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The Lewis acidity of fluorophosphonium salts: access to mixed valent phosphorus(III)/(V) species†

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Oxidative fluorination of the electron-deficient phosphine $Ph_2P(C_6F_5)$ using XeF_2, followed by fluoride ion abstraction from the resulting difluorophosphorane $Ph_2P(F)_2(C_6F_5)$, produces electrophilic fluorophosphonium salts $[Ph_2P(F)(C_6F_5)][X]$ (X = $FB(C_6F_5)_3$ or O_3SCF_3). Variable temperature NMR spectroscopic analysis of $[Ph_2P(F)(C_6F_5)][FB(C_6F_5)_3]$ demonstrates a fluxional process attributed to fluoride ion exchange between $B(C_6F_5)_3$ and $[Ph_2P(F)(C_6F_5)]^+$, suggesting that these species have comparable Lewis acidities. This exchange can also be illustrated by adding phosphine Ph_3P to $[Ph_2P(F)(C_6F_5)][FB(C_6F_5)_3]$ at ambient temperature to produce $Ph_2P(F)_2(C_6F_5)$ and $Ph_3P–B(C_6F_5)_3$, while heating this mixture results in thermally induced *para*-substitution of Ph_3P at the C_6F_5 group of the phosphonium ion to generate $[Ph_3P(C_6F_4)P(F)_2Ph_2][FB(C_6F_5)_3]$. Such frustrated Lewis pair reactivity also can be exploited by reacting $[Ph_2P(F)(C_6F_5)][O_3SCF_3]$ with silylphosphine Ph_2PSiMe_3 to afford the unique mixed-valent salt $[Ph_2P(C_6F_4)P(F)Ph_2][O_3SCF_3]$, which upon the addition of fluoride is converted to $Ph_2P(C_6F_4)P(F)_2Ph_2$. XeF_2 reacts with $[Ph_2P(C_6F_4)P(F)Ph_2][O_3SCF_3]$ at ambient temperature, producing equal proportions of the dicationic salt $[Ph_2P(F)(C_6F_4)P(F)Ph_2][O_3SCF_3]_2$ and the bis(difluorophosphorane) $Ph_2P(F)_2(C_6F_4)P(F)_2Ph_2$, the latter of which can then be quantitatively converted to the former by adding one equiv of $Me_3SiO_3SCF_3$.

Introduction

Phosphorus compounds are well known as ligands in transition metal chemistry. Indeed these Lewis bases are ubiquitously employed in the stoichiometric and catalytic processes familiar to synthetic inorganic, organic and organometallic chemists. On the other hand, the Lewis acidity of phosphonium salts has garnered much less attention.[1,2] Nonetheless, diverse applications of phosphonium salts as Lewis acid catalysts for C–C, C–O, C–N bond formations and asymmetric transformations have been reviewed.[3] Gabbaï and coworkers[4] have exploited the Lewis acidity of proximal phosphonium centres to enhance the fluoride affinity of boranes, generating highly sensitive fluoride sequestering agents. While the majority of these studies employed alkyl or aryl phosphonium salts, Terada and Kouchi[5] reported that the presence of electron-withdrawing substituents at a phosphonium centre enhances the energetic accessibility of σ* orbitals to provide an effective Lewis acid catalyst for Diels–Alder reactions.

Apart from the above applications in organocatalysis, the reactivity of electron-deficient phosphonium salts has remained largely underexplored. The chemistry of frustrated Lewis pairs (FLPs) has thus far focused principally on the reactivity of systems derived from sterically encumbered group 13 Lewis acids in combination with a variety of group 15 bases.[6–15] Indeed many researchers have exploited these FLPs to activate a wide variety of small molecules, perhaps most notably H_2.[16–19] Some efforts have extended FLPs to group 14 Lewis acids,[20–24] however our interests, together with the precedent of electrophilic phosphorus chemistry, prompted us to turn our attention to the Lewis acidity of high-valent phosphorus compounds. We have previously utilized the Lewis acidity of P(V) in strained amidophosphoranes for the capture of CO_2.[25] Herein, we demonstrate that fluorophosphonium salts exhibit Lewis acidity comparable to $B(C_6F_5)_3$, while highlighting reactions with phosphine bases that provide unique routes to mixed-valent P(III)/P(V) compounds or phosphorus-based FLPs.

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Experimental section

General procedures

All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under

vacuum before use. $Me_3SiO_3SCF_3$, Ph_3P, Ph_2PSiMe_3 and $[NBu_4][Ph_3SiF_2]$ were purchased from Aldrich and used without further purification. XeF_2 and $Ph_2P(C_6F_5)$ were purchased from Apollo Scientific and used without further purification. $B(C_6F_5)_3$ was purchased from Boulder Chemicals and used without further purification. All glassware was oven-dried and cooled under vacuum before use. CH_2Cl_2, Et_2O, *n*-pentane, and toluene were dried using an Innovative Technologies solvent purification system. CD_2Cl_2 (Aldrich) was 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.

Preparation of $Ph_2P(F)_2(C_6F_5)$ (1)

A solution of $Ph_2P(C_6F_5)$ (48 mg, 136 μmol) in 5 mL of CH_2Cl_2 was added to a solution XeF_2 (23 mg, 136 μmol) in 5 mL of CH_2Cl_2, resulting immediately in a colourless, effervescing solution. After approx. 1 min, effervescence had ceased and the solvent volume was reduced to approx. 1 mL *in vacuo*, then 2 mL of *n*-pentane were added. Slow evaporation of solvent from the colourless solution yielded diffraction-quality crystals (53 mg, >99%, Anal. Calcd for $C_{18}H_{10}F_7P$: C, 55.40; H, 2.58%. Found: C, 55.50; H, 2.82%). ^{1}H NMR (CD_2Cl_2, 400 MHz, Me_4Si): δ 8.12 (m, 4H, *o*-C_6H_5), 7.61 (m, 2H, *p*-C_6H_5), 7.52 (m, 4H, *m*-C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −34.5 (dt, $^1J_{PF}$ = 688 Hz, $^4J_{FF}$ = 14 Hz, 2F, P*F*$_2$), −134.2 (m, 2F, *o*-C_6F_5), −153.3 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), −162.6 (m, 2F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ −57.3 (td, $^1J_{PF}$ = 687 Hz, $^3J_{PF}$ = 14 Hz, *P*F_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, Me_4Si): δ 145.8 (dm, $^1J_{FC}$ = 245 Hz, *o*-C_6F_5), 142.5 (dm, $^1J_{FC}$ = 272 Hz, *p*-C_6F_5), 137.9 (dm, $^1J_{FC}$ = 250 Hz, *m*-C_6F_5), 135.8 (dt, $^2J_{PC}$ = 14 Hz, $^3J_{FC}$ = 11 Hz, *o*-C_6H_5), 133.5 (dt, $^1J_{PC}$ = 182 Hz, $^2J_{FC}$ = 25 Hz, i-C_6H_5), 133.2 (dt, $^4J_{PC}$ = 4 Hz, $^5J_{FC}$ = 1 Hz, *p*-C_6H_5), 129.1 (dt, $^3J_{PC}$ = 17 Hz, $^4J_{FC}$ = 2 Hz, *m*-C_6H_5), i-C_6F_5 signal not observed.

Preparation of $[Ph_2P(F)(C_6F_5)][FB(C_6F_5)_3]$ (2)

A solution of **1** (137 mg, 351 μmol) in 5 mL CH_2Cl_2 was added to a vial containing a solution of $B(C_6F_5)_3$ (179 mg, 350 μmol) in 5 mL of CH_2Cl_2, producing a colourless solution. The solvent volume was reduced to approx. 1 mL, then 5 mL of *n*-pentane were added, resulting in a white precipitate, which was allowed to settle before decanting the supernatant. The solid was dried *in vacuo* and isolated as a white powder (307 mg, 97%, Anal. Calcd for $C_{36}H_{10}BF_{22}P$: C, 47.92; H, 1.12%. Found: C, 47.19; H, 1.38%). ^{1}H NMR (CD_2Cl_2, 400 MHz, Me_4Si): δ 8.10 (m, 2H, *p*-C_6H_5), 7.97–7.79 (8H, *o*, *m*-C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −123.4 (dt/br, $^1J_{PF}$ = 1020 Hz, $^4J_{FF}$ = 17 Hz, 1F, P*F*), −124.1 (s/br, 2F, P(*o*-C_6F_5)), −131.3 (s/br, 1F, P(*p*-C_6F_5)), −135.6 (d/br, $^3J_{FF}$ = 16 Hz, 6F, B(*o*-C_6F_5)), −153.9 (m/br, 2F, P(*m*-C_6F_5)), −161.6 (s/br, 3H, B(*p*-C_6F_5)), −166.7 (m/br, 6F, B(*m*-C_6F_5)), −190.4 (s/br, 1F, B*F*). ^{11}B NMR (CD_2Cl_2, 128 MHz, $BF_3{\cdot}OEt_2$): δ 1.9 (s/br, *B*F). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 87.2 (d/br, $^1J_{PF}$ = 1020 Hz, *P*F). ^{13}C{^{1}H} NMR (partial, CD_2Cl_2, 100 MHz, Me_4Si): δ 148.4 (dm, $^1J_{FC}$ = 240 Hz, B(*o*-C_6F_5)), 140.0 (s, *p*-C_6H_5), 139.2 (dm, $^1J_{FC}$ = 206 Hz, B(*p*-C_6F_5)), 136.9 (dm, $^1J_{FC}$ = 231 Hz, B(*m*-C_6F_5)), 134.2 (d, $^2J_{PC}$ = 15 Hz, *o*-C_6H_5), 131.5 (d, $^3J_{PC}$ = 16 Hz, *m*-C_6H_5), broad, unresolved B(i-C_6F_5), P(C_6F_5) and P(i-C_6H_5) signals not observed.

Preparation of $[Ph_2P(F)(C_6F_5)][O_3SCF_3]$ (3)

In a glovebox, a 20 mL flask was charged with $Ph_2P(C_6F_5)$ (221 mg, 626 μmol), a stir bar and 10 mL of CH_2Cl_2. XeF_2 (106 mg, 626 μmol) was weighed in a separate flask. The XeF_2 solution was carefully transferred to the $Ph_2P(C_6F_5)$ solution and the colourless effervescing mixture was stirred for 30 min. The solution was then transferred to a vial containing $Me_3SiO_3SCF_3$ (140 mg, 626 mmol) and the colourless effervescing solution was stirred for another 30 min. The solvent volume was then reduced to approx. 2 mL *in vacuo* and 10 mL of *n*-pentane was added to the solution resulting in the formation of a white, oily precipitate. The mixture was stirred for 5 minutes before the precipitate was allowed to settle. The supernatant was decanted and discarded, and the solid was dried *in vacuo* and isolated as a white powder (243 mg, 75%, Calcd for $C_{19}H_{10}F_9O_3PS$: C, 43.86; H, 1.94%. Found: C, 43.59; H, 2.23%). ^{1}H NMR (CD_2Cl_2, Me_4Si, 400 MHz): δ 8.14–8.02 (6H, *o*,*p*-C_6H_5), 7.87 (m, 4H, *m*-C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −79.1 (s, 3F, C*F*$_3$), −123.0 (dt, $^1J_{PF}$ = 1016 Hz, $^4J_{FF}$ = 17 Hz, 1F, P*F*), −125.2 (m, 2F, *o*-C_6F_5), −133.5 (m, 1F, *p*-C_6F_5), −155.8 (m, 2F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2, H_3PO_4, 81 MHz): δ 87.1 (dt, $^1J_{PF}$ = 1016 Hz, $^3J_{PF}$ = 6 Hz, *P*F). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, Me_4Si): δ 149.4 (dm, $^1J_{FC}$ = 273 Hz, *p*-C_6F_5), 149.3 (dm, $^1J_{FC}$ = 261 Hz, *o*-C_6F_5), 139.6 (dm, $^1J_{FC}$ = 257 Hz, *m*-C_6F_5), 139.6 (dd, $^4J_{PC}$ = 3 Hz, $^5J_{FC}$ = 2 Hz, *p*-C_6H_5), 134.6 (d, $^2J_{PC}$ = 15 Hz, *o*-C_6H_5), 131.4 (d, $^3J_{PC}$ = 16 Hz, *m*-C_6H_5), 121.0 (q, $^1J_{FC}$ = 321 Hz, *C*F$_3$), 115.8 (dd, $^1J_{PC}$ = 114 Hz, $^2J_{FC}$ = 14 Hz, i-C_6H_5), i-C_6F_5 signal not observed.

Preparation of $[Ph_3P(C_6F_4)P(F)_2Ph_2][FB(C_6F_5)_3]$ (4)

A solution of Ph_3P (12 mg, 46 μmol) in 2 mL of CH_2Cl_2 was added to a solution of **2** (43 mg, 47 μmol) in 2 mL of CH_2Cl_2 instantly producing a white precipitate. The mixture was heated to 40 °C for 15 min, over which time the precipitate gradually dissolved to form a colourless solution. The solvent volume was reduced to approx. 0.5 mL *in vacuo* and 1 mL of Et_2O was added, followed by 1 mL of *n*-pentane. Slow evaporation of solvents from the solution produced colourless, diffraction-quality crystals (53 mg, 99%, Calcd for $C_{54}H_{25}BF_{22}P_2$: C, 55.66; H, 2.16%. Found: C, 55.16; H, 2.58%). ^{1}H NMR (CD_2Cl_2, Me_4Si, 400 MHz): δ 8.17 (m, 4H, C_6H_5), 7.92 (m, 3H, C_6H_5), 7.79–7.61 (14H, C_6H_5), 7.55 (m, 4H, C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −36.8 (dt, $^1J_{PF}$ = 699 Hz, $^4J_{FF}$ = 12 Hz, 2F, *P*F_2), −123.5 (m, 2F, P(C_6F_4)), −128.5 (m, 2F, P(C_6F_4)), −136.6 (m/br, 6F, B(*o*-C_6F_5)), −163.5 (t, $^3J_{FF}$ = 20 Hz, 3F, B(*p*-C_6F_5)), −167.9 (m, 6F, B(*m*-C_6F_5)), −191.4 (m/br, 1F, B*F*). ^{11}B NMR (CD_2Cl_2, 128 MHz, $BF_3{\cdot}OEt_2$): δ −0.6 (d, $^1J_{FB}$ = 65 Hz, *B*F). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 16.1 (t, $^3J_{PF}$ = 6 Hz, 1P, Ph_3P), −58.4 (tm, $^1J_{PF}$ = 699 Hz, 1P, *P*F_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, Me_4Si): δ 136.8 (d, $^4J_{PC}$ = 3 Hz, P(*p*-C_6H_5)),

Table 1 Crystallographic data

	3	**4**·0.25C_6H_{14}	**6**	**8**
Formula	$C_{19}H_{10}F_9O_3PS$	$C_{55.5}H_{28.5}BF_{22}P_2$	$C_{32}H_{20}F_{12}O_6P_2S_2$	$C_{30}H_{20}F_6P_2$
Formula wt	520.30	1186.03	854.54	556.40
Cryst. Sys.	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	17.5800(11)	10.7377(6)	14.5862(6)	16.4223(17)
b (Å)	12.4210(7)	13.3608(8)	14.4109(6)	8.9674(10)
c (Å)	18.6519(12)	18.5330(11)	17.6835(8)	18.0179(17)
α (°)	90	85.615(3)	90	90
β (°)	90	89.546(4)	110.851(2)	104.440(5)
γ (°)	90	71.427(3)	90	90
V (Å^3)	4072.9(4)	2512.6(3)	3473.6(3)	2569.6(5)
Z	8	2	4	4
d (g cm^{-3})	1.697	1.568	1.634	1.438
μ (mm^{-1})	0.339	0.208	0.354	0.231
Total data	34 987	47 216	32 487	21 903
Unique data	5704	12 691	8380	5797
$I > 2\sigma(I^2)$	3355	9213	4555	3673
Variables	298	739	487	343
R_1	0.0446	0.0534	0.0739	0.0465
wR_2	0.1051	0.1673	0.2478	0.1139
GOF	1.000	1.029	1.037	0.983

136.2 (dt, $^2J_{PC}$ = 14 Hz, $^3J_{FC}$ = 11 Hz, P(*o*-C_6H_5)), 134.3 (d, $^3J_{PC}$ = 11 Hz, P(*m*-C_6H_5)), 133.8 (d, $^4J_{PC}$ = 4 Hz, P(*p*-C_6H_5)), 131.2 (d, $^2J_{PC}$ = 14 Hz, P(*o*-C_6H_5)), 129.5 (dt, $^3J_{PC}$ = 18 Hz, $^4J_{FC}$ = 2 Hz, P(*m*-C_6H_5)), 129.4 (dt, $^1J_{PC}$ = 65 Hz, $^2J_{FC}$ = 16 Hz, P(i-C_6H_5)), 116.1 (d, $^1J_{PC}$ = 92 Hz, P(i-C_6H_5), signals for broad, unresolved C_6F_5 groups are not reported.

Preparation of $[Ph_2P(C_6F_4)P(F)Ph_2][O_3SCF_3]$ (5)

A colourless solution of Ph_2PSiMe_3 (80 mg, 310 μmol) in 2 mL of C_6H_5Br was added to a flask containing solid **3** (150 mg, 288 μmol). Agitation of the mixture for several minutes produced a yellow solution containing trace particles, which was then filtered through a Kimwipe® plug in a glass pipette. The solvent and volatile Me_3SiF were removed *in vacuo*, resulting in a clear, viscous, yellow oil. Et_2O (10 mL) was then added, and the mixture was agitated thoroughly for 5 min. A yellow oil settled out from the colourless supernatant, which was then decanted, and the residue was dried *in vacuo*. *n*-Pentane (10 mL) was then added, and the mixture was triturated to a fine suspension before the precipitate was allowed to settle. The supernatant was decanted and the solid was dried *in vacuo* yielding a light-yellow powder (147 mg, 74%, Calcd for $C_{31}H_{20}F_8O_3P_2S$: C, 54.24; H, 2.94%. Found: C, 52.53; H, 3.05%). Although elemental data are insufficient to support the compound's formulation, NMR spectra (see ESI,† Fig. 3–5) reveal the presence of **5** along with minor impurities. ^{1}H NMR (CD_2Cl_2, Me_4Si, 400 MHz): δ 8.18–8.03 (6H, X$_6H_5$), 7.92 (m, 4H, C_6H_5), 7.63 (m, 4H, C_6H_5), 7.51–7.42 (6H, C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −78.9 (s, CF_3, 3F), −123.1 (m, C_6F_4, 2F), −124.4 (dt, $^1J_{PF}$ = 1011 Hz, $^4J_{FF}$ = 14 Hz, P*F*, 1F), −125.9 (m, C_6F_4, 2F). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 86.8 (dt, $^1J_{PF}$ = 1011 Hz, $^3J_{PF}$ = 7 Hz, *P*F, 1P), −15.0 (t, $^3J_{PF}$ = 23 Hz, Ph_2P, 1P). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, Me_4Si): δ 148.5 (dm, $^1J_{FC}$ = 260 Hz, C_6F_4), 147.7 (dm, $^1J_{FC}$ = 267 Hz, C_6F_4), 139.6 (dd, J_{PC} = 3 Hz, J_{FC} = 2 Hz, C_6H_5), 134.3 (d, J_{PC} = 38 Hz, C_6H_5), 134.4 (s, C_6H_5), 131.4 (d, J_{PC} = 16 Hz, C_6H_5), 130.7 (s, C_6H_5), 129.4 (d, J_{PC} = 8 Hz, C_6H_5), 121.0 (q, $^1J_{FC}$ = 321 Hz, CF_3), 116.4 (dm, $^1J_{PC}$ = 113 Hz, $^2J_{FC}$ = 12 Hz, i-C_6H_5), 115.2 (d, $^1J_{PC}$ = 14 Hz, i-C_6H_5), i-C_6F_4 signals not observed.

Preparation of $[Ph_2P(F)(C_6F_4)P(F)Ph_2][O_3SCF_3]_2$ (6)

A colourless solution of XeF_2 (40 mg, 236 μmol) in 5 mL of CH_2Cl_2 was added to a yellow solution of **5** (160 mg, 233 μmol) in 5 mL of CH_2Cl_2, and agitation of the mixture yielded a colourless solution. The solvent volume was reduced to approx. 1 mL *in vacuo* and 10 mL of *n*-pentane was added to the white slurry. The mixture was vigorously agitated for 2 min and the precipitate was allowed to settle. The supernatant was decanted and the solid was dried *in vacuo* and isolated as a white powder (162 mg, 81%, Calcd for $C_{32}H_{20}F_{12}O_6P_2S_2$: C, 44.98; H, 2.36%. Found: C, 44.43; H, 2.89%). ^{1}H NMR (CD_2Cl_2, Me_4Si, 400 MHz): δ 8.40–7.68 (20H, C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −78.8 (s, 6F, CF_3), −121.6 (m, 4F, C_6F_4) −123.2 (dm, $^1J_{PF}$ = 1033 Hz, 2F, P*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 86.7 (dm, $^1J_{PF}$ = 1033 Hz, *P*F). ^{13}C{^{1}H} NMR spectra could not obtained due to the exceedingly low solubility of the compound in all common NMR solvents. Diffraction-quality crystals were grown by slow evaporation of a saturated CD_2Cl_2 solution.

Preparation of $Ph_2P(C_6F_4)P(F)_2Ph_2$ (8)

A colourless solution of $[NBu_4][Ph_3SiF_2]$ (36 mg, 67 μmol) in 2 mL of CH_2Cl_2 was added to a yellow solution of **5** (46 mg, 67 μmol) in 2 mL of CH_2Cl_2, instantly producing a colourless solution. The solvent volume was reduced to approx. 0.5 mL *in vacuo* and 10 mL of *n*-pentane were added. The mixture was agitated vigorously for 5 min and was left to settle for 10 min, after which point a light-pink oil had settled out from the colourless supernatant. The supernatant was decanted and the solvent was allowed to evaporate slowly. A white, crystalline

substance, covered in a colourless oil, remained after solvent evaporation was complete. The crystalline residue was triturated with 10 mL of cold *n*-pentane (to remove residual Ph_3SiF), dried *in vacuo*, and isolated as a white, microcrystalline powder (23 mg, 62%, Calcd for $C_{30}H_{20}F_6P_2$: C, 64.76; H, 3.62%. Found: C, 64.78; H, 3.99%). ^{1}H NMR (CD_2Cl_2, Me_4Si, 400 MHz): δ 8.09–7.25 (20H, C_6H_5). ^{19}F NMR (CD_2Cl_2, 377 MHz, $CFCl_3$): δ −34.6 (dt, $^1J_{PF}$ = 684 Hz, $^4J_{FF}$ = 12 Hz, PF_2, 2F), −128.1 (m, C_6F_4, 2F), −133.3 (m, C_6F_4, 2F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ −23.6 (t, $^3J_{PF}$ = 36 Hz, Ph_2P, 1P), −57.2 (tm, $^1J_{PF}$ = 684 Hz, PF_2, 1P). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, Me_4Si): δ 148.1 (dm, $^1J_{FC}$ = 246 Hz, C_6F_4), 145.2 (dm, $^1J_{FC}$ = 260 Hz, C_6F_4), 135.8 (dt, J_{PC} = 15 Hz, J_{FC} = 9 Hz, C_6H_5), 133.8 (dm, $^1J_{PC}$ = 11 Hz, C_6H_5), 133.6 (dt, $^1J_{PC}$ = 182 Hz, i-C_6H_5), 133.4 (dt, J_{PC} = 21 Hz, J_{FC} = 1 Hz, C_6H_5), 133.1 (dt, J_{PC} = 4 Hz, J_{FC} = 1 Hz, C_6H_5), 131.5 (d, J_{PC} = 11 Hz, C_6H_5), 129.1 (dt, J_{PC} = 17 Hz, J_{FC} = 2 Hz, C_6H_5), 129.1 (d, J_{PC} = 7 Hz, C_6H_5), i-C_6F_4 signals not observed.

X-Ray data collection, reduction, solution and refinement

Single crystals were coated in Paratone-N oil in the glovebox, 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 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.[26] 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 (see Table 1 and ESI†).

Results and discussion

Reaction of XeF_2 with the commercially available, electron-deficient phosphine, $Ph_2P(C_6F_5)$, cleanly generates the difluorophosphorane, $Ph_2P(F)_2(C_6F_5)$ **1** (Scheme 1), and subsequent fluoride ion abstractions with either $B(C_6F_5)_3$ or $Me_3SiO_3SCF_3$ generate electrophilic phosphonium salts of the formula $[Ph_2P(F)(C_6F_5)][X]$ (**2**: X = $FB(C_6F_5)_3$; **3**: X = O_3SCF_3). The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a sharp doublet of triplets at δ 87.1 ($^1J_{PF}$ = 1016 Hz, $^3J_{PF}$ = 6 Hz) resulting from coupling to the P-bound fluoride and the *ortho*-fluorines of the C_6F_5 ring, while the ^{19}F spectrum reveals similar multiplicity for the P*F* resonance at δ −123.0 ($^1J_{PF}$ = 1016 Hz, $^4J_{FF}$ = 17 Hz). The X-ray structure of **3** (Fig. 1) shows the expected tetrahedral geometry at phosphorus with a P–F bond length of 1.547(2) Å.

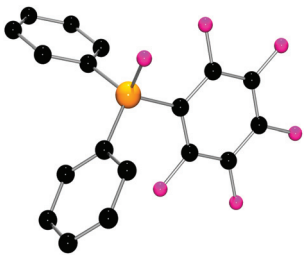
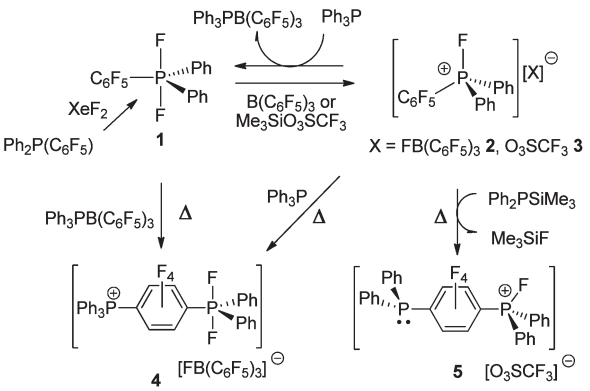


Fig. 1 POV-ray depiction of the cation of **3**.

In contrast to the sharp NMR signals observed for **3**, the $^{31}P\{^1H\}$ and ^{19}F resonances of **2** are somewhat broad at ambient temperature, with no discernible coupling. These signals sharpen with decreasing temperature so that the P–F couplings are resolved at −39 °C, and broaden dramatically upon increasing the temperature to 60 °C. This temperature dependent behaviour, which is not observed for the triflate derivative **3**, suggests fluoride delivery from the $[FB(C_6F_5)_3]^-$ anion to the Lewis acidic fluorophosphonium cation. This interpretation is further supported by the ambient temperature addition of Ph_3P to **2** in CD_2Cl_2, which immediately generated a white precipitate, identified as the adduct, Ph_3P–$B(C_6F_5)_3$[27] (Scheme 1). $^{31}P\{^1H\}$ NMR analysis of the supernatant confirmed the presence of difluorophosphorane **1**. Transfer of fluoride from the fluoroborate anion to the fluorophosphonium cation, suggests that this cation has similar fluorophilicity to $B(C_6F_5)_3$.

Interestingly, heating the mixture of Ph_3P–$B(C_6F_5)_3$ and **1** to reflux for 10 min resulted in the immediate formation of a new species **4**. The $^{31}P\{^1H\}$ NMR spectrum of this product shows two new triplet resonances at δ 16.1 ($^3J_{PF}$ = 6 Hz) and −58.4 ($^1J_{PF}$ = 699 Hz). The ^{19}F NMR spectrum of **4** exhibited seven signals, consistent with attack of Ph_3P at the *para*-position of the phosphonium ion's C_6F_5 group. The resulting phosphonium–phosphorane, $[Ph_3P(C_6F_4)P(F)_2Ph_2][FB(C_6F_5)_3]$ **4** (Scheme 1), was crystallized and characterized by X-ray structural analysis (Fig. 2). The axially disposed fluorine atoms of the phosphorane moiety give rise to an F(1)–P(2)–F(2) angle of 175.20(14)°. The P(2)–F(1) and P(2)–F(2) bond lengths of 1.656(3) and 1.657(3) Å, respectively, are typical of difluorotriarylphosphorane species.[25,28] The reaction producing **4** is thought to proceed *via* initial fluoride abstraction from **1** by thermally liberated $B(C_6F_5)_3$. Subsequent attack of Ph_3P at the fluorophosphonium cation occurs with concomitant migration of fluoride ion to the Lewis acidic fluorophosphonium centre, producing **4**. This reactivity is analogous to the thermally-



Scheme 1 Synthesis of **1–5**.

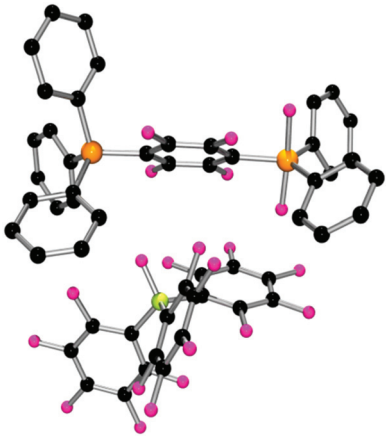
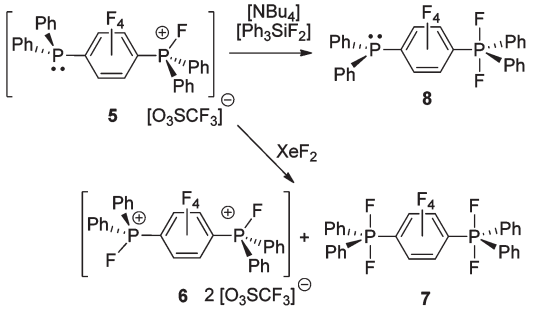


Fig. 2 POV-ray depiction of **4**.

induced *para*-substitution reaction of Ph_3P with $B(C_6F_5)_3$ affording $Ph_3P(C_6F_4)B(F)(C_6F_5)_2$,[27] thus the formation of **4** further illustrates the Lewis acidity of the phosphonium cation, $[Ph_2P(F)(C_6F_5)]^+$.

A related species is derived from the ambient temperature reaction of **3** with the silylphosphine Ph_2PSiMe_3 in C_6D_5Br. This reaction produced a brilliant, yellow solution of **5** (Scheme 1), which exhibits a $^{31}P\{^1H\}$ NMR spectrum with a doublet of triplets at δ 86.8 ($^1J_{PF}$ = 1011 Hz, $^3J_{PF}$ = 7 Hz) and a triplet at δ −15.0 ($^3J_{PF}$ = 23 Hz). These signals are consistent with the presence of Ph_2P and PF fragments occupying mutually *para* positions of a C_6F_4 ring, and thus the formulation of **5** as $[Ph_2P(C_6F_4)P(F)Ph_2][O_3SCF_3]$. The bright yellow colour of **5** can presumably be attributed to charge transfer from the phosphine through the arene to the *para*-disposed phosphonium electrophile further supporting Lewis acidity of the fluorophosphonium cation. The formation of **5** is a rare example of a reaction between a phosphonium cation and neutral base.[29] In addition, compound **5** is analogous to $R_2P(C_6F_4)B(C_6F_5)_2$ in that it contains both Lewis acidic and basic centres. As such **5** can be described as an all-phosphorus intramolecular FLP.

Compound **5** reacts with XeF_2 in CH_2Cl_2 solution with immediate loss of colour, generating two new $^{31}P\{^1H\}$ NMR signals of equal intensity at δ 86.7 (dm, $^1J_{PF}$ = 1033 Hz) and −57.2 (tm, $^1J_{PF}$ = 685 Hz). These signals are consistent with the presence of fluorophosphonium and difluorophosphorane fragments. Upon standing, colourless crystals of a species **6** were obtained from the reaction mixture. This product accounts for the $^{31}P\{^1H\}$ NMR signal at δ 86.7. X-ray structural analysis revealed **6** to be the symmetrical bis(phosphonium) salt, $[Ph_2P(F)(C_6F_4)P(F)Ph_2][O_3SCF_3]_2$ (Scheme 2). Not surprisingly, this dicationic salt is quite insoluble in all common solvents, although NMR spectroscopic analysis could be carried out on a dilute CD_2Cl_2 solution. The X-ray structure of **6** (Fig. 3) shows the presence of the two *para*-disposed fluorophosphonium functionalities about the C_6F_4 group with an average P–F bond length of 1.54 Å. The remaining metric



Scheme 2 Reactivity of **5**.

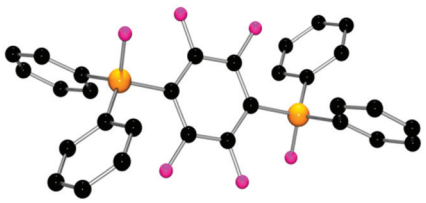


Fig. 3 POV-ray depiction of the dication of **6**.

parameters are unexceptional. The second product from the reaction of **5** with XeF_2 was observed in the supernatant by its $^{31}P\{^1H\}$ NMR signal at δ −57.2, and formulated as the bis(difluorophosphorane), $Ph_2(F)_2P(C_6F_4)P(F)_2Ph_2$ **7**. Support for this observation was obtained by the reaction of **7** with $Me_3SiO_3SCF_3$, which quantitatively produced the dicationic salt **6**.

The addition of $[NBu_4][Ph_3SiF_2]$ to **5** in CH_2Cl_2 also instantly resulted in disappearance of the solution's yellow colour, and a $^{31}P\{^1H\}$ NMR spectrum of the mixture reveals phosphine–phosphorane **8** (Scheme 2) with two new triplet resonances at δ −23.6 ($^3J_{PF}$ = 36 Hz) and −57.2 ($^1J_{PF}$ = 684 Hz). Compound **8** and Ph_3SiF were simultaneously extracted from the concentrated reaction mixture with *n*-pentane, and slow evaporation of the solvent produced diffraction-quality crystals of the mixed-valent product. The by-product Ph_3SiF could then be removed by washing the crystals with *n*-pentane to afford **8** as an analytically pure solid. X-ray structural analysis of **8** (Fig. 4) clearly shows the *para*-disposed phosphorane and phosphine functionalities of the fluorinated arene. The respective geometries of the two phosphorus centres are

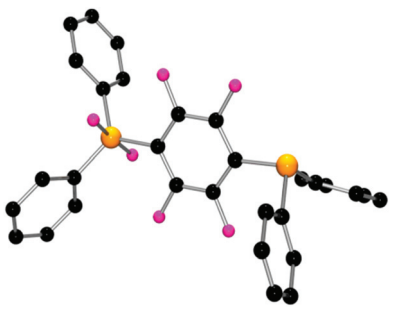
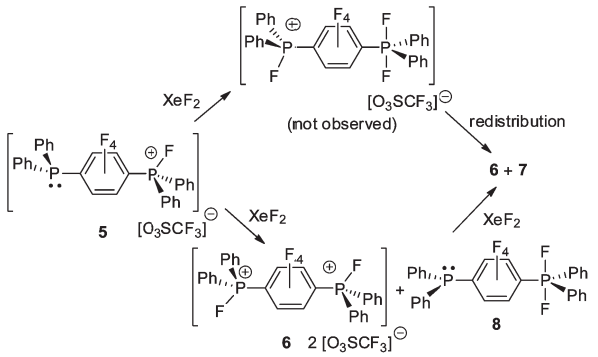


Fig. 4 POV-ray depiction of **8**.



Scheme 3 Proposed pathways for the reaction of **5** with XeF_2.

pseudo-trigonal bipyramidal and *pseudo*-trigonal pyramidal, with the P–F bond distances of the former averaging 1.66 Å. The formation of **8** affirms the Lewis acidic nature of the fluorophosphonium centre of **5**. Moreover, this observation supports the description of **5** as an FLP.

Two possible reaction pathways can be envisioned for the formation of **6** and **7** from **5** and XeF_2 (Scheme 3). Direct oxidation of the phosphine centre in **5** with XeF_2 could generate the intermediate $[Ph_2PF(C_6F_4)P(F)_2Ph_2]^+$. In this species, Lewis acidity of the phosphonium centre should be enhanced by the *para*-disposed phosphorane, prompting intermolecular fluoride redistribution to form **6** and **7** (Scheme 3). Alternatively, one can consider that activation of XeF_2 between the acidic and basic functionalities of two independent cations would generate **6** and $Ph_2P(C_6F_4)P(F)_2Ph_2$ **8**. Subsequent oxidation of **8** by XeF_2 would produce **7**. Efforts to discern the operative pathway *via* low temperature reactions were unsuccessful. It is noteworthy that in the former mechanism the proposed intermediate is analogous to the isolated species **4**, whereas in the latter pathway the proposed intermediate **8** was prepared and isolated independently. These observations suggest that the independent pathways may be competitive.

Conclusions

In summary, Lewis acidic fluorophosphonium salts are readily prepared by oxidation of a phosphine with XeF_2 and subsequent fluoride abstraction. Reactions of the resulting fluorophosphonium salts with Ph_3P and Ph_2PSiMe_3 yield **4** and **5**, respectively, demonstrating the fluorophilicity of these Lewis acids, which readily undergo *para*-attack at the C_6F_5 group. This reactivity is reminiscent of that observed for related P/B FLP systems.[27,30] While compound **5** reacts with XeF_2 to give **6** and **7**, it also reacts with a source of fluoride to give **8**. Compounds **5** and **8** represent rare examples of mixed-valent P(III)/(V) compounds,[31–37] and **8** is, to the best of our knowledge, the first crystallographically characterized species containing both phosphine and phosphorane functionalities. In addition, the Lewis acidity of fluorophosphonium cations provides routes to these unprecedented mixed-valent phosphorus compounds, thus affording all-phosphorus FLPs. The demonstration that fluorophosphonium cations are of comparable Lewis acidity to $B(C_6F_5)_3$ augurs well for applications of P-based Lewis acids in synthesis and catalysis. Such developments are the subject of on-going efforts in our laboratories.

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