal data and structure refinement parameters are given in Table 1.†

Results and discussion

Classical Lewis adducts

Following published procedures, a range of phosphines were combined in toluene with $B(C_6F_5)_3$ and stirred for 1 hour at 25 °C. Concentration of the solvent afforded the series of adducts, $(CyPH_2)B(C_6F_5)_3$ **1**, $((C_5H_9)_2PH)B(C_6F_5)_3$ **2**, $(Cy_2PH)B(C_6F_5)_3$ **3**,[24] $(Et_2PH)B(C_6F_5)_3$ **4**, $(Ph_2PH)B(C_6F_5)_3$ **6**,[24] $(Mes_2PH)B(C_6F_5)_3$ **7**, $(Me_3P)B(C_6F_5)_3$ **8**,[25–27] $(Et_3P)B(C_6F_5)_3$ **9**, $(n\text{-}Bu_3P)B(C_6F_5)_3$ **10** and $(Ph_3P)B(C_6F_5)_3$ **11**[28,29] (Scheme 2). All products were readily characterized by ^1H, ^{11}B,$^{13}C\{^1H\}$, ^{19}F and ^{31}P NMR spectroscopy (Table 2). These adducts exhibit a gap in the ^{19}F NMR resonances attributable to the *meta* and *para* fluorine atoms and a ^{11}B chemical shift that is characteristic of a four-coordinate boron center.[36–41] In addition, the solid state structures of **4**, **5**, **6** and **9** were determined



Scheme 2 Synthesis of compounds **1**–**35**.

Table 1 Crystallographic data[a]

	4[b]	5·0.5C$_7$H$_8$	6	9	14	15[b]	27	28	31	33·C$_6$H$_5$Br	34	36	37·CH$_2$Cl$_2$
Formula	$C_{22}H_{11}BF_{15}P$	$C_{29.5}H_{23}BF_{15}P$	$C_{30}H_{11}BF_{15}P$	$C_{24}H_{15}BF_{15}P$	$C_{28}H_{23}BF_{15}OP$	$C_{40}H_{41}BF_{15}OP$	$C_{28}H_{15}BF_{15}P$	$C_{31}H_{21}BF_{15}P$	$C_{30}H_{27}BF_{15}P$	$C_{42}H_{20}BBrF_{15}P$	$C_{36}H_{12}BF_{18}P$	$C_{18}H_5BF_{10}$	$C_{37}H_{40}BCl_2F_{10}P$
Formula wt	602.09	704.26	698.17	630.14	702.2	864.5	678.18	720.26	714.30	931.27	828.24	422.03	787.37
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Phca$	$P\bar{1}$
a/Å	8.2030(16)	9.3182(19)	16.064(2)	13.197(2)	10.3288(17)	12.2670(39)	23.155(5)	11.819(5)	9.2247(16)	12.9407(16)	12.9545(15)	10.6539(13)	11.635(3)
b/Å	16.295(3)	10.374(2)	8.3163(11)	10.5908(18)	12.0825(20)	13.0763(42)	10.399(2)	12.003(6)	16.029(3)	13.0760(16)	13.2370(16)	16.736(2)	12.659(3)
c/Å	8.4244(17)	15.635(3)	21.102(3)	18.211(3)	13.0835(21)	24.4486(78)	23.014(5)	14.964(7)	21.638(4)	13.2779(16)	13.5614(16)	19.095(2)	13.371(3)
α/°	90	88.96(3)	90	90	94.234(2)	90.0	90	66.442(5)	90	68.326(2)	66.727(2)	90	73.387(3)
β/°	97.57(3)	85.90(3)	102.364(2)	93.850(2)	105.527(2)	90.0	93.67(3)	69.594(5)	100.781(2)	65.310(2)	63.9130(10)	90	77.620(3)
γ/°	90	78.03(3)	90	90	106.696(2)	90.0	90	74.705(6)	90	72.050(2)	72.990(2)	90	82.653(3)
V/Å^3	1116.3(4)	1474.7(5)	2753.8(6)	2539.6(7)	1486.64(17)	3921.73(22)	5530.4(19)	1772.1(14)	3143.0(9)	1865.3(4)	1898.7(4)	3404.7(7)	1838.7(7)
Z	2	2	4	4	2	4	8	2	4	2	2	8	2
d(calc)/g cm^{-3}	1.791	1.586	1.684	1.648	1.57	1.46	1.629	1.350	1.507	1.658	1.449	1.647	1.422
μ/cm^{-1}	0.260	0.209	0.224	0.232	0.210	0.174	0.220	0.176	0.197	1.253	0.186	0.172	0.298
Data collected	6659	13213	25561	23727	14171	37516	25443	16895	29420	18019	18290	36577	17839
R_{int}	0.0364	0.1255	0.0311	0.0766	0.0451	0.1140	0.1158	0.0389	0.0287	0.0210	0.0210	0.0401	0.0262
Data $F_o^2 > 3\sigma(F_o^2)$	3553	4977	4837	4463	5216	6900	4840	6214	5502	6552	6669	4098	6441
Variables	356	412	428	386	409	523	410	437	424	541	505	262	464
R	0.0400	0.0744	0.0378	0.0479	0.0742	0.0470	0.0685	0.0486	0.0557	0.0448	0.0445	0.0484	0.0687
R_w	0.1007	0.1808	0.0892	0.0968	0.1973	0.0737	0.1469	0.1078	0.1483	0.1185	0.1216	0.1241	0.1954
GOF	1.030	0.988	1.045	1.014	1.011	0.985	1.027	0.907	1.032	0.957	1.019	1.002	1.046

[a] Data collected at 20 °C with Mo Kα radiation ($\lambda = 0.71073$ Å). $R = \sum(F_o - F_c)/\sum F_o$, $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] Flack parameters: **4**: –0.08(12), **15**: –0.19(14).

Table 2 Chemical shifts and structural data for free phosphine, (phosphine)$B(C_6F_5)_3$ adducts and $R_2PR'(C_6F_4)BF(C_6F_5)_2$

Phosphine		$B(C_6F_5)_3$ adduct				$R_2PR'(C_6F_4)BF(C_6F_5)_2$		
	$^{31}P(^1J_{PH})$	Cmpd	$^{31}P(^1J_{PH})$	^{11}B	P–B/Å	Cmpd	$^{31}P(^1J_{PH})$	^{11}B
H_3P					2.046(8)[59]			
tBuPH$_2$					2.015(3)[60]			
PhPH$_2$					2.039(3)[61]			
CyPH$_2$[a]	−110.1(184)	**1**	−30.0(392)	−17.5				
$(C_5H_9)_2PH$[b]	−35.2(191)	**2**	11.2(408)	−15.9	2.0243(3)	**22**	12.7(508)	−0.1
Cy$_2$PH[c,27]	−27.5(192)	**3**	9.3(406)	−13.5	2.0270(14)[24]	**23**	11.5(480)	−0.2
Et$_2$PH[c,24]	−55.5(190)	**4**	5.7(412)	−16.2	2.036(4)			
tBu$_2$PH[c]	20.1(199)	**5**	17.4(394)	−12.8	2.094(7)	**24**	34.2(465)	0.8
Ph$_2$PH	−40.1(215)	**6**	0.9(411)	−9.4	2.098(3)	**25**	6.5(500)	−1.0
Mes$_2$PH[c]	−92.7(229)	**7**	−67.7	23.6		**26**	−37.7(503)	0.4
tBuPhPH[b]	−5.3(208)					**27**	14.7(487)	0.4
tBuMesPH[d]	−49.1(214)					**28**	−2.9(505)	0.4
Me$_3$P[24]	−63.3	**8**	−6.1	−14.7	2.061(4)[25]			
Et$_3$P[c]	−19.1	**9**	5.6	−13.4	2.081(4)	**29**	39.1	0.5
iPr$_3$P[24]	19.3					**30**	53.2	−0.9
nBu$_3$P[c]	−31.6	**10**	−0.6	−13.5		**31**	33.1	−0.8
Cy$_3$P[c]	11.1					**32**	41.6	−0.7
Ph$_3$P[c]	−4.6	**11**	−5.2	−2.5	2.180(6)[17]	**33**	15.1	−0.3
$(p$-C$_6$H$_4$F$)_3$P[c]	−9					**34**	14.1	−0.2
$(o$-C$_6$H$_4$OMe$)_3$P[c]	−29.3					**35**	10.9	−0.5

[a] C_6D_5Br solvent for NMR spectra. [b] CD_2Cl_2 solvent for NMR spectra. [c] C_6D_6 solvent for NMR spectra. [d] THF solvent for NMR spectra.

by X-ray crystallography (Fig. 1, Table 1), while those of **2**, **3**,[24] **8**[25] and **10**[29] had been previously determined. As expected the geometries at the B and P atoms are both pseudo-tetrahedral in each case. In the present compounds, the P–B bond distances range from 2.024(3) to 2.180(6) Å (Table 2) and appear to vary with both the relative steric bulk and basicity of the phosphine. The bulky phosphine adduct **7** was isolated, but only as a minor product. The ^{31}P and ^{11}B NMR spectra of **7** are very broad signals at −67 and 23 ppm, respectively, while the ^{19}F NMR spectrum exhibits three broad resonances for the *ortho*, *meta* and *para* fluorine atoms of the C_6F_5 rings. Upon cooling to −70 °C, the three broad fluorine resonances split into 13 sharp peaks with 2 of double intensity, corresponding to 15 inequivalent fluorine atoms.

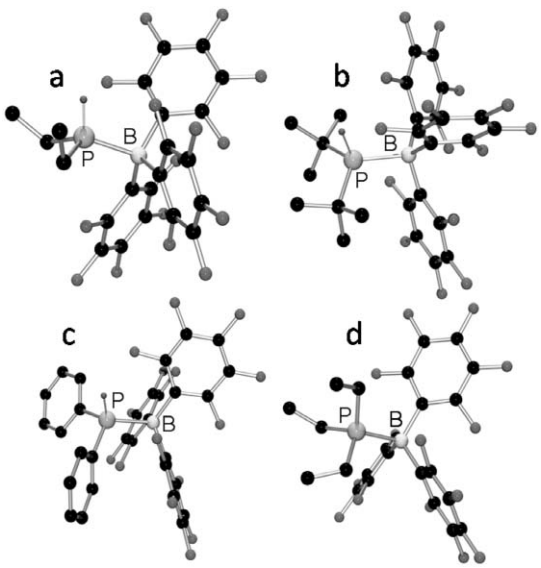


Fig. 1 POV-ray drawings of (a) **4** (b) **5** (c) **6** (d) **9**.

These NMR data support the notation that Mes$_2$PH forms a weak adduct with $B(C_6F_5)_3$ at 25 °C and at low temperatures exhibits PH···FC interactions rendering the inequivalence of fluorine atoms. A similar phenomenon has been previously observed for amine-$B(C_6F_5)_3$ adducts.[42] Similarly, weak P–B interactions were observed between tBu(Mes)PH and $B(C_6F_5)_3$ and thus an adduct was not isolated. In such crowded systems, the steric interactions have been rationalised in terms of the sum of repulsive Pauli and attractive electrostatic and van der Waals interactions by Erker, Grimme and co-workers.[43]

In the case of tBu$_2$PH, evidence of formation of adduct (tBu$_2$PH)$B(C_6F_5)_3$ **5** was observed on cooling of solutions of the phosphine in the presence of $B(C_6F_5)_3$ to −60 °C. Such solutions gave rise to a broad ^{31}P NMR resonance at 17.4 ppm and a ^{11}B NMR signal at −12.8 ppm. The ^{19}F NMR spectrum of **5** shows eight signals consistent with inequivalent C_6F_5 ring environments. Nonetheless, the adduct **5** was not stable as alternate chemistry occurs on warming to 25 °C (*vide infra*).

Larger phosphines such as $(o$-C$_6$H$_3$Me$_2)_3$P, $(o$-C$_6$H$_4$Me$)_3$P, (C$_6$H$_2$Me$_3)_3$P or tBu$_3$P appear to effect no reaction with $B(C_6F_5)_3$ in toluene-d_8 or CD_2Cl_2 in the temperature range of 25 °C to −70 °C as evidenced by ^1H, ^{31}P, ^{11}B, and ^{19}F NMR spectroscopy. Such mixtures of Lewis acids and Lewis bases, where steric demands preclude quenching of the Lewis acidity and basicity, have been described as 'frustrated Lewis pairs' and have been shown to exhibit unique reactivity with small molecules.[44–48] As noted previously, the combination of Mes$_3$P and $B(C_6F_5)_3$ gave rise to a violet solution; in contrast to combinations of Ph$_2$MeN and $B(C_6F_5)_3$ where formal electron transfer is proposed,[4] reaction mixtures of Mes$_3$P and $B(C_6F_5)_3$ were found to be EPR silent.

THF ring-opening

Intuitively an alternative to the procedure above to generate $B(C_6F_5)_3$ adducts involves the displacement of THF from

$(THF)B(C_6F_5)_3$. Indeed this approach has been employed to obtain **3** and **6**.[24] However, the analogous reactions employing tBu_2PH, Mes_2PH and Cy_3P do not proceed in this fashion; rather, reaction of $(THF)B(C_6F_5)_3$ with these phosphine effects the ring-opening of THF affording the products **12**, **13**, and **15** in 81, 79 and 98% yields, respectively. The ^{11}B NMR spectra revealed single resonances at *ca.* −2.1 to −2.8 ppm indicative of four-coordinate boron centers, while the ^{31}P NMR spectra gives rise to downfield resonances. The ^{1}H NMR data are consistent with the presence of four methylene resonances. These NMR data are consistent with the formulation of the products as the THF ring-opened phosphonium borates $tBu_2PH(C_4H_8O)B(C_6F_5)_3$ **12**, $Mes_2PH(C_4H_8O)B(C_6F_5)_3$ **13** and $Cy_3P(C_4H_8O)B(C_6F_5)_3$ **15** (Scheme 2). In a similar fashion, the adduct **9** was dissolved in THF and heated to 80 °C for 6 hours to give a white solid formulated as $Et_3PC_4H_8OB(C_6F_5)_3$ **14** in 81% yield. It is noteworthy that prolonged heating of **4** in THF to 80 °C showed no such rearrangement. This presumably reflects the stronger P–B bond in **4** relative to that in **9**. The formulations of the zwitterions above were also supported by X-ray data for **12**, **13**,[18] **14** and **15** (Fig. 2). The THF ring-opening reaction products exhibit B–O bond lengths of 1.415(18)–1.459(4) Å, which are in the range seen for the related compound tBuNTe(μ-NtBu)$_2$TeN(tBu)(CH$_2$)4OB(C$_6$F$_5$)$_3$ (1.444(4) Å)[49] and are shorter than that found in the anion $[HOB(C_6F_5)_3]^-$ (B–O = 1.480(11) Å).[50] The remaining metric parameters are unexceptional.

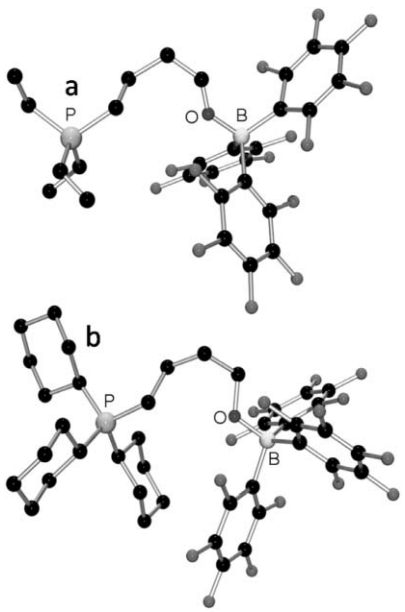


Fig. 2 POV-ray drawings of (a) **14** (b) **15**.

Related anionic phosphine-borates are readily derived from **12** *via* treatment with tBuLi or, alternatively, by treating $B(C_6F_5)_3$ with a lithium phosphide (R_2PLi, R = tBu, Ph Mes) to afford **16**–**19** in THF. These approaches, depending on the solvent used, afford the species $[Li(THF)_2][tBu_2P(C_4H_8O)B(C_6F_5)_3]$ **16**, $[Li][tBu_2P(C_4H_8O)B(C_6F_5)_3]$ **17**, $[Li(THF)_2][Ph_2P(C_4H_8O)B(C_6F_5)_3]$ **18** and $[Li(THF)_2][Mes_2P(C_4H_8O)B(C_6F_5)_3]$ **19** as confirmed by NMR data (Scheme 2). Indeed this latter approach can be extended to a 2 : 1 reaction, as treatment of $(THF)B(C_6F_5)_3$ with two equivalents of a lithium phosphide affords the species $[Li][tBu_2P(C_4H_8OB(C_6F_5)_3)_2]$ **20** and $[Li(THF)_4][Mes_2P(C_4H_8OB(C_6F_5)_3)_2]$ **21**. The X-ray structures of **19** and **20** have been previously communicated.[18] It should be noted that **20** is observed in preparations of **16** performed at room temperature, while **16** is generated cleanly at −78 °C, consistent with the ability of **16** to effect also THF ring-opening.

Aromatic substitution

In the majority of cases, the classical borane-phosphine adducts were found to undergo rearrangement reactions, yet requiring prolonged heating in some cases. For example, heating **2** in a sealed reaction bomb to 125 °C for 24 h in toluene resulted in the formation of a white precipitate. Subsequent workup afforded **22** as a white solid in 73% yield (Scheme 2). The ^{11}B NMR signal for **22** was observed at −0.2 ppm, which is shifted dramatically from that seen for **2** (−13.5 ppm). Similarly, the ^{31}P NMR resonance shifted downfield slightly to 11.5 ppm and notably exhibited a $^{1}J_{PH}$ coupling constant of 480 Hz typical of a phosphonium salt. A new ^{19}F NMR signal was observed at −191.5 ppm attributable to a B–F unit, while resonances at −129.2 and −131.9 ppm confirmed the presence of a 1,4-disubstituted C_6F_4 aryl ring. Collectively, these data are consistent with the formulation of **22** as $(C_5H_9)_2PH(C_6F_4)BF(C_6F_5)_2$. In a similar fashion, the adducts **3**, **6**, **8**, **9**, **10** and **11** underwent similar thermal rearrangements to give the corresponding zwitterionic species $Cy_2PH(C_6F_4)BF(C_6F_5)_2$ **23**, $Ph_2PH(C_6F_4)BF(C_6F_5)_2$ **25**, $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ **26**, $Et_3P(C_6F_4)BF(C_6F_5)_2$ **29**, $nBu_3P(C_6F_4)BF(C_6F_5)_2$ **31** and $Ph_3P(C_6F_4)BF(C_6F_5)_2$ **33**, in near quantitative yields, respectively (Scheme 2). Although such rearrangements of Lewis acid–base adducts have only rare precedent,[17] the nucleophilic substitution of at the *para*-position of a pentafluorophenyl ring is well known.[51,52]

In the case of bulky basic phosphine, the attack of the fluorinated aromatic rings is even more facile. For example and as mentioned above, isolation of the $B(C_6F_5)_3$ adduct of tBu_2PH is challenging; however, on stirring at room temperature, attack at a *para*-carbon atom proceeds easily to give $tBu_2PH(C_6F_4)BF(C_6F_5)_2$ **24**. Similarly, monitoring the reaction of Cy_3P and $B(C_6F_5)_3$ showed no evidence of the formation of the adduct, but rather the rapid formation of $Cy_3P(C_6F_4)BF(C_6F_5)_2$ **32**. In the same fashion, the species $(t$Bu$)(Ph)PH(C_6F_4)BF(C_6F_5)_2$ **27**, $(t$Bu$)(Mes)PH(C_6F_4)BF(C_6F_5)_2$ **28**, $iPr_3P(C_6F_4)BF(C_6F_5)_2$ **30** and $(o\text{-}C_6H_4OMe)_3P(C_6F_4)BF(C_6F_5)_2$ **35**, were prepared and isolated (Scheme 2). The spectral data for these zwitterionic species are all similar to those described above for **22**, each exhibiting the characteristic ^{31}P, ^{11}B, ^{19}F and ^{1}H NMR resonances (Table 2). In each case, the sterically congested environment about the phosphorus atom disfavors coordination to boron thus prompting nucleophilic aromatic substitution at the electrophilic *para*-carbon atom of an arene ring followed by fluoride transfer to boron.

X-Ray structural data for **27**, **28**, **31**, **33** and **34** are reported herein (Fig. 3 and 4) confirming the zwitterionic nature of these species. In each species the phosphorus and boron centers are pseudo-tetrahedral. The B–F bond lengths range from 1.413(4) Å to 1.436(6) Å and compare well to those found in the zwitterions 1,4-$Ph_3PCH_2(C_6F_4)BF(C_6F_5)_2$ (1.392(12) Å),[17] 1,4-$Ph_2MeP(C_6H_4)BF(Mes)_2$ (1.467(4) Å),[53] and the anions $(C_6F_5)_3BF$ (1.428 Å),[54] and $(o\text{-}(C_6F_5)C_6F_4)_3BF$ (1.472 (11) Å),[55] while they are

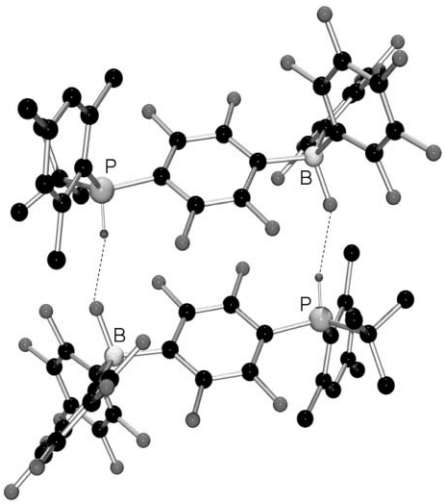


Fig. 3 POV-ray drawings of two adjacent molecules of **28**. The dashed lines indicate the close approach of the BF and PH fragments.

longer than those found in the diarylboranes Mes_2BF (1.339(2) Å) and $(o,p\text{-}C_6H_3(CF_3)_2)_2BF$ (1.313(3) Å).[56] In the solid state, the molecules of **28**, like **24**, pack in a head-to-tail fashion accommodating intermolecular P–H···F–B interactions of 2.55(3) Å and 2.20(2) Å respectively (Fig. 4). This orientation also provides parallel yet offset π-stacking of the phosphorus and boron substituted (PC_6F_4B) arene rings. Additionally the PH moiety is oriented parallel to an *o*-fluorine of the bridging C_6F_4 unit resulting in intramolecular P–H···F–C contacts of 2.50(3) Å and 2.47(2) Å for **24** and **28**, respectively.[57] The remaining metric parameters were unexceptional and similar to those communicated for **22**, **24**, **26**, **30** and **32**. It should be noted that recently, Royo and co-workers have reported the formation of a related zwitterion $Ph_3P(C_6F_4)BMe(C_6F_5)_2$ as a by-product of a mixture of Ph_3P and the ion pair $[Zr\{C_5H_3[SiMe_2(\eta^1\text{-}N\mathit{t}Bu)]_2\}][RB(C_6F_5)_3]$ left at 80 °C for one week.[58]

While the aromatic substitution seems to tolerate a variety of substituents on phosphorus, it is noteworthy that no reaction was observed with prolonged heating of the solutions of adducts **1**, **4** and **8** to 140 °C for several days.[62] The inability of these adducts to undergo thermal rearrangement demonstrates that small, highly basic phosphines form strong P–B bonds with $B(C_6F_5)_3$ that are thermally stable. This notion is consistent with the relatively short P–B bond lengths seen in **4** and **8** in comparison to those determined for **6** to **9** for which thermal rearrangement does proceed (Table 2). In the case of **1** and **4**, secondary H···F contacts analogous to those seen for amine adducts[24] also strengthen the Lewis acid–base interaction. Short inter- and intra-molecular CH···F contacts have been described for **7**[25] and are thought to contribute to its poor solubility in organic solvents. Short intramolecular CH···F and PH···F and intermolecular CH···F contacts less than the sum of the van der Waals radii (<2.55 Å) are found in **4**.[57] Bradley *et al.*[60] have attributed the strength of the adduct $(\mathit{t}BuPH_2)B(C_6F_5)_3$ *vs.* $(H_3P)B(C_6F_5)_3$ to both short inter- and intra-molecular H···F interactions present in the former. In each case, the CH···F and/or PH···F interactions are not retained in solution as determined using ^{19}F NMR spectroscopy, indicating that such interactions are significantly weaker than similar NH···F contacts, which are typically observed in solution.[24]

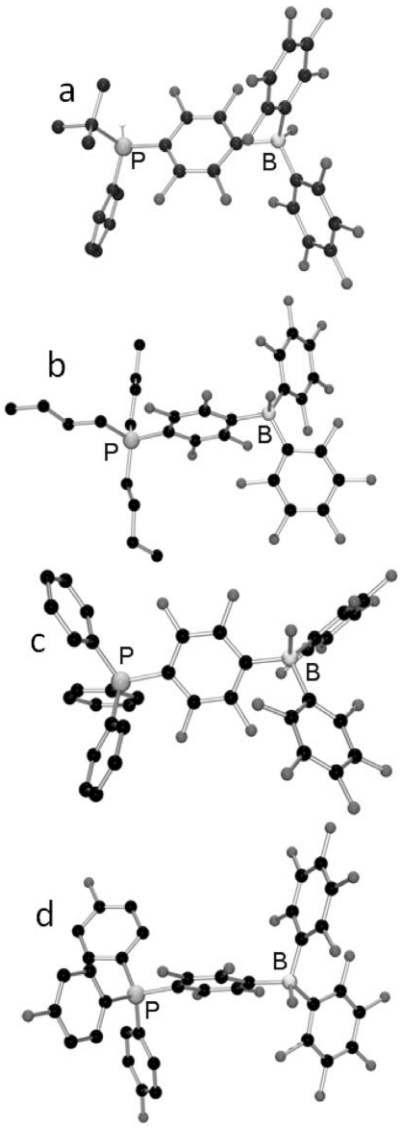


Fig. 4 POV-ray drawings of (a) **27** (b) **31** (c) **33** (d) **34**.

Interestingly, the solid state structure of the adduct **6** exhibits a short intramolecular PH···F contact of 2.27(2) Å,[57] yet it still thermally rearranges to give the zwitterions **25**, albeit only at a higher temperature. Hence while such secondary interactions may play a role, clearly the sterics and basicity of the phosphine dominate in determining the strength of the P–B bond.

To examine the impact of alternative substitution at the boron atom the species $PhB(C_6F_5)_2$ **36**,[31] known to have a diminished degree of Lewis acidity[63,64] compared to $B(C_6F_5)_3$, was prepared. Crystals of $PhB(C_6F_5)_2$ were obtained and the solid-state structure determined by X-ray diffraction (Fig. 5(a)). The structure is planar at B ($\sum_{C\text{-}B\text{-}C} = 360°$) and exhibits a propeller shape with the two C_6F_5 rings turned 43° and 50° out of the BC_3 plane and the C_6H_5 ring rotated 24° out of the BC_3 plane as is typical for related triarylboranes.[56,65–71] Upon addition of Cy_3P to a toluene solution of $PhB(C_6F_5)_2$ at 25 °C, a white solid precipitated and was identified as the phosphonium borate $Cy_3P(C_6F_4)BF(Ph)(C_6F_5)$ **37** (Fig. 5(b)). The ^{31}P NMR spectrum is very similar to that of **32**, while the ^{11}B NMR resonance is shifted downfield 3 ppm from

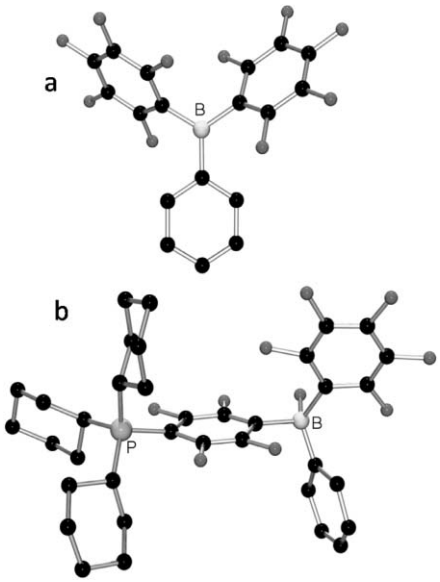


Fig. 5 POV-ray drawings of (a) **36** (b) **37**.

that of **32**, while the gap between the *meta*- and *para*-resonances ($\Delta_{p\text{-}m}$ = 4 ppm) is slightly smaller than in **32** ($\Delta_{p\text{-}m}$ = 5 ppm). The solid-state structure of **37** was determined by X-ray diffraction. While the metric parameters are as expected and unexceptional, the structure confirms the preferential attack of the phosphine at the electron deficient C_6F_5 ring. This is consistent with experiments where mixtures of Ph_3B and Cy_3P or tBu_2PH showed no evidence of aromatic substitution at 125 °C by ^{11}B or ^{31}P NMR spectroscopy. In line with this, no reactivity was observed between Cy_3P and the borane B(*m*-$C_6H_3(CF_3)_2)_3$.

Mechanistic insights

Dissociation of (phosphine)$B(C_6F_5)_3$ adducts permits attack at the *para*-carbon of a C_6F_5 ring on $B(C_6F_5)_3$ to give zwitterions of the form $R'R_2P(C_6F_4)BF(C_6F_5)_2$. Mechanistically it is thought that the first step in the reaction involves nucleophilic attack by phosphine at a *para*-carbon atom forming a dearomatized intermediate. This step is followed by fluoride transfer to the boron atom. The strength of the newly formed P–C and B–F bonds renders the reaction irreversible. A similar mechanism was described by Erker and co-workers[17] for the generation of $(Ph_3PCHPh)C_6F_4BF(C_6F_5)_2$. Similarly, the reaction of tertiary phosphines with trityl cation proceeds in a similar fashion, initially giving the (4-benzhydrylidene-cyclohexa-2,5-dienyl)phosphonium cations $[R_3P(C_6H_5)=CPh_2]^+$ and subsequent (*p*-benzhydryl)phenylphosphonium cations $[R_3P(C_6H_4)CHPh_2]^+$ (Scheme 1).[16] Efforts to observe a dearomatized intermediate in the reaction of phosphine and $B(C_6F_5)_3$ by NMR spectroscopy were unsuccessful. Nonetheless, the general trend in reactivity seems to parallel steric bulk, consistent with the proposed mechanism; small phosphines form robust adducts, larger phosphines rearrange to give aromatic substitution under thermal duress, larger still phosphines form weak adducts and effect aromatic substitution rapidly, while very large phosphines show no reactivity at all towards $B(C_6F_5)_3$.

In summary, it has been demonstrated that the reactivity between Lewis basic phosphines and the Lewis acid $B(C_6F_5)_3$ is not limited to simple adduct formation. Instead, novel phosphonium borate zwitterions derived from THF ring-opening and nucleophilic aromatic substitution are accessible depending on the conditions. Extremely bulky tertiary phosphines do not react at all with $B(C_6F_5)_3$ thus yielding 'frustrated Lewis pairs'. We continue to examine the chemistry of each class of these products. While we are currently exploring the potential of these two classes of zwitterions as ligands, we also continue to explore the fundamental reactivity of Lewis acids and bases and in particular that of 'frustrated Lewis pairs'.

Acknowledgements

Financial support from NSERC of Canada and NOVA Chemicals Corporation is gratefully acknowledged. G. C. W. is grateful for the award of an NSERC-postgraduate scholarship. M. A. D. is grateful for the award of an Ontario graduate scholarship.

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