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Synthesis and Lewis Acidity of Fluorophosphonium Cations

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A series of fluorophosphonium salts, [R3PF][X] (R = alkyl or aryl; X = FB(C6F5)3, [B(C6F5)4]), have been prepared by reactions of phosphine / borane frustrated Lewis pairs (FLPs) with XeF2 or difluorophosphoranes with [Et3Si][B(C6F5)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 catalysis5-8 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 H2.23 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 H2.

The electrophilicity of higher oxidation state phosphorus-species have also been exploited in the classic Wittig24 and Staudinger25 reactions. In addition, phosphonium Lewis acids have been employed in catalytic transformation, 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 fluorene 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 N2 atmosphere using standard Schlenk and 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. CH2Cl2, Et2O,
Synthesis of [\(\text{BF}_3\text{P}\text{O}_3\)] [\(\text{BF}(\text{CF}_3)\text{C}_2\text{F}_3\)] (2) This procedure was utilized to synthesize this product the first involving addition of \(\text{XeF}_2\) to the \(\text{FPPand the second involving initial phosphine oxidation followed by borane abstraction of fluoride. Both are described below. (1) A solution of \(\text{BF}_3\text{P}\) (40 mg, 195 \(\mu\text{mol}\)) in 5 mL of dichloromethane was added to \(\text{B}(\text{CF}_3)\text{C}_2\text{F}_3\) (100 mg, 195 \(\mu\text{mol}\)). This solution was added to \(\text{XeF}_2\) (33 mg, 195 \(\mu\text{mol}\)) in 5 mL of dichloromethane, resulting in immediate effervescence. The reaction was allowed to stir for 10 minutes and the solvent was removed in \(\text{vacuo}\) producing a colorless solid that was washed with pentane (3 x 2 mL) and was dried in \(\text{vacuo}\). (2) A solution of \(\text{BF}_3\text{P}\) (40 mg, 195 \(\mu\text{mol}\)) in 5 mL of dichloromethane was added to a solution of \(\text{XeF}_2\) (33 mg, 195 \(\mu\text{mol}\)) 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. \(\text{B}(\text{CF}_3)\text{C}_2\text{F}_3\) (100 mg, 195 \(\mu\text{mol}\)) was added and the solution was removed in \(\text{vacuo}\) producing a colorless solid that was washed with pentane (3 x 2 mL) and was dried in \(\text{vacuo}\).
(14): Anal. Caled. for C36H27BF21P (900.36): found C 48.02, H 3.02; found C 48.00, H 3.06. **H NMR (499.7 MHz, CDCl3, MeSi): δ = 1.65 ppm (dd, JHF = 15.8 Hz, JHH = 1.7 Hz); **B[11]H NMR (128.4 MHz, CDCl3, BF3·OEt2): δ = −1.67 ppm (s, ν1/2 = 26 Hz); **C[13]H NMR (125.7 MHz, CDCl3, MeSi): δ = 148.5 (JCP = 99.1 Hz, CF = 7.6 Hz, CF3), 136.7 (JCP = 245.7 Hz, CF3), 124.2 (br, i-CF3), 41.6 (dd, JCP = 26.5 Hz, JCF = 7.7 Hz, CHs), 27.7 ppm (m, CHs); **F NMR (376.6 MHz, CDCl3, CFCls): δ = −130.0 (m, 6F, o-CF3), −163.7 (t, JHF = 20.4 Hz, 4F, p-CF3), −167.8 ppm (m, 8F, m-CF3), −171.6 ppm (d, JHF = 1019 Hz, 1F, PF); **P[31]H NMR (162.0 MHz, CDCl3, H3PO4): δ = −147.5 ppm (t, JHF = 1019 Hz).

(16): Yield: 414 mg (92%); Anal. Caled. for C38H25B2F2(1H) (900.36): found C 56.38, H 3.06; found C 57.52, H 3.29. **H NMR (499.7 MHz, CDCl3, MeSi): δ = 7.22 (d, JHF = 3.26 Hz, 3H, CH2Me), 7.07 (d, JHF = 6.35 Hz, 3H, C2H2Me2), 2.40 (s, 9H, C2H2Me2-δ), 2.34 (d, JHF = 6.17 Hz, 9H, C2H2Me2-δ), 1.96 ppm (s, 9H, C2H2Me2-δ); **B[11]H NMR (128.4 MHz, CDCl3, BF3·OEt2): δ = −16.77 ppm (s, ν1/2 = 26 Hz); **C[13]H NMR (125.7 MHz, CDCl3, MeSi): δ = 149.5 (dd, JCP = 99.1 Hz, CF = 2.6 Hz, JCP = 1.5 Hz, CF3), 148.6 (dd, JCP = 248.0 Hz, CF3), 145.6 (dd, JCP = 81.8 Hz, JCP = 1.4 Hz, CF3), 144.0 (dd, JCP = 18.2 Hz, JCP = 3.1 Hz, CF3), 138.6 (d, JCP = 244.8 Hz, CF3), 136.7 (d, JCP = 246.1 Hz, CF3), 133.6 (dd, JCP = 14.0 Hz, 2CH2), 124.2 (br, i-CF3), 117.2 (dd, JCP = 99.1 Hz, JCP = 13.2 Hz, CF3), 22.6 (dd, JCP = 7.67 Hz, JCP = 5.2 Hz, CHs), 21.7 ppm (m, CHs); **F NMR (376.6 MHz, CDCl3, CFCls): δ = −115.6 (JHF = 940 Hz, 1F, PF), −133.1 (m, 8F, o-CF3), −163.8 (t, JHF = 20.3 Hz, 4F, p-CF3), −167.6 ppm (m, 8F, m-CF3); **P[31]H NMR (162.0 MHz, CDCl3, H3PO4): δ = 93.0 ppm (d, JHF = 940 Hz).

Synthesis of [R(R’F)PF][BF(C6F4)3] (R = R’ = Bu (16), Me (17), o-Tol (18), Ph (19), p-C6H4F (20), p-C6H4F (21), R = Ph, R’ = C6F5 (22)) A solution of RPF2 in toluene (8 mL) was added to a slurry of [EtSiS][BF(C6F4)04] (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 CH2Cl2 (2 mL) and dried in vacuo yielding the product as a colorless fine powder. Crystals suitable for X-ray analysis were obtained from a CH2Cl2 solution at −35 °C after several days for 14, 16, 17 and 18.

(17): Yield: 472 mg (87%); Anal. Caled. for C38H25B2F2(1H) (1086.57): found C 56.38, H 3.06; found C 57.52, H 3.29. **H NMR (499.7 MHz, CDCl3, MeSi): δ = 7.22 (d, JHF = 3.26 Hz, 3H, CH2Me), 7.07 (d, JHF = 6.35 Hz, 3H, C2H2Me2), 2.40 (s, 9H, C2H2Me2-δ), 2.34 (d, JHF = 6.17 Hz, 9H, C2H2Me2-δ), 1.96 ppm (s, 9H, C2H2Me2-δ); **B[11]H NMR (128.4 MHz, CDCl3, BF3·OEt2): δ = −16.77 ppm (s, ν1/2 = 26 Hz); **C[13]H NMR (125.7 MHz, CDCl3, MeSi): δ = 149.5 (dd, JCP = 99.1 Hz, CF = 2.6 Hz, JCP = 1.5 Hz, CF3), 148.6 (dd, JCP = 248.0 Hz, CF3), 145.6 (dd, JCP = 81.8 Hz, JCP = 1.4 Hz, CF3), 144.0 (dd, JCP = 18.2 Hz, JCP = 3.1 Hz, CF3), 138.6 (d, JCP = 244.8 Hz, CF3), 136.7 (d, JCP = 246.1 Hz, CF3), 133.6 (dd, JCP = 14.0 Hz, 2CH2), 124.2 (br, i-CF3), 117.2 (dd, JCP = 99.1 Hz, JCP = 13.2 Hz, CF3), 22.6 (dd, JCP = 7.67 Hz, JCP = 5.2 Hz, CHs), 21.7 ppm (m, CHs); **F NMR (376.6 MHz, CDCl3, CFCls): δ = −115.6 (JHF = 940 Hz, 1F, PF), −133.1 (m, 8F, o-CF3), −163.8 (t, JHF = 20.3 Hz, 4F, p-CF3), −167.6 ppm (m, 8F, m-CF3); **P[31]H NMR (162.0 MHz, CDCl3, H3PO4): δ = 93.0 ppm (d, JHF = 940 Hz).
(18): Yield: 431 mg (86%); Anal. Caled. for C25H12BF3P: calcd C 52.53, H 1.52; found C 52.53, H 1.52. 1H NMR (497.9 MHz, CD2Cl2, MeSi): δ = 8.06 (m, 1H, CH), 7.08 ppm (m, 4H, CH); 19F NMR (128.4 MHz, CD2Cl2, BF3·OEt2): δ = 167 ppm (s, ν12 = 26 Hz); 13C{1H} NMR (125.7 MHz, CD2Cl2, MeSi): δ = 148.5 (d, 1JC = 240.5 Hz, Cδ3), 114.5 (dd, δJC = 8.5 Hz, δJC = 1.5 Hz, CH3), 138.6 (d, 1JC = 240.0 Hz, Cδ3), 137.7 (d, δJC = 2.7 Hz, δJC = 1.3 Hz, CH3), 136.7 (d, 1JC = 242.0 Hz, Cδ3), 135.6 (dd, δJC = 18.4 Hz, δJC = 2.2 Hz, CH3), 134.5 (d, δJC = 12.0 Hz, CH3), 128.3 (d, δJC = 15.7 Hz, CH3), 124.1 (br, i-C6F5), 115.7 (dd, 1JC = 105.2 Hz, 1JC = 12.8 Hz, Cδ3), 22.0 (dd, δJC = 5.0 Hz, δJC = 2.8 Hz, CH3).19F NMR (376.6 MHz, CD2Cl2, CFCl3): δ = −125.5 (d, 1JFP = 993 Hz, 1F, PF) −133.0 (m, 8F, o-CF3), −163.6 (t, 1JFP = 20.2 Hz, 4F, p-CF3), −167.5 ppm (m, 8F, m-CF3); 31P{1H} NMR (162.0 MHz, CD2Cl2, 25 °C): δ = 103.2 ppm (d, 1JFP = 993 Hz).

(19): Yield: 384 mg (80%); Anal. Caled. for C25H12BF3P: calcd C 52.53, H 1.57; found C 52.53, H 1.52. 1H NMR (497.9 MHz, CD2Cl2, MeSi): δ = 8.06 (m, 1H, CH), 7.08 ppm (m, 4H, CH); 19F NMR (128.4 MHz, CD2Cl2, BF3·OEt2): δ = 167 ppm (s, ν12 = 26 Hz); 13C{1H} NMR (125.7 MHz, CD2Cl2, MeSi): δ = 148.5 (d, 1JC = 240.5 Hz, Cδ3), 114.5 (dd, δJC = 8.5 Hz, δJC = 1.5 Hz, CH3), 138.6 (d, 1JC = 240.0 Hz, Cδ3), 137.7 (d, δJC = 2.7 Hz, δJC = 1.3 Hz, CH3), 136.7 (d, 1JC = 242.0 Hz, Cδ3), 135.6 (dd, δJC = 18.4 Hz, δJC = 2.2 Hz, CH3), 134.5 (d, δJC = 12.0 Hz, CH3), 128.3 (d, δJC = 15.7 Hz, CH3), 124.1 (br, i-C6F5), 115.7 (dd, 1JC = 105.2 Hz, 1JC = 12.8 Hz, Cδ3), 22.0 (dd, δJC = 5.0 Hz, δJC = 2.8 Hz, CH3).19F NMR (376.6 MHz, CD2Cl2, CFCl3): δ = −125.5 (d, 1JFP = 993 Hz, 1F, PF) −133.0 (m, 8F, o-CF3), −163.6 (t, 1JFP = 20.2 Hz, 4F, p-CF3), −167.5 ppm (m, 8F, m-CF3); 31P{1H} NMR (162.0 MHz, CD2Cl2, H2PO4): δ = 94.8 ppm (d, 1JFP = 997.8 Hz).

(20): Yield: 451 mg (89%); Anal. Caled. for C25H12BF3P: calcd C 52.53, H 1.19; found C 49.69, H 0.87. 1H NMR (497.9 MHz, CD2Cl2, MeSi): δ = 7.80 (m, 2H, CH), 7.54 ppm (m, 2H, CH); 19F NMR (128.4 MHz, CD2Cl2, BF3·OEt2): δ = 167 ppm (s, ν12 = 26 Hz); 13C{1H} NMR (125.7 MHz, CD2Cl2, MeSi): δ = 169.6 (dd, 1JC = 242.0 Hz, JCP = 3.27 Hz, JC = 1.60 Hz, CF), 148.5 (d, 1JC = 240.5 Hz, Cβ), 138.6 (d, 1JC = 244.0 Hz, Cδ3), 137.7 (dd, δJC = 15.2 Hz, δJC = 10.8 Hz, δJC = 1.0 Hz, CH3), 136.6 (d, 1JC = 242.0 Hz, Cδ3), 124.1 (br, i-C6F5), 119.7 (dd, δJC = 22.8 Hz, δJC = 16.1 Hz, CH3), 112.0 ppm (dd, 1JC = 116.1 Hz, 1JC = 5.7 Hz, 1JC = 3.4 Hz, Cδ3); 13F NMR (376.6 MHz, CD2Cl2, CFCl3): δ = −92.3 (m, 3F, CF), −122.9 (d, 1JFP = 1000 Hz, 1F, PF) −133.1 (m, 8F, o-CF3), −163.6 (t, 1JFP = 20.2 Hz, 4F, p-CF3), −167.5 ppm (m, 8F, m-CF3); 31P{1H} NMR (162.0 MHz, CD2Cl2, H2PO4): δ = 94.8 ppm (d, 1JFP = 1000 Hz, 1JPF = 1.8 Hz).

(21): Yield: 470 mg (80%); Anal. Caled. for C25H11BF3P: calcd C 42.89, H 0.26; found C 42.36, H 0.56. 1H NMR (499.7 MHz, CD2Cl2, MeSi): δ = 8.03 ppm (m, CH3); 19F NMR (128.4 MHz, CD2Cl2, BF3·OEt2): δ = −167 ppm (s, ν12 = 26 Hz); 13F NMR (376.6 MHz, CD2Cl2, CFCl3): δ = −124.4 (dm, 1JFP = 1060 Hz, 1F, PF), −125.7 (m, 6F, o-CF3-H), −128.2 (m, 6F, m-CF3-H), −133.3 (m, 8F, o-CF3), −163.9 (t, 1JFP = 20.3 Hz, 4F, p-CF3), −167.8 ppm (m, 8F, m-CF3); 31P{1H} NMR (162.0 MHz, CD2Cl2, H2PO4): δ = 70.1 ppm (dsept, 1JFP = 1060 Hz, 3JPF = 8.5 Hz).

X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were coated with Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(s+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 F2 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 CD3Cl2 solution containing 1:1 Bu4PBF5/[B(C6F5)3] to XeF2 at ambient temperature immediately resulted in vigorous effervescence to produce the fluorophosphonium fluoroborate salt, [Bu4P][BF(C6F5)3] (1; Scheme I), which could be isolated in quantitative yield as a colourless, analytically pure solid. 31P{1H} NMR spectroscopy of the resulting mixture shows a doublet signal at δ = 148.5 ppm (1Jpf = 1019 Hz), while the 19F NMR spectrum shows the corresponding doublet resonance at δ = −171.6 ppm, consistent with the formulation. The selective production of 1 suggests that the FLP reacts with XeF2 by a mechanism involving phosphine oxidation and fluoride ion abstraction by B(C6F5)3. The observed reactivity is in stark contrast to that of reaction of intramolecular P/B FLP systems with XeF2, where complexation of the borane to BuNC was required to achieve clean oxidation to the corresponding fluorophosphonium fluoroborate.

The aforementioned reactivity was extended to a series of variously substituted organophosphene precursors, including MesP, (o-Tol)2P, PhP, and (p-C6Me3SiF3)P. In the presence of 1 equiv. of B(C6F5)3, the resulting FLPs reacted with XeF2 to yield salts of the...
formaldehyde, [R3PF][FB(C6F5)3], where R = Mes (2), o-Tol (3), Ph (4), or p-C6H4F (5) (Scheme 2). NMR data for triarylphosphonium salts 2 and 3 each show significantly upfield-shifted 31P NMR resonances (δ 92.9 and 104.3, respectively), and downfield-shifted 19F signals (δ -116.7 and -125.5, respectively) relative to that of trialkylphosphonium salt 1, which can be crystallized from a mixture of CH2Cl2 and n-pentane. X-ray structural analysis of 1 shows the expected tetrahedral geometry around both P and B centers (Figure 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.

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

A crystallographic analysis of 3 (Figure 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 difference is attributed to the more steric demands of the tBu 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), suggesting that favorable π-stacking and Coulombic interactions between these ions instead stabilize their mutual orientation in the solid state.

Scheme 2. Reaction of XeF2 with phosphine / borane FLPs.

With the exception of Ph3P, the apparent rate of reactions between XeF2 and phosphine / B(C6F5)3 FLPs is noticeably reduced as increasingly electron-withdrawing substituents are appended to P. Our previous report describing the reaction between XeF2 and the electron-deficient phosphine / borane FLPs demonstrated the anticipated formation of salt 6. Interestingly however, 6 was found to exist in equilibrium with free B(C6F5)3 and the difluorophosphorane, Ph2(C6F5)PF2, by rapid fluoride ion transfer between P and B centers, made evident by variable temperature 31P{1H} and 19F NMR spectroscopy. Analogous reactions using the phosphines Ph(C6F5)P, (p-C6F4H)PF and (C6F5)3P also result in their oxidation to the difluorophosphoranes. In these cases however, B(C6F5)3 does not abstract fluoride from the corresponding difluorophosphoranes, indicating that the targeted fluorophosphonium cations are more Lewis acidic than B(C6F5)3 towards fluoride. Nonetheless, fluoride ion abstraction from the difluorophosphoranes can be achieved employing the harder electrophiles such as Al(C6F5)3 or [Et3Si][B(C6F5)4]. We have previously utilized this technique to access highly electrophilic fluorophosphonium cations, [(C6F5)2PhPF]+ (7) and [(C6F5)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(C6F5)3]+ anion. Thus, initial oxidation of the phosphines with XeF2 yields the difluorophosphoranes R2PF2, [R, R' = tBu (9), Mes (10), o-Tol (11), Ph (12), p-C6H4F (13), and p-C6F4H (14), R = Ph, R' = C6F5 (15)] in quantitatively yields. Subsequently fluoride abstraction of the difluorophosphoranes with [Et3Si][B(C6F5)4] yield the salts of the formula [R2PF][B(C6F5)3], where R = tBu (16), Mes (17), o-Tol (18), Ph (19), p-C6H4F (20), and p-C6F4H (21), R =
Ph, R’ = C6F5 (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(C6F5)4] anion give rise to signals in the 11B and 19F NMR spectra at δ = −16.7 and −133.0 (α-C6F5), −163.7 (p-C6F5) and −167.8 (m-C6F5), respectively.

Figure 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.

Crystals suitable for X-ray crystallographic studies of compound 17, 19, 20, 21 and 22 were obtained from a concentrated CH2Cl2 solution at −35 °C (Figure 2). The P–F bond lengths of the Mes (17), Ph (19), p-C6H4F (20) p-C6F4H (21) and Ph2(C6F5) (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-CF3H substituents in 21. This value is similar to that see for the P–F bond length in [(C6F5)2PhPF][F(Al(C6F5)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(C6F5)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 31P{1H} NMR chemical shift decreases with increasingly electron-withdrawing substituents (Figure 3). Conversely, 19F 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 discrepancy is perhaps best attributed to the impact of the increased steric crowding in this triarylphosphonium cation, which may affect shielding of the 31P and/or 19F nuclei. Nonetheless, these observation suggest that the 31P and 19F chemical shifts are correlated with the expected Lewis acidity of these fluorophosphonium cations.

Figure 3. Stack plot of the 31P{1H} NMR data for a series of 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 test32 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,\textsuperscript{43-44} addition of one equivalent of Et3PO to the least Lewis acidic compounds among the series, 1, 2 or 3 resulted in no observable change in the \(^{31}\text{P}\) NMR chemical shifts indicative of no interaction of the phosphate-oxide with these Lewis acids. In contrast, addition of Et3PO to the more electron-deficient salt 4 led to the generation of the difluorophosphorane, Ph$_3$PF$_2$ and the adduct (Et$_3$PO)B(C$_6$F$_5$)$_3$. This observation confirms fluoride ion transfer from B to P with concurrent sequestration of the phosphate-oxide by the freed borane (Scheme 4).

A similar result was previously observed with the more Lewis acidic salt 6.\textsuperscript{33} Interestingly combination of 19 where the [B(C$_6$F$_5$)$_3$] anion circumvents the reaction of phosphate-oxide with the anion, no interaction of the cation with EtPO was evident from the \(^{31}\text{P}\) NMR spectroscopy. We have previously reported that Et3PO coordinates to the cation of 8 affording a shift of the \(^{31}\text{P}\) signal for the phosphate oxide to 91.1 ppm and thus a Gutmann-Beckett \(\Delta \delta\) of 40.4.\textsuperscript{30} The combination of the tetrafluorophenyl-substituted fluorophosphonium (21) with Et3PO in CD$_2$Cl$_2$ gave rise of a signal for the coordinated phosphate oxide at 89.5 ppm in the \(^{31}\text{P}\) NMR spectrum and thus \(\Delta \delta\) of 38.8. This suggests that 21 is about 5% less Lewis acidic than [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_3$]. This situation is analogous to the Lewis acidities of B(p-C$_6$F$_4$H)$_3$ and B(C$_6$F$_5$)$_3$.\textsuperscript{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.

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\text{Scheme 4: Reactions of 6 and 19 with Et}_3\text{PO.}
\]

An alternative strategy to assess Lewis acidity to these experimental methods, is a method developed by Bartlett,\textsuperscript{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.\textsuperscript{47-48} In addition, Slattery et al. have calculated the FIA of a number of free phosphonium cations and the results show that certain free phosphonium cations have the potential to be as Lewis acidic as silylium cations.\textsuperscript{49} In this method two computational approaches were used. The first involved the calculation of enthalpy (\(\Delta H\)) using WB97XD/def2TZV level of theory\textsuperscript{50-51} in conjunction with the conductor-like polarizable continuum solvation model (CPCM)\textsuperscript{52-55} in dichloromethane for the reaction of F\(^-\) with [R$_3$PF]$^+$ forming the corresponding difluorophosphorane (Eq’n 1). The FIA is then defined as the negative of the enthalpy \(\Delta H\).\textsuperscript{46, 56-57} The second approach utilized a gas phase pseudo-isodesmic reaction between the fluorophosphonium cations and [COF$_2$]$^-$ acting as F$^-$ donor forming corresponding difluorophosphorane and COF$_2$. These latter calculations are anchored to an experimental \(\Delta H\) value of the addition of F$^-$ to COF$_2$ forming [COF$_3$]$^-$ of 209 kJ/mol.\textsuperscript{49, 56} In addition, the \(^{31}\text{P}\) NMR chemical shifts the phosphonium cations were calculated using gauge-including atomic orbital method (GIAO)\textsuperscript{58-59} at WB97XD/def2TZV level of theory (Table 1). The calculated \(^{31}\text{P}\) NMR chemical shifts were referred to chemical shift of [Me$_3$PF]$^+$, and although there is some divergence from the experimental observations the computed shifts follow the same trends.

\[
[R_3PF]^+ + F^- \xrightarrow{\Delta H = \text{FIA}} R_3PF_2
\]

\textbf{Table 1. NMR data and FIA for fluorophosphonium cations.}

<table>
<thead>
<tr>
<th>Cation</th>
<th>(^{31}\text{P})</th>
<th>(^{19}\text{F})</th>
<th>(^{31}\text{P}_{\text{calc}})</th>
<th>FIA ((^{19}\text{F}))</th>
<th>FIA (COF$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtBu.PF]$^+$</td>
<td>148.5</td>
<td>-171.6</td>
<td>181.6</td>
<td>163</td>
<td>148</td>
</tr>
<tr>
<td>[Mes$_3$PF]$^+$</td>
<td>92.9</td>
<td>-116.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[o-tol.PF]$^+$</td>
<td>104.3</td>
<td>-125.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Ph.PF]$^+$</td>
<td>94.7</td>
<td>-128.3</td>
<td>108.1</td>
<td>200</td>
<td>165</td>
</tr>
<tr>
<td>[p-C$_6$H$_4$Cl.PF]$^+$</td>
<td>93.3</td>
<td>-123.8</td>
<td>103.7</td>
<td>220</td>
<td>214</td>
</tr>
<tr>
<td>[Ph$_2$(C$_6$F$_5$).PF]$^+$</td>
<td>87.2</td>
<td>-123.4</td>
<td>90.9</td>
<td>238</td>
<td>227</td>
</tr>
<tr>
<td>[(C$_6$F$_5$)$_3$.PF]$^+$</td>
<td>77.7</td>
<td>-121.9</td>
<td>71.6</td>
<td>275</td>
<td>280</td>
</tr>
<tr>
<td>[p-C$_6$H$_4$.F.PF]$^+$</td>
<td>70.1</td>
<td>-124.4</td>
<td>-</td>
<td>296</td>
<td>287</td>
</tr>
<tr>
<td>[(C$_6$F$_5$)$_2$.PF]$^+$</td>
<td>68.0</td>
<td>-120.7</td>
<td>53.2</td>
<td>311</td>
<td>323</td>
</tr>
</tbody>
</table>

Interestingly the calculated FIA values are well correlated with implications of the observed \(^{31}\text{P}\) and \(^{19}\text{F}\) 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 acidity. Furthermore, the FIA of B(C$_6$F$_5$)$_3$, 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$_6$F$_5$)$_3$ from the alkyl and aryl substituted difluorophosphoranes with FIA values lower than that of the B(C$_6$F$_5$)$_3$. At the same time this is also consistent with the observation that B(C$_6$F$_5$)$_3$ does not abstract fluoride from bis- and tris-pentafluorophenyl substituted difluorophosphoranes, where the FIA is computed to be higher than that of B(C$_6$F$_5$)$_3$.

\textbf{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$_6$F$_5$)$_3$ is not a strong enough Lewis acid to abstract the fluoride; a notion that is supported by a comparison of the calculated FIA values. The aforementioned fluorophosphonium cations were also generated using [Et$_3$Si][B(C$_6$F$_5$)$_3$] in an effort to remove the non-innocent [FB(C$_6$F$_5$)$_3$]$^+$ anion. The \(^{31}\text{P}\) and \(^{19}\text{F}\) chemical shifts and the computed FIA values 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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