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Synthesis and Lewis acidity of fluorophosphonium cations†

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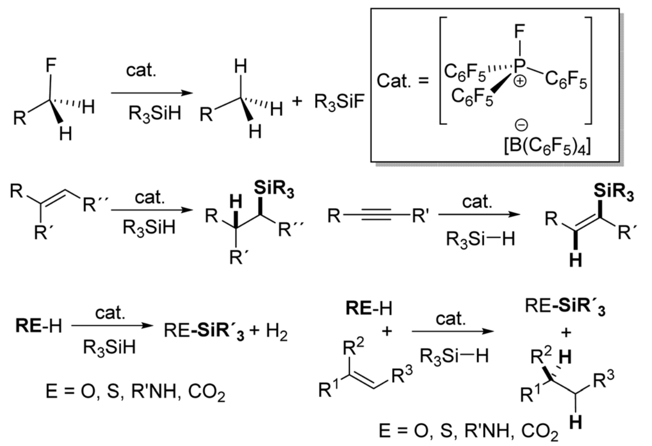
A series of fluorophosphonium salts, $[R_3PF][X]$ (R = alkyl or aryl; X = $FB(C_6F_5)_3$, $[B(C_6F_5)_4]$), have been prepared by reactions of phosphine/borane frustrated Lewis pairs (FLPs) with XeF_2 or difluorophosphoranes with $[Et_3Si][B(C_6F_5)_4]$. As the substituents bound to phosphorus become increasingly electron withdrawing, the corresponding fluorophosphonium salts are shown to be increasingly Lewis acidic. Calculations were also performed to determine the relative fluoride ion affinities (FIA) of these fluorophosphonium cations.

The p-block elements which have been exploited for their Lewis acidic properties have thus far mainly consisted of boron,[1] aluminium,[2] and silicon,[3] although heavier elements have also been investigated to a lesser extent.[4] Such group 13 and 14 electrophiles have found utility in a range of Lewis acid chemistry and catalysis[5–8] as well as in the domain of frustrated Lewis pair (FLP) chemistry.[1] In contrast, group 15 compounds have mainly been exploited for their Lewis basic properties and thus as σ-donor for applications in transition metal coordination, organometallic chemistry and catalysis.[9–13] An overlooked subset of phosphorus chemistry is the ability for these compounds to act as acceptors. Phosphenium or P(III) cations contain both a lone pair of electrons and an empty p-orbital. Such systems have been shown to exhibit nucleophilic and electrophilic character acting as both donors and acceptors.[14–22] In a recent result we have described the direct reaction of a triphosphabenzene derivative with H_2.[23] In this case, computational work supports an FLP-type mechanism in which P and C acts as Lewis acidic and Lewis basic centers respectively in the heterolytic cleavage of H_2.

The electrophilicity of higher oxidation state phosphorus-species have also been exploited in the classic Wittig[24] and Staudinger[25] reactions. In addition, phosphonium Lewis acids have been employed in catalytic transformations, including Diels–Alder cyclization reactions,[26] addition reactions to polar unsaturates,[27] and as sensors for fluoride ions.[28] More recently, we have utilized electron withdrawing fluorine and pentafluorophenyl substituents to develop highly electrophilic fluorophosphonium cations. These cations have been shown to be highly effective Lewis acids for the stoichiometric sequestration of carbon dioxide,[29] as well as the catalytic hydrodefluorination of fluoroalkanes,[30] hydrosilylation of olefins and alkynes,[31] dehydrocoupling of amines, alcohols, acids and thiols with silanes as well as tandem transfer hydrogenation of olefins (Scheme 1).[32]



Scheme 1 Reactions of electrophilic phosphonium cations.

In this full report we described the facile synthesis and full characterization of a series of fluorophosphonium salts. In an effort to rank these Lewis acids with known systems, various approaches to Lewis acidity evaluation are considered and discussed.

Experimental section

General procedures

All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and

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glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals or Apollo Scientific, and were used without further purification unless indicated otherwise. CH_2Cl_2, Et_2O, *n*-pentane, and toluene were dried using an Innovative Technologies solvent purification system. CD_2Cl_2 and $CDCl_3$ (Aldrich) were deoxygenated, distilled over CaH_2, then stored over 4 Å molecular sieves before use. C_6D_5Br (Aldrich) was deoxygenated and stored over 4 Å molecular sieves before use. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer. ^{1}H NMR data, referenced to external Me_4Si, are reported as follows: chemical shift (δ/ppm), coupling constant (Hz), normalized integrals. $^{13}C\{^1H\}$ NMR chemical shifts (δ/ppm) are referenced to external Me_4Si. $[Ph_2(C_6F_5)PF][FB(C_6F_5)_3]$ (**6**), $[Ph(C_6F_5)_2PF][B(C_6F_5)_4]$ (**7**), and $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (**8**), were prepared by the reported procedures.[30,33] F_2PR_3 (R = *t*Bu,[34] Mes,[35] *o*-Tol,[35] Ph,[36] *p*-C_6H_4F[37] are literature known but were synthesized by different routes. NMR spectroscopic data match with the literature values.

Synthesis of $[^tBu_3PF][FB(C_6F_5)_3]$ (1). Two procedures can be utilized to synthesize this product, the first involving addition of XeF_2 to the FLP and the second involving initial phosphine oxidation followed by borane abstraction of fluoride. Both are described below. (1) A solution of tBu_3P (40 mg, 195 μmol) in 5 mL of dichloromethane was added to $B(C_6F_5)_3$ (100 mg, 195 μmol). This solution was added to XeF_2 (33 mg, 195 μmol) in 5 mL of dichloromethane, resulting in immediate effervescence. The reaction was allowed to stir for 10 minutes and the solvent was removed *in vacuo* producing a colorless solid that was washed with pentane (3 × 2 mL) and was dried *in vacuo*. (2) A solution of $^tBu_3P$ (40 mg, 195 μmol) in 5 mL of dichloromethane was added to a solution of XeF_2 (33 mg, 195 μmol) in 5 mL of dichloromethane, resulting in immediate effervescence. When effervescence had ceased (~1 minute), the colourless solution was allowed to stir for an additional 5 minutes. $B(C_6F_5)_3$ (100 mg, 195 μmol) was added and the solvent was removed *in vacuo* producing a colorless solid that was washed with pentane (3 × 2 mL) and was dried *in vacuo*. Diffraction quality crystals were grown from a saturated solution of dichloromethane and *n*-pentane (139 mg, 95%, Anal. Calcd for $C_{30}H_{27}BF_{17}P$: C, 47.90; H: 3.62%. Found C, 47.78; H: 3.73%). **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 1.63 (dd, $^3J_{PH}$ = 15.9 Hz, $^4J_{FH}$ = 1.4 Hz, 27H, CH_3). **^{11}B NMR** (CD_2Cl_2, 128 MHz, $BF_3\cdot OEt_2$): δ −0.6 (d, $^1J_{FB}$ = 70 Hz, *B*F). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −136.6 (m, 6F, *o*-C_6F_5), −162.7 (t, $^3J_{FF}$ = 20 Hz, 3F *p*-C_6F_5), −167.0 (m, 6F, *m*-C_6F_5), −171.6 (d, $^1J_{PF}$ = 1019 Hz, 1F, P*F*), −190.3 (q/br, $^1J_{FB}$ = 70 Hz, 1F, B*F*). **$^{31}P\{^1H\}$** NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 148.5 (d, $^1J_{PF}$ = 1019 Hz, *P*F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, Me_4Si): δ 148.2 (dm, $^1J_{FC}$ = 240 Hz, 6C, C_6F_5), 139.1 (dm, $^1J_{FC}$ = 206 Hz, 3C, *p*-C_6F_5), 136.8 (dm, $^1J_{FC}$ = 231 Hz, 6C, C_6F_5), 41.4 (dd, $^1J_{PC}$ = 26 Hz, $^2J_{FC}$ = 7 Hz, 3C, $C(CH_3)_3)_3$), 27.9 (dd, $^2J_{PC}$ = 2 Hz, $^3J_{FC}$ = 1 Hz, 9C, $C(CH_3)_3)_3$), not observed i-C_6F_5.

Synthesis of $[Mes_3PF][FB(C_6F_5)_3]$ (2). The compound was prepared in a manner similar to that of 1 using Mes_3P (76 mg, 195 μmol), XeF_2 (33 mg, 195 μmol), $B(C_6F_5)_3$ (100 mg, 195 μmol), and was isolated as a white solid (153 mg, 163 μmol, 84% yield). Anal. Calcd for $C_{45}H_{33}BF_{17}P$: C, 57.59; H, 3.54%. Found: C, 57.54; H: 3.76%. **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 7.22 (d, $^4J_{PH}$ = 3.8 Hz, 3H, *m*-Mes), 7.08 (d, $^4J_{PH}$ = 6.6 Hz, 3H, *m*-Mes), 2.41 (s, 9H, *o*-CH_3), 2.34 (d, $^4J_{PH}$ = 6.1 Hz, 9H, *o*-CH_3), 1.96 (s, 9H, *p*-CH_3). **^{11}B NMR** (CD_2Cl_2, 128 MHz, $BF_3\cdot OEt_2$): δ −0.6 (d, $^1J_{FB}$ = 69 Hz, *B*F). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −116.7 (d, $^1J_{PF}$ = 940 Hz, 1F, P*F*), −136.6 (m, 6F, *o*-C_6F_5), −163.7 (t, $^3J_{FF}$ = 20 Hz, 3F *p*-C_6F_5), −168.0 (m, 6F, *m*-C_6F_5), −190.9 (q/br, $^1J_{FB}$ = 69 Hz, 1F, B*F*). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 92.9 (d, $^1J_{PF}$ = 940 Hz, *P*F). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 100 MHz, Me_4Si): δ 149.4 (dd, J_{PC} = 3 Hz, J_{FC} = 1 Hz, 3C, Mes), 148.3 (dm, $^1J_{FC}$ = 240 Hz, 6C, C_6F_5), 145.5 (dd, J_{PC} = 8 Hz, J_{FC} = 1 Hz, 3C, Mes), 144.0 (dd, J_{PC} = 18 Hz, J_{FC} = 3 Hz, 3C, Mes), 139.1 (dm, $^1J_{FC}$ = 206 Hz, 3C, *p*-C_6F_5), 136.8 (dm, $^1J_{FC}$ = 231 Hz, 6C, C_6F_5), 133.5 (d, J_{PC} = 14 Hz, 3C, Mes), 133.5 (d, 11 Hz, 3C, Mes), 117.1 (dd, $^1J_{PC}$ = 99 Hz, $^2J_{FC}$ = 13 Hz, 3C, i-Mes), 23.3 (d, $^3J_{PC}$ = 6 Hz, 3C, *o*-Me), 22.5 (dd, J_{FC} = 7 Hz, J_{PC} = 5 Hz, 3C, *o*-Me), 21.7 (s, 3C, *p*-Me), not observed i-C_6F_5.

Synthesis of $[(o\text{-}Tol)_3PF][FB(C_6F_5)_3]$ (3). The compound was prepared in a manner similar to that of **1** using $(o\text{-}Tol)_3P$ (59 mg, 195 μmol), XeF_2 (33 mg, 195 μmol), $B(C_6F_5)_3$ (100 mg, 195 μmol), and was isolated as a white solid (151 mg, 130 μmol, 91%). **Anal. Calcd** for $C_{39}H_{21}BF_{17}P$: C, 54.83; H, 2.48%. Found: C, 54.26; H, 2.46%. **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 7.92 (m, 3H, Tol), 7.68 (m, 3H, Tol), 7.51 (m, 3H, Tol), 7.22 (m, 3H, Tol), 2.47 (d, $^3J_{HH}$ = 2.6 Hz, 9H, CH_3). **^{11}B NMR** (CD_2Cl_2, 128 MHz, $BF_3\cdot OEt_2$): δ −0.6 (d/br, $^1J_{FB}$ = 70 Hz, *B*F). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −125.5 (d, $^1J_{PF}$ = 994 Hz, 1F, P*F*), −135.6 (m, 6F, *o*-C_6F_5), −162.7 (t, $^3J_{FF}$ = 21 Hz, 3F *p*-C_6F_5), −167.0 (m, 6F, *m*-C_6F_5), −190.9 (s/br, 1F, B*F*). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 104.3 (d, $^1J_{PF}$ = 994 Hz, *P*F). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 100 MHz, Me_4Si): δ 148.2 (dm, $^1J_{FC}$ = 240 Hz, 6C, C_6F_5), 145.4 (dd, J_{PC} = 9 Hz, J_{FC} = 1 Hz, 3C, Tol), 139.2 (dm, $^1J_{FC}$ = 206 Hz, 3C *p*-C_6F_5), 138.8 (dd, J_{PC} = 3 Hz, J_{FC} = 1 Hz, 3C, Tol), 136.9 (dm, $^1J_{FC}$ = 231 Hz, 6C, C_6F_5), 135.6 (dd, J_{PC} = 18 Hz, J_{FC} = 2 Hz, 3C, Tol), 134.4 (d, J_{PC} = 12 Hz, 3C, Tol), 128.3 (d, J_{PC} = 16 Hz, 3C, Tol), 115.7 (dd, $^1J_{PC}$ = 105 Hz, $^2J_{FC}$ = 13 Hz, 3C, i-Tol), 22.0 (dd, $^3J_{PC}$ = Hz, $^4J_{FC}$ = Hz, 3C, *o*-Me), not observed i-C_6F_5.

Synthesis of $[Ph_3PF][FB(C_6F_5)_3]$ (4). The compound was prepared in a manner similar to that of **1** using Ph_3P (51 mg, 195 μmol), XeF_2 (33 mg, 195 μmol), $B(C_6F_5)_3$ (100 mg, 195 μmol), and was isolated as a white solid (157 mg, 193 μmol, 99%). **Anal. Calcd** for $C_{36}H_{15}BF_{17}P$: C, 53.23; H, 1.86%. Found: C, 52.80; H, 1.71%. **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 8.04 (m, 3H, Ph), 7.85–7.74 (12H, Ph). **^{11}B NMR** (CD_2Cl_2, 128 MHz, $BF_3\cdot OEt_2$): δ −0.6 (d/br, $^1J_{FB}$ = 57 Hz, *B*F). **^{19}F NMR** (CD_2Cl_2, $CFCl_3$, 377 MHz): δ −128.3 (d, $^1J_{PF}$ = 996 Hz, 1F, P*F*), −135.6 (d, $^3J_{FF}$ = 20 Hz, 6F, *o*-C_6F_5), −162.4 (t, $^3J_{FF}$ = 19 Hz, 3F, *p*-C_6F_5), −166.9 (m, 6F, *m*-C_6F_5), −190.9 (s/br, 1F, B*F*). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 94.7 (d, $^1J_{PF}$ = 996 Hz, *P*F). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 100 MHz, Me_4Si): δ 148.4 (dm, $^1J_{FC}$ = 240 Hz, 6C, C_6F_5), 139.2 (dm, $^1J_{FC}$ = 206 Hz, 3C

p-C_6F_5), 138.9 (dd, $^4J_{PC}$ = 3 Hz, $^5J_{FC}$ = 2 Hz, 3C, p-Ph), 136.9 (dm, $^1J_{FC}$ = 231 Hz, 6C, C_6F_5), 134.3 (dd, J_{PC} = 13 Hz, J_{FC} = 1 Hz, 6C, Ph), 131.2 (d, J_{PC} = 14 Hz, 6C, Ph), 116.5 (dd, $^1J_{PC}$ = 109 Hz, $^2J_{FC}$ = 15 Hz, 3C, i-Ph), not observed i-C_6F_5.

Synthesis of [(*p*-$C_6H_4F)_3PF$][$FB(C_6F_5)_3$] (5). The compound was prepared in a manner similar to that of **5** using (p-$C_6H_4F)_3P$ (62 mg, 195 μmol), XeF_2 (33 mg, 195 μmol), $B(C_6F_5)_3$ (100 mg, 195 μmol), and was isolated as a white solid (149 mg, 172 μmol, 88%). **Anal. Calcd** for $C_{36}H_{12}BF_{20}P$: C, 49.92; H, 1.40%. Found: C, 49.36; H, 1.60%. **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 7.84 (m, 6H, C_6H_4F), 7.48 (m, 6H, C_6H_4F). **^{11}B NMR** (CD_2Cl_2, 128 MHz, $BF_3\cdot OEt_2$): δ −0.6 (d/br, $^1J_{FB}$ = 62 Hz, BF). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −93.9 (s, 3F, C_6H_4F), −123.8 (d, $^1J_{PF}$ = 994 Hz, 1F, PF), −135.6 (d, $^3J_{FF}$ = 20 Hz, 6F, o-C_6F_5), −162.4 (t, $^3J_{FF}$ = 19 Hz, 3F, p-C_6F_5), −166.9 (m, 6F, m-C_6F_5), −190.9 (s/br, 1F, BF). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 93.3 (d, $^1J_{PF}$ = 998 Hz, PF). ^{13}C{^{1}H} NMR not obtained due to insolubility.

Synthesis of (*p*-$C_6F_4H)_3P$. i-PrMgCl (10.9 mL, 21.8 mmol, 2 M) was added to a solution of p-C_6F_4HBr (5.00 g, 21.8 mmol) in Et_2O (100 mL) and stirred for 1 hour at ambient temperature. To the cloudy solution was added copper(I) iodide (416 mg, 2.2 mmol) and a solution of PCl_3 (1.00 g, 7.3 mmol) in Et_2O (5 mL). The suspension was stirred for an additional 2 h and filtered. The residue was washed with 10 mL Et_2O and the solvent was removed from the collected extracts *in vacuo* to give a colorless solid as the crude product. Recrystallization from hexane yield the product as crystalline, colorless solid. Yield: 3.30 g (94%). NMR spectroscopic data match previously reported.[38] **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 7.25 ppm (m, CH); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 147.3 (dm, $^1J_{CF}$ = 248 Hz), 145.9 (dm, $^1J_{CF}$ = 249 Hz), 111.3–110.7 (m, i-C), 108.9 ppm (t, $^2J_{CF}$ = 22.8 Hz, CH); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −131.2 (m, 6F, o-C_6F_4H), −138.2 ppm (m, 6F, m-C_6F_4H); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −72.3 ppm (sept, $^3J_{PF}$ = 36.4 Hz).

Synthesis of R_3PF_2 (R = *t*Bu (9), Mes (10), *o*-Tol (11), Ph (12), *p*-C_6H_4F (13), *p*-C_6H_4F (14)). To a solution of R_3P (262.3 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added a solution of XeF_2 (169.3 mg, 1.0 mmol) in CH_2Cl_2 (10 mL). After 1 hour at ambient temperature the solvent was removed *in vacuo* and the remaining solid was washed with n-pentane (5 mL). The solid was dried *in vacuo* yielding the product as a colorless powder in quantitatively yield.

(**9**): **^{1}H NMR** (400.2 MHz, C_6D_6, Me_4Si): δ = 1.32 ppm (dt, $^3J_{HP}$ = 17.1 Hz, $^4J_{HF}$ = 2.6 Hz); **^{19}F NMR** (376.6 MHz, C_6D_6, $CFCl_3$): δ = −59.0 ppm (d, $^1J_{PF}$ = 793 Hz, PF_2); **^{31}P{^{1}H}** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −20.9 ppm (t, $^1J_{PF}$ = 793 Hz).

(**10**): **^{1}H NMR** (400.2 MHz, CD_2Cl_2, Me_4Si): δ = 6.89 (d, $^4J_{PH}$ = 5.6 Hz, 2H, $C_6H_2Me_3$), 2.29 (s, 3H, C_6H_2Me-4), 2.18 ppm (s, 6H, $C_6H_2Me_2$-2,6); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −25.7 (d, $^1J_{PF}$ = 654 Hz, PF_2); **^{31}P{^{1}H}** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −39.7 ppm (t, $^1J_{PF}$ = 654 Hz);

(**11**): **^{1}H NMR** (400.2 MHz, CD_2Cl_2, Me_4Si): δ = 7.62 (m, 1H, CH), 7.42 (m, 1H, CH), 7.31–7.23 (m, 2H, CH), 2.28 (s, 3H, CH_3); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −25.7 (d, $^1J_{PF}$ = 654 Hz, PF_2); **^{31}P{^{1}H}** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −35.0 ppm (t, $^1J_{PF}$ = 626 Hz).

(**12**): **^{1}H NMR** (400.2 MHz, CD_2Cl_2, Me_4Si): δ = 8.05 (m, 2H, CH), 7.51 ppm (m, 3H, CH); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −39.4 (d, $^1J_{PF}$ = 660 Hz, PF_2); **^{31}P{^{1}H}** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −54.8 ppm (t, $^1J_{PF}$ = 660 Hz).

(**13**): **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 8.04 (m, 2H, CH), 7.17 ppm (m, 2H, CH); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −39.8 (d, $^1J_{PF}$ = 670 Hz, PF_2), −105.5 ppm (m, C_6H_4F); **^{31}P{^{1}H}** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −58.9 ppm (t, $^1J_{PF}$ = 670 Hz).

(**14**): **Anal. Calcd** for $C_{18}H_3F_{14}P$ (516.17) C 41.88, H 0.59; found C 41.60, H 0.38. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 7.41 ppm (m, CH); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 146.1 (dm, $^1J_{CF}$ = 253 Hz), 145.3 (dm, $^1J_{CF}$ = 254 Hz), 114.5 (dm, $^1J_{PC}$ = 198 Hz, i-C), 110.3 ppm (t, $^2J_{CF}$ = 22.5 Hz, CH); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −2.2 (dsept, $^1J_{PF}$ = 690 Hz, $^4J_{FF}$ = 15 Hz, 2F, PF_2), −133.5 (m, 6F, o-C_6F_4H), −137.0 ppm (m, 6F, m-C_6F_4H); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = −47.9 ppm (tsept, $^1J_{PF}$ = 690 Hz, $^3J_{PF}$ = 11.7 Hz).

Synthesis of [$R_2R'PF$][$B(C_6F_5)_4$] (R = R′ = *t*Bu (16), Mes (17), *o*-Tol (18), Ph (19), *p*-C_6H_4F (20), *p*-C_6F_4H (21), R = Ph, R′ = C_6F_5 (22)). A solution of R_3PF_2 in toluene (8 mL) was added to a slurry of [Et_3Si][$B(C_6F_5)_4$] (489 mg, 0.5 mmol) in toluene (8 mL). The resulting suspension was stirred for 5 min. The new formed precipitate was allowed to settle and the supernatant was decanted. The colorless solid was washed with CH_2Cl_2 (2 mL) and dried *in vacuo* yielding the product as a colorless fine powder. Crystals suitable for X-ray analysis were obtained from a CH_2Cl_2 solution at −35 °C after several days for **14**, **16**, **17** and **18**.

(**16**): Yield: 414 mg (92%); **Anal. Calcd** for $C_{36}H_{27}BF_{21}P$ (900.36): calcd C 48.02, H 3.02; found C 48.00, H 3.06. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 1.65 ppm (dd, $^3J_{HP}$ = 15.8 Hz, $^4J_{HF}$ = 1.7 Hz); **^{11}B{^{1}H} NMR** (128.4 MHz, CD_2Cl_2, $BF_3\cdot OEt_2$): δ = −16.7 ppm (s, $\nu_{1/2}$ = 26 Hz); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 148.5 (d, $^1J_{CF}$ = 241.0 Hz, C_6F_5), 138.6 (d, $^1J_{CF}$ = 245.6 Hz, C_6F_5), 136.7 (d, $^1J_{CF}$ = 245.7 Hz, C_6F_5), 124.2 (br, i-C_6F_5), 41.6 (dd, $^1J_{CP}$ = 26.5 Hz, $^2J_{CF}$ = 7.7 Hz, CH_3), 27.7 ppm (m, CH_3); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −133.0 (m, 8F, o-C_6F_5), −163.7 (t, $^3J_{FF}$ = 20.4 Hz, 4F, p-C_6F_5), −167.8 ppm (m, 8F, m-C_6F_5), −171.6 ppm (d, $^1J_{PF}$ = 1019 Hz, 1F, PF); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = 147.5 ppm (t, $^1J_{PF}$ = 1019 Hz).

(**17**): Yield: 472 mg (87%); **Anal. Calcd** for $C_{51}H_{33}BF_{21}P$ (1086.57): calcd C 56.38, H 3.06; found C 57.52, H 3.29. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 7.22 (d, $^4J_{HP}$ = 3.26 Hz, 3H, $C_6H_2Me_3$), 7.07 (d, $^4J_{HP}$ = 6.35 Hz, 3H, $C_6H_2Me_3$), 2.40 (s, 9H, $C_6H_2Me_2$-4), 2.34 (d, $^4J_{HP}$ = 6.17 Hz, 9H, $C_6H_2Me_2$-2,6), 1.96 ppm (s, 9H, C_6H_2Me-2,6); **^{11}B{^{1}H} NMR** (128.4 MHz, CD_2Cl_2, $BF_3\cdot OEt_2$): δ = −16.7 ppm (s, $\nu_{1/2}$ = 26 Hz); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 149.5 (dd, J_{CP} = 2.6 Hz, J_{CF} = 1.5 Hz, C_q), 148.6 (d, $^1J_{CF}$ = 248.0 Hz, C_6F_5), 145.6 (dd, J_{CP} = 8.1 Hz, J_{CF} = 1.4 Hz, C_q), 144.0 (dd, J_{CP} = 18.2 Hz, J_{CF} = 3.1 Hz, C_q), 138.6 (d, $^1J_{CF}$ = 244.8 Hz, C_6F_5), 136.7 (d, $^1J_{CF}$ =

246.1 Hz, C_6F_5), 133.6 (dm, J_{CP} = 14.0 Hz, 2X*C*H), 124.2 (br, i-C_6F_5), 117.2 (dd, J_{CP} = 99.1 Hz, J_{CF} = 13.2 Hz, C_q), 23.3 (dd, J_{CP} = 5.6 Hz, J_{CF} = 1.0 Hz, CH_3), 22.6 (dd, J_{CF} = 7.6 Hz, J_{CP} = 5.2 Hz, CH_3), 21.7 ppm (m, CH_3); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −115.6 (d, $^1J_{PF}$ = 940 Hz, 1F, PF), −133.1 (m, 8F, *o*-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 4F, *p*-C_6F_5), −167.6 ppm (m, 8F, *m*-C_6F_5); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = 93.0 ppm (d, $^1J_{PF}$ = 940 Hz).

(**18**): Yield: 431 mg (86%); **Anal. Calcd** for $C_{45}H_{21}BF_{21}P$ (1002.41): calcd C 53.92, H 2.11; found C 54.21, H 2.21. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 7.90 (m, 1H, C*H*), 7.68 (m, 1H, C*H*), 7.50 (m, 1H, C*H*), 7.23 (m, 1H, C*H*), 2.47 ppm (m, 3H, CH_3); **^{11}B{^{1}H} NMR** (128.4 MHz, CD_2Cl_2, $BF_3{\cdot}OEt_2$): δ = −16.7 ppm (s, $\nu_{1/2}$ = 26 Hz); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 148.5 (d, $^1J_{CF}$ = 240.5 Hz, C_6F_5), 145.4 (dd, J_{CP} = 8.5 Hz, J_{CF} = 1.5 Hz, *C*H), 138.6 (d, $^1J_{CF}$ = 244.0 Hz, C_6F_5), 137.7 (dd, J_{CP} = 2.7 Hz, J_{CF} = 1.3 Hz, *C*H), 136.7 (d, $^1J_{CF}$ = 242.0 Hz, C_6F_5), 135.6 (dd, J_{CP} = 18.4 Hz, J_{CF} = 2.2 Hz, *C*H), 134.5 (d, J_{CP} = 12.0 Hz, *C*H), 128.3 (d, J_{CP} = 15.7 Hz, *C*H), 124.1 (br, i-C_6F_5), 115.7 (dd, $^1J_{CP}$ = 105.2 Hz, $^2J_{CF}$ = 12.8 Hz, C_q), 22.0 (dd, J_{CP} = 5.0 Hz, J_{CF} = 2.8 Hz, CH_3); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −125.5 (d, $^1J_{PF}$ = 993 Hz, 1F, PF) −133.0 (m, 8F, *o*-C_6F_5), −163.6 (t, $^3J_{FF}$ = 20.2 Hz, 4F, *p*-C_6F_5), −167.5 ppm (m, 8F, *m*-C_6F_5); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 25 °C): δ = 103.2 ppm (d, $^1J_{PF}$ = 993 Hz).

(**19**): Yield: 384 mg (80%); **Anal. Calcd** for $C_{22}H_{15}BF_{21}P$ (960.33): calcd C 52.53, H 1.57; found C 52.53, H 1.52. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 8.06 (m, 1H, C*H*), 7.08 ppm (m, 4H, C*H*); **^{11}B{^{1}H} NMR** (128.4 MHz, CD_2Cl_2, $BF_3{\cdot}OEt_2$): δ = −16.7 ppm (s, $\nu_{1/2}$ = 26 Hz); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 148.5 (d, $^1J_{CF}$ = 240.5 Hz, C_6F_5), 138.6 (d, $^1J_{CF}$ = 244.0 Hz, C_6F_5), 139.0 (dd, J_{CP} = 2.8 Hz, J_{CF} = 1.7 Hz, *C*H), 136.7 (d, $^1J_{CF}$ = 242.0 Hz, C_6F_5), 134.3 (d, J_{CP} = 14.5 Hz, *C*H), 131.3 (d, J_{CP} = 14.5 Hz, *C*H), 124.3 (br, i-C_6F_5), 116.5 ppm (dd, J_{CP} = 108.9 Hz, J_{CF} = 14.5 Hz, i-C_6H_5); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −128.2 (d, $^1J_{PF}$ = 997.8 Hz, 1F, PF), −133.0 (m, 8F, *o*-C_6F_5), −163.6 (t, $^3J_{FF}$ = 20.3 Hz, 4F, *p*-C_6F_5), −167.5 ppm (m, 8F, *m*-C_6F_5); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = 94.8 ppm (d, $^1J_{PF}$ = 997.8 Hz).

(**20**): Yield: 451 mg (89%); **Anal. Calcd** for $C_{42}H_{12}BF_{24}P$ (1014.04): calcd C 49.73, H 1.19; found C 49.69, H 0.87. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 7.80 (m, 2H, C*H*), 7.54 ppm (m, 2H, C*H*); **^{11}B{^{1}H} NMR** (128.4 MHz, CD_2Cl_2, $BF_3{\cdot}OEt_2$): δ = −16.7 ppm (s, $\nu_{1/2}$ = 26 Hz); **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2, Me_4Si): δ = 169.6 (ddd, $^1J_{CF}$ = 242.0 Hz, J_{CP} = 3.27 Hz, J_{CF} = 1.60 Hz, *C*F), 148.5 (d, $^1J_{CF}$ = 240.5 Hz, C_6F_5), 138.6 (d, $^1J_{CF}$ = 244.0 Hz, C_6F_5), 137.7 (ddd, J_{CP} = 15.2 Hz, J_{CF} = 10.8 Hz, J_{CF} = 1.0 Hz, *C*H), 136.7 (d, $^1J_{CF}$ = 242.0 Hz, C_6F_5), 124.1 (br, i-C_6F_5), 119.7 (dd, J_{CP} = 22.8 Hz, J_{CF} = 16.1 Hz, *C*H), 112.0 ppm (ddd, $^1J_{CP}$ = 116.1 Hz, $^2J_{CF}$ = 15.7 Hz, $^4J_{CF}$ = 3.4 Hz, C_q); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −92.3 (m, 3F, CF), −122.9 (d, $^1J_{PF}$ = 1000 Hz, 1F, PF) −133.1 (m, 8F, *o*-C_6F_5), −163.6 (t, $^3J_{FF}$ = 20.2 Hz, 4F, *p*-C_6F_5), −167.5 ppm (m, 8F, *m*-C_6F_5); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = 94.8 ppm (dd, $^1J_{PF}$ = 1000 Hz, $^5J_{PF}$ = 1.8 Hz).

(**21**): Yield: 470 mg (80%). **Anal. Calcd** for $C_{42}H_3BF_{33}P$ (1076.21): calcd C 42.89, H 0.26; found C 42.36, H 0.56. **^{1}H NMR** (499.7 MHz, CD_2Cl_2, Me_4Si): δ = 8.03 ppm (m, C*H*); **^{11}B-{^{1}H} NMR** (128.4 MHz, CD_2Cl_2, $BF_3{\cdot}OEt_2$): δ = −16.7 ppm (s, $\nu_{1/2}$ = 26 Hz); **^{19}F NMR** (376.6 MHz, CD_2Cl_2, $CFCl_3$): δ = −124.4 (dm, $^1J_{PF}$ = 1060 Hz, 1F, PF), −125.7 (m, 6F, *o*-C_6F_4H), −128.2 (m, 6F, *m*-C_6F_4H), −133.3 (m, 8F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 4F, *p*-C_6F_5), −167.8 ppm (m, 8F, *m*-C_6F_5); **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, H_3PO_4): δ = 70.1 ppm (dsept, $^1J_{PF}$ = 1060 Hz, $^3J_{PF}$ = 8.5 Hz). **^{13}C{^{1}H} NMR:** Could not be obtained due to low solubility of the compound in all common NMR solvents.

(**22**): This reaction was performed on a smaller scale using 32 mg (820 μmol) of $(C_6F_5)Ph_2PF_2$ and using 100 mg of **8** (813 μmol) as opposed to $[Et_3Si][B(C_6F_5)_4]$ to abstract a fluoride ion. Yield: 71 mg (83%). **Anal. Calcd** for $C_{42}H_{10}BF_{26}P$ (1050.28): calcd C 48.03, H 0.96; found C 47.45, H 1.17. **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 8.15 (m, 2H, *p*-C_6H_5), 7.89 (m, 8H, *o*, *m*-C_6H_5). **^{11}B NMR** (CD_2Cl_2, 128 MHz, $BF_3{\cdot}OEt_2$): δ −16.7 (s, *B*$(C_6F_5)_4$) **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −123.54 (dt, $^1J_{PF}$ = 1023 Hz, $^4J_{FF}$ = 19 Hz, 1F, P*F*), −123.83 (m, 2F, P(*o*-C_6F_5)), −130.13 (m, 1F, P(*p*-C_6F_5)), −133.18 (m, 8F, B(*o*-C_6F_5)), −152.80 (m, 2F, P(*m*-C_6F_5)), −163.75 (t, $^3J_{FF}$ = 20 Hz, 4F, B(*p*-C_6F_5)), −167.65 (t/br, $^3J_{FF}$ = 19 Hz, 8F, B(*m*-C_6F_5)). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 87.6 (dt, $^1J_{PF}$ = 1023 Hz, $^3J_{PF}$ = 7 Hz *P*F). **^{13}C{^{1}H} NMR:** (CD_2Cl_2, 100 MHz, Me_4Si): δ 148.5 (d, $^1J_{CF}$ = 240 Hz, C_6F_5), 140.59 (CH aromatic), 138.6 (d, $^1J_{CF}$ = 246 Hz, C_6F_5), 136.7 (d, $^1J_{CF}$ = 245 Hz, C_6F_5), 134.0 (d, $^2J_{PC}$ = 14 Hz), 131.8 (d, $^3J_{PC}$ = 15 Hz, CH aromatic).

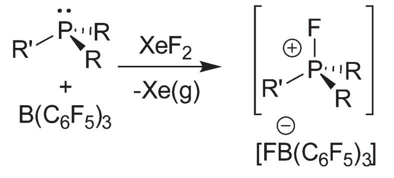
X-ray data collection, reduction, solution and refinement

Single crystals were coated in Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N_2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. Data reduction was performed using the SAINT software package, and an absorption correction was applied using SADABS. 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. 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.

Results and discussion

Synthesis

The careful addition of a CD_2Cl_2 solution containing 1 : 1 $tBu_3P/B(C_6F_5)_3$ to XeF_2 at ambient temperature immediately resulted in vigorous effervescence to produce the fluorophosphonium fluoroborate salt, $[tBu_3PF][FB(C_6F_5)_3]$ (**1**; Scheme 1), which could be isolated in quantitative yield as a colourless, analytically pure solid. ^{31}P{^{1}H} NMR spectroscopy of the resulting mixture shows a doublet signal at δ 148.5 ppm ($^1J_{PF}$ = 1019 Hz), while the ^{19}F NMR spectrum shows the corresponding



Scheme 2 Reaction of XeF_2 with phosphine/borane FLPs.

doublet resonance at δ −171.6 ppm, consistent with the formulation. The selective production of **1** suggests that the FLP reacts with XeF_2 by a mechanism involving phosphine oxidation and fluoride ion abstraction by $B(C_6F_5)_3$. The observed reactivity is in stark contrast to that of reaction of intramolecular P/B FLP systems with XeF_2 [39] where complexation of the borane to *t*BuNC was required to achieve clean oxidation to the corresponding fluorophosphonium fluoroborate.

The aforementioned reactivity was extended to a series of variously substituted organophosphine precursors, including Mes_3P, $(o\text{-Tol})_3P$, Ph_3P and $(p\text{-}C_6H_4F)_3P$. In the presence of 1 equiv. of $B(C_6F_5)_3$, the resulting FLPs reacted with XeF_2 to yield salts of the formula $[R_3PF][FB(C_6F_5)_3]$, where R = Mes (**2**), *o*-Tol (**3**), Ph (**4**), or *p*-C_6H_4F (**5**) (Scheme 2). NMR data for triarylphosphonium salts **2** and **3** each show significantly upfield-shifted ^{31}P NMR resonances (δ 92.9 and 104.3, respectively), and downfield-shifted ^{19}F signals (δ −116.7 and −125.5, respectively) relative to that of trialkylphosphonium salt **1**, which can be crystallized from a mixture of CH_2Cl_2 and *n*-pentane. X-ray structural analysis of **1** shows the expected tetrahedral geometry around both P and B centers (Fig. 1). The P–F and B–F bond lengths are normal at 1.628(2) Å and 1.427(3) Å, respectively, and there appear to be no strong interactions between the cation and the anion.

A crystallographic analysis of **3** (Fig. 1) also shows a typical B–F bond length of 1.418(6) Å, although its P–F bond length of 1.554(3) Å is substantially shorter than that in **1**. This differences is attributed to the more steric demands of the *t*Bu groups in **1** in comparison to the *ortho*-tolyl groups in **3** which more readily accommodates a pseudo tetrahedral geometry. This difference in the geometry at P is also illustrated by the sum of the C–P–C angles which is 344.4° in **1** and 337.2° in **3**. In addition, the P center in **3** is more electron deficient and thus accommodates a shorter P–F bond. Interestingly, compound **3** also seems to exhibit a weak cation–anion interaction, although the (B)F⋯P(F) separation of *ca.* 3.55 Å is greater than the sum of the van der Waals radii of these atoms (3.24 Å),[40] suggesting that favorable π-stacking and Coulombic interactions between these ions instead stabilize their mutual orientation in the solid state.

The reaction between $Ph_3P/B(C_6F_5)_3$ and XeF_2 is much slower, proceeding over several days to gradually yield **4** as the product. Such sluggish reactivity is attributable to the competing reaction in which Ph_3P forms an adduct with $B(C_6F_5)_3$ at ambient temperature. Nevertheless, the dissociation equilibrium of $Ph_3P\text{–}B(C_6F_5)_3$ in solution allows for gradual

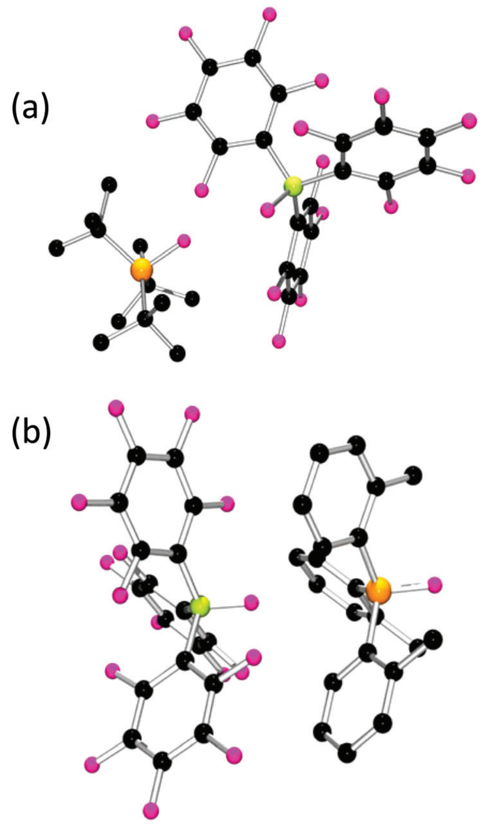


Fig. 1 POV-Ray depictions of compounds (a) **1** and (b) **3**. P: orange; F: pink; B: green; C: black.

oxidation of free Ph_3P to the unobserved intermediate difluorophosphorane, Ph_3PF_2, which immediately undergoes fluoride abstraction by $B(C_6F_5)_3$ to yield $[Ph_3PF][FB(C_6F_5)_3]$ (**4**). Supporting this mechanistic interpretation is the observation that combining Ph_3P and XeF_2 in solution without $B(C_6F_5)_3$ results in immediate effervescence, and subsequent addition of $B(C_6F_5)_3$ yields (**4**) in a matter of minutes. It is also interesting to note that in a recent investigation in collaboration with the Erker group,[39] we described the reactions of intramolecular FLPs with XeF_2. These reactions proceed in a similar fashion to those with other halogenating reagents.[41]

With the exception of Ph_3P, the apparent rate of reactions between XeF_2 and phosphine/$B(C_6F_5)_3$ FLPs are noticeably reduced as increasingly electron-withdrawing substituents are appended to P. Our previous report describing the reaction between XeF_2 and the electron-deficient phosphine/borane combination, $Ph_2(C_6F_5)P/B(C_6F_5)_3$, demonstrated the anticipated formation of salt **6**. Interestingly however, **6** was found to exist in equilibrium with free $B(C_6F_5)_3$ and the difluorophosphorane, $Ph_2(C_6F_5)PF_2$, by rapid fluoride ion transfer between P and B centers, made evident by variable temperature $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy.[33] Analogous reactions using the phosphines $Ph(C_6F_5)_2P$, $(p\text{-}C_6F_4H)_3P$[38] and $(C_6F_5)_3P$ also result in their oxidation to the difluorophosphorane. In these cases however, $B(C_6F_5)_3$ does not abstract fluoride from the corresponding difluorophosphoranes, indicating that the targeted fluorophosphonium cations are more Lewis acidic than $B(C_6F_5)_3$ towards fluoride. Nonetheless, fluoride ion abstraction from the difluorophosphoranes can be achieved employing the harder electrophiles such as $Al(C_6F_5)_3$ or $[Et_3Si][B(C_6F_5)_4]$. We have previously utilized this technique to access highly electrophilic fluorophosphonium cations, $[(C_6F_5)_2PhPF]^+$ (**7**) and $[(C_6F_5)_3PF]^+$ (**8**), which have shown a wide range of reactivity (*vide supra*).

This synthetic approach was subsequently applied to all previously synthesized phosphonium cations to eliminate the non-innocent $[FB(C_6F_5)_3]^-$ anion. Thus, initial oxidation of the phosphines with XeF_2 yields the difluorophosphoranes $R'R_2PF_2$, [R,R′ = *t*Bu (**9**), Mes (**10**), *o*-Tol (**11**), Ph (**12**), *p*-C_6H_4F (**13**), and *p*-C_6F_4H (**14**), R = Ph, R′ = C_6F_5 (**15**)] in quantitatively yields. Subsequently fluoride abstraction of the difluorophosphoranes with $[Et_3Si][B(C_6F_5)_4]$ yield the salts of the formula $[R'R_2PF][B(C_6F_5)_4]$, where R,R′ = *t*Bu (**16**), Mes (**17**), *o*-Tol (**18**), Ph (**19**), *p*-C_6H_4F (**20**), and *p*-C_6F_4H (**21**), R = Ph, R′ = C_6F_5 (**22**) (Scheme 3). NMR data for **9–15** were consistent with the formulations while the data for the cations of compounds **16–20** are consistent with that described for **1–5**. In each of **16–22**, the $[B(C_6F_5)_4]$ anion give rise to signals in the ^{11}B and ^{19}F NMR spectra at δ −16.7 and −133.0 (*o*-C_6F_5), −163.7 (*p*-C_6F_5) and −167.8 (*m*-C_6F_5), respectively.

Crystals suitable for X-ray crystallographic studies of compound **17**, **19**, **20**, **21** and **22** were obtained from a concentrated CH_2Cl_2 solution at −35 °C (Fig. 2). The P–F bond lengths of the Mes (**17**), Ph (**19**), *p*-C_6H_4F (**20**) *p*-C_6F_4H (**21**) and $Ph_2(C_6F_5)$ (**22**) substituted fluorophosphonium cations were found to be 1.561(1), 1.556(2), 1.553(1), 1.527(4) Å and 1.540(3) Å, respectively. The shortest P–F distances is consistent with the presence of the most electron withdrawing *p*-C_6F_4H substituents in **21**. This value is similar to that see for the P–F bond length in $[(C_6F_5)_2PhPF][F(Al(C_6F_5)_3)_2]$ with 1.533(2) Å.[30] The sum of the C–P–C angles for the more sterically encumbered phosphonium cation **17** has values of 344.3°. With decreasing bulkiness around the phosphorus atom the sum of C–P–C angles adopt smaller values of 339.7° in **19**, 336.3° in **20**, 338.8° in **21** and 336.2° in **22**, respectively. In all structures the parameters of the anion $[B(C_6F_5)_4]$ are unexceptional.

It is interesting to note some trends observed in the spectroscopic data of the fluorophosphonium cations. For the series of fluorophosphonium cations the $^{31}P\{^1H\}$ NMR chemical shift decreases with increasingly electron-withdrawing substituents (Fig. 3). Conversely, ^{19}F NMR chemical shifts attributable to the P-bound F atom generally increase with Lewis acidity. It is interesting that the mesityl- substituted derivative (**2**) does not strictly adhere to this trend. This discre-

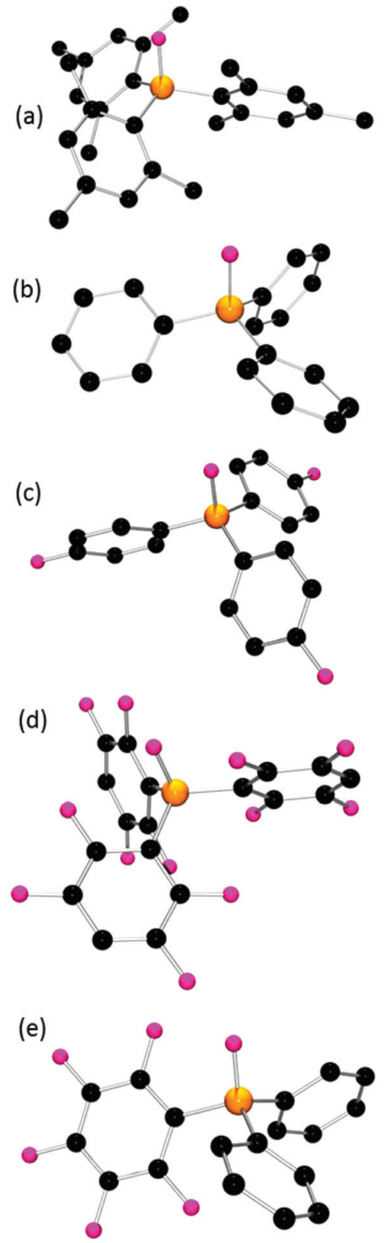
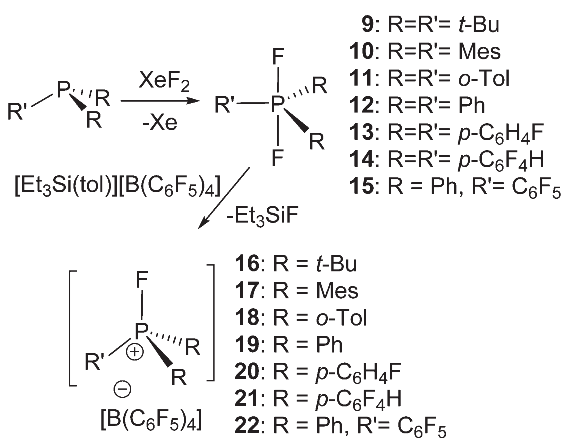


Fig. 2 POV-Ray depictions of the cations of (a) **17** (b) **19**, (c) **20**, (d) **21**, (e) **22**. Hydrogen atoms are omitted for clarity. P: orange; F: pink; B: green; C: black.



Scheme 3 Synthesis of fluorophosphonium salts.

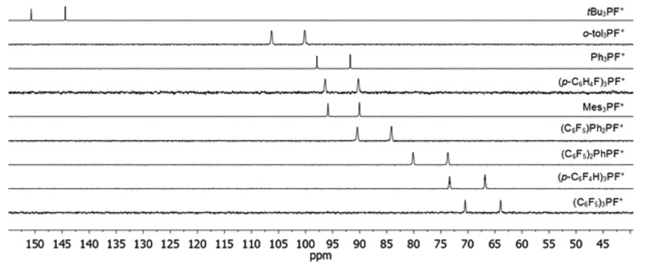


Fig. 3 Stack plot of the $^{31}P\{^{1}H\}$ NMR data for a series of fluorophosphonium cations.

Table 1 NMR data and FIA for fluorophosphonium cations

Cation	^{31}P	^{19}F	$^{31}P_{calc}$	FIA (F^-)	FIA ($(COF_3)^-$)
$[tBu_3PF]^+$	148.5	−171.6	181.6	163	148
$[Mes_3PF]^+$	92.9	−116.7	—	—	—
$[o\text{-}tol_3PF]^+$	104.3	−125.5	—	—	—
$[Ph_3PF]^+$	94.7	−128.3	108.1	200	165
$[(p\text{-}C_6H_4F)_3PF]^+$	93.3	−123.8	103.7	220	214
$[Ph_2(C_6F_5)PF]^+$	87.2	−123.4	90.9	238	227
$[(C_6F_5)_2PhPF]^+$	77.7	−121.9	71.6	275	280
$[(p\text{-}C_6HF_4)_3PF]^+$	70.1	−124.4	—	296	287
$[(C_6F_5)_3PF]^+$	68.0	−120.7	53.2	311	323

pancy is perhaps best attributed to the impact of the increased steric crowding in this triarylphosphonium cation, which may affect shielding of the ^{31}P and/or ^{19}F nuclei. Nonetheless, these observation suggest that the ^{31}P and ^{19}F chemical shifts are correlated with the expected Lewis acidity of these fluorophosphonium cations.

To further probe the Lewis acidity of these phosphonium cations, efforts were made to employ standardized methods employed to rank these Lewis acids. Initially efforts to use the Child's test[42] proved unsuccessful as the combination of crotonaldehyde with fluorophosphonium salts resulted in the formation of a complex mixture of products. Employing the Gutmann–Beckett protocol,[43,44] addition of one equivalent of Et_3PO to the least Lewis acidic compounds among the series, **1**, **2** or **3** resulted in no observable change in the ^{31}P NMR chemical shifts indicative of no interaction of the phosphine-oxide with these Lewis acids. In contrast, addition of Et_3PO to the more electron-deficient salt **4** led to the generation of the difluorophosphorane, Ph_3PF_2 and the adduct $(Et_3PO)B(C_6F_5)_3$. This observation confirms fluoride ion transfer from B to P with concurrent sequestration of the phosphine-oxide by the freed borane (Scheme 4). A similar result was previously observed with the more Lewis acidic salt **6**.[33] Interestingly combination of **19** where the $[B(C_6F_5)_4]$ counterion circumvents the reaction of phosphine-oxide with the anion, no interaction of the cation with Et_3PO was evident from the ^{31}P NMR spectroscopy. We have previously reported that Et_3PO coordinates to the cation of **8** affording a shift of the ^{31}P signal for the phosphine oxide to 91.1 ppm and thus a Gutmann–Beckett $\Delta\delta$ of 40.4.[30] The combination of the tetrafluorophenyl-substituted fluorophosphonium (**21**) with Et_3PO in CD_2Cl_2 gave rise of a signal for the coordinated phosphine oxide at 89.5 ppm in the ^{31}P NMR spectrum and thus $\Delta\delta$ of 38.8. This suggests that **21** is about 5% less Lewis acidic than $[(C_6F_5)_3PF][B(C_6F_5)_4]$. This situation is analogous to the Lewis acidities of $B(p\text{-}C_6F_4H)_3$ and $B(C_6F_5)_3$.[45] Nonetheless, the present results indicate that both the Child's and Gutmann–Beckett methods have limited utility in efforts to establish a ranking of the Lewis acidities of fluorophosphonium cations with other known Lewis acids.

An alternative strategy to assess Lewis acidity to these experimental methods, is a method developed by Bartlett,[46] in which the fluoride ion affinity (FIA) is computed. The Krossing group used this approach to determine the relative Lewis acidities for a number of neutral Lewis acids[47,48] In addition, Slattery *et al.* have calculated the FIA of a number of free phosphenium cations and the results show that certain free phosphenium cations have the potential to be as Lewis acidic as silylium cations.[49] In this method two computational approaches were used. The first involved the calculation of enthalpy (ΔH) using WB97XD/def2TZV level of theory[50,51] in conjunction with the conductor-like polarizable continuum solvation model (CPCM)[52–55] in dichloromethane for the reaction of F^- with $[R_3PF]^+$ forming the corresponding difluorophosphorane (eqn (1)). The FIA is then defined as the negative of the enthalpy ΔH.[46,56,57] The second approach utilized a gas phase pseudo-isodesmic reaction between the fluorophosphonium cations and $[COF_3]^-$ acting as F^- donor forming corresponding difluorophosphorane and COF_2. These latter calculations are anchored to an experimental ΔH value of the addition of F^- to COF_2 forming $[COF_3]^-$ of 209 kJ mol^{-1}.[49,56] In addition, the ^{31}P NMR chemical shifts for the phosphonium cations were calculated using gauge-including atomic orbital method (GIAO)[58,59] at WB97XD/def2TZV level of theory (Table 1). The calculated ^{31}P NMR chemical shifts were referenced to chemical shift of $[Me_3PF]^+$, and although there is some divergence from the experimental observations the computed shifts follow the same trends.

$$[R_3PF]^+ + F \xrightarrow{\Delta H = -FIA} R_3PF_2 \qquad (1)$$

Interestingly the calculated FIA values are well correlated with implications of the observed ^{31}P and ^{19}F NMR chemical shifts for the fluorophosphonium cations, For example, the 5% difference in Lewis acidity between **21** and **8** inferred by the Gutmann–Beckett method is also predicted by the FIA calculations. Thus, stronger electron withdrawing substituents on P leads to higher FIA values consistent with greater Lewis

$$\underset{\mathbf{6}}{[Ph_3PF][FB(C_6F_5)_3]} \xrightarrow{Et_3PO} Ph_3PF_2 + (Et_3PO)B(C_6F_5)_3$$

$$\underset{\mathbf{19}}{[Ph_3PF][B(C_6F_5)_4]} \xrightarrow{Et_3PO} NR$$

Scheme 4 Reactions of **6** and **19** with Et_3PO.

acidity. Furthermore, the FIA of $B(C_6F_5)_3$ calculated at the same level of theory was found to be 260 kJ mol^{-1}, in good agreement with experimental observation that a fluoride anion can be abstracted by $B(C_6F_5)_3$ from the alkyl and aryl substituted difluorophosphoranes with FIA values lower than that of the $B(C_6F_5)_3$. At the same time this is also consistent with the observation that $B(C_6F_5)_3$ does not abstract fluoride from bis- and tris-pentafluorophenyl substituted difluorophosphoranes, where the FIA is computed to be higher than that of $B(C_6F_5)_3$.

Conclusions

The reaction of a variety of phosphine/borane FLPs with XeF_2 proceeds cleanly to afford the resulting fluorophosphonium fluoroborate salts. These fluorophosphonium cations become increasingly electrophilic as the substituents become more electron withdrawing. When there are two or more pentafluorophenyl substituents on the phosphine, $B(C_6F_5)_3$ is not a strong enough Lewis acid to abstract the fluoride; a notion that is supported by a comparison of the calculated FIAs. The aforementioned fluorophosphonium cations were also generated using $[Et_3Si][B(C_6F_5)_4]$ in an effort to remove the non-innocent $[FB(C_6F_5)_3]^-$ anion. The ^{31}P and ^{19}F chemical shifts and the computed FIAs of these fluorophosphonium cations correlate with the rankings of the relative Lewis acidities. Thus the NMR data can be employed as an indication of relative Lewis acidity within the series of fluorophosphonium cations, while the computed FIA provides a basis for comparison with other Lewis acid systems. The electrophilicity of fluorophosphonium cations is a topic of research which we continue to explore in our laboratory.

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