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Pyridinium-Phosphonium Dications: Highly Electrophilic Phosphorus-based Lewis Acid Catalysts

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Using commercially available 2-pyridyldiphenylphosphine (*o*-NC_5H_4)PPh_2, a family of electrophilic phosphonium cations [(*o*-NC_5H_4)$PFPh_2$]$^+$ (**2**) and dications [(*o*-$MeNC_5H_4$)$PRPh_2$]$^{2+}$ (R = F (**4**); Me (**5**)) were prepared. The Lewis acidity of these pyridinium-phosphonium dications was probed in Friedel-crafts dimerization, hydrodefluorination, hydrosilylation, dehydrocoupling and hydrodeoxygenation reactions. The influence of the counterion on the catalytic activity of the electrophilic phosphonium cations is also discussed.

Introduction

Metal-free catalysis is an emerging alternative to conventional transition metal catalyst technologies. Among the various metal-free strategies, catalysts based on main group species have garnered significant attention in the past decade. Many of these efforts have been prompted by the development of frustrated Lewis pairs (FLPs) by our group in 2006,[1] which led to the first metal-free hydrogenation technologies. Many different combinations of Lewis acids and bases have been exploited as FLPs, but typically the Lewis acids have been limited to boron-based species although other Lewis acids such as Al, C, Ti and Zr among others have also been explored.[2-3] In an attempt to broaden the scope of main group Lewis acids our group has explored the use of phosphorus-based Lewis acids in FLP chemistry and catalysis.[4]

Many research groups have studied electrophilic phosphorus compounds and their applications in stoichiometric and catalytic reactions.[4] For instance, P(III) dicoordinate phosphenium cations have been shown to activate C-C/H and P-P bonds,[10-12] and form Lewis acid-base adducts with nucleophilic amidines[13] and 4-*N*-*N*-dimethylaminopyridine.[14] Interestingly, a triphosphabenzene derivative was also shown to activate H_2 via an intramolecular FLP-type mechanism in which a carbanion acts as the base and a P(III) centre acted as the Lewis acid.[15] Similarly, PF_5 phosphoranes have formed Lewis acid-base adducts with *N*-trimethylsilyl imidazole and pyrazole derivatives.[16] The synergistic use of tetracoordinate P(V) phosphonium cations in combination with a B-Lewis acid have been used to capture fluoride ions in sensor applications[17] and to facilitate addition to polar unsaturates.[18] In this context, the addition of P-based ylides to ketones in Wittig reactions is also driven by the electrophilic nature of the P centre[19-20] A significant advance in this field was the development of the electrophilic phosphonium cation (EPC), $[(C_6F_5)_3PF][B(C_6F_5)_4]$,[21-22] which has been exploited as a catalyst for hydrodefluorination,[22] hydrosilylation,[23-24] transfer hydrogenation of olefins,[25] hydroarylation and hydrothiolation[26] and hydrodeoxygenation reactions.[27] The reactivity of this EPC is attributed to the energetically accessible σ* orbital oriented opposite the polar P-F bond.[21-22, 28-29] In an attempt to synthesize a broader range of fluorophosphonium cations, the fluorophosphonium dication, $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$, was prepared. This dication proved to be more Lewis acidic than $[(C_6F_5)_3PF][B(C_6F_5)_4]$[30] and consequently was an effective catalyst for the above reactions. Shortly after, a family of *bis*-fluorophosphonium dications in which two phosphonium cations are placed in close proximity was synthesized. These species also proved to be active catalysts in the aforementioned organic transformations.[31] A more recent advance includes the use of the EPC $[(C_6F_5)_3PF][B(C_6F_5)_4]$ in conjunction with sterically encumbered aryl-substituted amines to effect reversible H_2 activation and hydrogenation catalysis of olefins.[32] In addition, we have also synthesized a 1,2-diphosphonium dication, which effects E-H (E = C, Si, B, H) bond activations with phosphine Lewis bases.[33]

Despite these recent advances of EPCs, this area remains underexplored as the use of P-based metal-free Lewis acids in catalysis and FLP chemistry is still in its infancy. In an effort to further broaden the range of P-based dications available for catalysis, in this report we describe a facile synthetic route to a family of pyridinium-phosphonium cations. These species exhibit enhanced solubility and are shown to be effective catalysts in a variety of organic transformations. The effect of

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the counterion on both solubility and catalytic activity is also discussed.

Experimental Section

General Procedures: All manipulations were performed in a Glove box MB Unilab produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (CH_2Cl_2, and *n*-pentane) were prepared using an Innovative Technologies solvent purification system. CD_2Cl_2 and CD_3CN (Aldrich) were deoxygenated, distilled over CaH_2, then stored over 4 Å molecular sieves before use. C_6D_6 and C_6D_5Br (Aldrich) were deoxygenated and stored over 4 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ was prepared by the reported procedure.[34] 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. Assignments of individual resonances were done using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer. Elemental analyses were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyser.

Synthesis of $(o\text{-}NC_5H_4)PF_2Ph_2$ (1). A solution of 2-pyridyldiphenylphosphine (1.19 g, 4.53 mmol, 1.0 eq.) in CH_2Cl_2 (8 mL) was added to a suspension of XeF_2 (0.768 g, 4.54 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture, transparent and colourless, was stirred for 2 h at ambient temperature. All volatiles were removed *in vacuo* and the residue was washed with *n*-pentane (3 x 5 mL). The supernatant was removed and all volatiles were removed *in vacuo* to afford a white microcrystalline powder (1.28 g, 94%, Anal. Calcd for $C_{17}H_{14}F_2NP$: C, 67.77; H, 4.68; N, 4.65%. Found: C, 67.14; H, 4.69; N, 4.80%). **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 7.4 (m, 5H; Ph), 7.4 (m, 1H; *p*-py), 7.7 (m, 1H; *m*-py), 7.8 (m, 1H; *o*-py), 8.1 (m, 5H; Ph), 8.7 ppm (dm, $^4J_{PH}$ = 5 Hz, 1H; *m*-py). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -36.4 ppm (d, $^1J_{PF}$ = 670 Hz, 2F; PF_2). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ -52.7 ppm (t, $^1J_{PF}$ = 670 Hz, 1P). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 100 MHz, Me_4Si): δ 125.2 (d, $^4J_{PC}$ = 4 Hz, 1C; *p*-py), 126.5 (dt, $^2J_{PC}$ = 32 Hz, $^3J_{FC}$ = 5 Hz, 1C; *o*-py), 129.0 (dt, $^2J_{PC}$ = 16.5 Hz, $^3J_{FC}$ = 2 Hz, 4C; *o*-Ph), 132.5 (dt, $^4J_{PC}$ = 4 Hz, $^5J_{FC}$ = 2 Hz, 2C, *p*-Ph), 134.7 (dt, $^1J_{PC}$ = 177 Hz, $^2J_{FC}$ = 27 Hz, 2C, *i*-Ph), 135.3 (dt, $^3J_{PC}$ = 13 Hz, $^4J_{FC}$ = 10 Hz, 4C; *m*-Ph), 136.7 (d, $^3J_{PC}$ = 14 Hz, 1C; *m*-py), 150.0 (d, $^3J_{PC}$ = 27 Hz, 1C; *m*-py), 159.4 ppm (dt, $^1J_{PC}$ = 269 Hz, $^2J_{FC}$ = 36 Hz, 1C, *i*-py),. **HRMS (DART-TOF+)** : m/z 280.0899 (Calcd. for [(*o*-NC_5H_5)PPh_2O]+ : 280.0891),

Synthesis of $[(o\text{-}NC_5H_4)PFPh_2][O_3SCF_3]$ (2a). Trimethylsilyl trifluoromethanesulfonate ($Me_3SiO_3SCF_3$) (0.2 mL, 1.11 mmol, 1.1 eq.) was added dropwise to a solution of **1** (0.295 g, 1.05 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 15 min at ambient temperature. All volatiles were removed *in vacuo* and the residue was washed with *n*-pentane (3 x 5 mL). The supernatant was removed and all volatiles were removed *in vacuo* to afford a white microcrystalline powder. (0.390 g, 92%, Anal. Calcd for $C_{18}H_{14}F_4NO_3PS$: C, 50.12; H, 3.27; N, 3.25%. Found: C, 50.32; H, 3.65; N, 3.24%). **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 7.8 (m, 4H; *o*-Ph), 7.82 (m, 1H; *p*-py), 7.9 (dd, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 15 Hz, 4H; *m*-Ph), 7.97 (m, 2H; *p*-Ph), 8.2 (m, 2H; *m*- and *o*-py) 9.0 ppm (dm, $^4J_{PH}$ = 5 Hz, 1H; *m*-py). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -79.0 (s, 3F; O_3SCF_3), -136.8 ppm (d, $^1J_{PF}$ = 1004 Hz, 1F; PF). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 80.1 ppm (d, $^1J_{PF}$ = 1004 Hz, 1P). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 100 MHz, Me_4Si): δ 115.6 (dd, $^1J_{PC}$ = 94 Hz, $^2J_{FC}$ = 12 Hz, 2C; *i*-Ph), 130.4 (dd, $^4J_{PC}$ = 4 Hz, $^5J_{FC}$ = 1 Hz, 1C; *p*-py), 130.7 (d $^3J_{PC}$ = 14 Hz, 4C; *m*-Ph), 131.8 (d, $^2J_{PC}$ = 26 Hz, 1C; *o*-py), 134.2 (dd, $^2J_{PC}$ = 13 Hz, $^3J_{FC}$ = 2 Hz, 4C; *o*-Ph), 138.4 (dd, $^4J_{PC}$ = 3 Hz, $^5J_{FC}$ = 2 Hz, 2C; *p*-Ph), 138.7 (d, $^3J_{PC}$ = 11 Hz, 1C; *m*-py), 141.7 (dd, $^1J_{PC}$ = 148 Hz, $^2J_{FC}$ = 18 Hz, 1C; *i*-py), 152.7 ppm (dd, $^3J_{PC}$ = 24 Hz, $^4J_{FC}$ = 2 Hz, 1C; *m*-py), not observed O_3SCF_3. **HRMS (ESI-QTOF+)**: m/z 280.0894 (Calcd. for [(*o*-NC_5H_5)PPh_2O]+ : 280.0891).

Synthesis of $[(o\text{-}NC_5H_4)PFPh_2[B(C_6F_5)_4]$ (2b). A solution of freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (0.087 g, 0.089 mmol, 0.95 eq.) in C_6D_5Br (0.6 mL) was added to **1** (0.028 g, 0.093 mmol, 1.0 eq.) The solution was agitated for 2 minutes at ambient temperature. 3 mL of *n*-pentane was added resulting in the formation of an orange oil. The supernatant was decanted and the resulting oil was washed with *n*-pentane (3 x 3 mL). The supernatant was decanted and the residue was dried *in vacuo* affording a white microcrystalline solid (0.088 g, 97%, Anal. Calcd for $C_{41}H_{14}BF_{21}NP$: C, 51.23; H, 1.47; N, 1.46%. Found: C, 50.89; H, 1.54; N, 1.68%). **^{1}H NMR** (C_6D_5Br, 400 MHz, Me_4Si): δ 7.0 (m, 1H; *o/m*-py), 7.1 (m, 5H; *m*-Ph & *o/m*-py), 7.3 (m, 6H; *o*-Ph & *p*-Ph), 7.4 (m, 1H; *p*-py), 8.3 ppm (d, $^4J_{PH}$ = 5 Hz, 1H; *m*-py). **^{11}B NMR** (C_6D_5Br, 128 MHz, BF_3•OEt_2): δ -16.2 ppm (s, 1B). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -131.7 (m(br), 8F; B(*o*-$C_6F_5)_4$), -137.3 (d, $^1J_{PF}$ = 1004 Hz, 1F; PF), -161.9 (t, $^3J_{FF}$ = 21 Hz, 4F; B(*p*-$C_6F_5)_4$), -165.8 ppm (m(br), 8F; B(*m*-$C_6F_5)_4$). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 162 MHz, H_3PO_4): δ 78.2 ppm (d, $^1J_{PF}$ = 1004 Hz, 1P). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 100 MHz, Me_4Si): δ 115.9 (dd, $^1J_{PC}$ = 105 Hz, $^2J_{FC}$ = 13 Hz, 2C; *i*-Ph), 130.0 (d, $^4J_{PC}$ = 25 Hz, 1C; *p*-py), 130.3 (d, $^3J_{PC}$ = 14 Hz, 4C; *m*-Ph), 133.4 (dd, $^2J_{PC}$ = 13 Hz, $^3J_{FC}$ = 2 Hz, 4C; *o*-Ph), 134.3 (d, $^2J_{PC}$ = 20 Hz, 1C; *o*-py), 136.5 (d(br), $^1J_{FC}$ = 240 Hz, 8C; C_6F_5), 137.6 (d, $^3J_{PC}$ = 11 Hz, 1C; *m*-py), 138.1 (d, $^4J_{PC}$ = 3 Hz, 2C; *p*-Ph), 138.4 (d(br), $^1J_{FC}$ = 245 Hz, 4C; C_6F_5), 141.3 (dd, $^1J_{PC}$ = 149 Hz, $^2J_{FC}$ = 19 Hz, 1C; *i*-py), 148.6 (d(br), $^1J_{FC}$ = 243 Hz, 8C; C_6F_5), 152.3 ppm (d, $^3J_{PC}$ = 22 Hz, 1C; *m*-py), not observed *i*-B($C_6F_5)_4$. **HRMS (ESI-QTOF+)**: m/z 280.0895 (Calcd. for [(*o*-NC_5H_4)PPh_2O]+ : 280.0891).

Synthesis of $[(o\text{-}HNC_5H_4)PPh_2][O_3SCF_3]$. Trifluoromethanesulfonic acid (20.4 µL, 0.23 mmol, 1.0 eq.) was added to a solution of 2-pyridyldiphenylphosphine (0.061 g, 0.23 mmol, 1.0 eq.) in CD_2Cl_2 (0.6 mL). The reaction mixture was left at ambient temperature for 10 min resulting in a pale yellow solution. All volatiles were removed *in vacuo* and the residue was washed with *n*-pentane (3 x 5 mL), affording a pale yellow

oil. (0.090 g, 95% Yield). **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 7.5 (m, 10H; Ph), 7.9 (t, $^3J_{HH}$ = 7 Hz, 1H; *p*-py), 8.3 (t, $^3J_{HH}$ = 8 Hz, 1H; *m*-py), 8.9 (m, 1H; *m*-py), 14.7 ppm (s(br), 1H; NH), resonance for the H-substituent in *ortho*-position of the pyridyl-group was not observed. **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -78.8 ppm (s, 3F; O_3SCF_3). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 Hz, H_3PO_4): δ -5.2 ppm (s, 1P). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125 MHz, Me_4Si): δ 120.7 (q, $^1J_{FC}$ = 320 Hz, 1C; O_3SCF_3), 126.7 (d, $^4J_{PC}$ = 1 Hz, 1C; *p*-py), 130.2 (d, $^3J_{PC}$ = 8 Hz, 4C; *m*-Ph), 130.6 (d, $^1J_{PC}$ = 8 Hz, 2C; *i*-Ph), 131.8 (d, $^4J_{PC}$ = 1 Hz, 2C; *p*-Ph), 131.9 (d, $^2J_{PC}$ = 6 Hz, 1C; *o*-py), 135.1 (d, $^2J_{PC}$ = 22 Hz, 4C; *o*-Ph), 144.3 (d, $^3J_{PC}$ = 2 Hz, 1C; *m*-py), 146.0 (d, $^3J_{PC}$ = 1 Hz, 1C; *m*-py), 161.0 ppm (d, $^1J_{PC}$ = 36 Hz, 1C; *i*-py), **HRMS (DART-TOF+)** : m/z 264.0938 (Calcd. for $[(o\text{-}HNC_5H_4)PPh_2]^+$: 264.0942).

Synthesis of [(*o*-MeNC$_5$H$_4$)PF$_2$Ph$_2$][O$_3$SCF$_3$] (3). Methyl trifluoromethanesulfonate (MeO_3SCF_3, 1 mL, 8.83 mmol, 2.5 eq.) was added, dropwise, to a solution of **1** (1.05 g, 3.49 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 1.5 h at ambient temperature. The solution volume was reduced to *ca.* 1 mL and then 3 mL of *n*-pentane was added. After agitation for 2 min, a white solid settled out of solution. The supernatant was decanted and the solid was washed with *n*-pentane (3 x 5 mL). All volatiles/solvents were removed *in vacuo* to afford a white microcrystalline solid. (1.58 g, 98%, Anal. Calcd for $C_{19}H_{17}F_5NO_3PS$: C, 49.04; H, 3.68; N, 3.01%. Found: C, 48.88; H, 3.74; N, 3.04%). Single crystals of **3** suitable for X-ray diffraction were obtained from slow diffusion of pentane into a concentrated CH_2Cl_2 solution at -35 °C. **^{1}H NMR** (CD_2Cl_2, 400 MHz 25 °C, Me_4Si): δ 4.4 (s(br), 3H; N-CH_3), 7.6 (m, 4H; *o*-Ph), 7.7 (m, 2H; *p*-Ph), 7.97 (m, 1H; *m*-py), 8.0 (m, 1H; *o*-py), 8.2 (dd, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 15 Hz, 4H; *m*-Ph), 8.5 (m, 1H; *p*-py), 9.1 ppm (m, 1H; *m*-py). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ - 40.9 (d, $^1J_{PF}$ = 705 Hz, 2F; PF_2), -79.0 ppm (s, 3F; O_3SCF_3). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 Hz, H_3PO_4): δ -55.6 ppm (t, $^1J_{PF}$ = 705 Hz, 1P). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125 MHz, Me_4Si): δ 50.3 (m, 1C; N-CH_3), 121.4 (q, $^1J_{FC}$ = 321 Hz, 1C; O_3SCF_3), 129.5, (d, $^4J_{PC}$ = 2 Hz, 2C; *p*-Ph), 130.4 (dt, $^2J_{PC}$ = 17 Hz, $^3J_{FC}$ = 2 Hz, 4C; *o*-Ph), 130.9 (dt, $^1J_{PC}$ = 177 Hz, $^2J_{FC}$ = 24 Hz, 2C; *i*-Ph), 134.9 (dt, $^4J_{PC}$ = 4 Hz, $^5J_{FC}$ = 1 Hz, 1C; *p*-py), 136.6 (dt, $^3J_{PC}$ = 14 Hz, $^4J_{FC}$ = 11 Hz, 4C; *m*-Ph), 145.9 (d, $^3J_{PC}$ = 12 Hz, 1C; *m*-py), 149.0 (d, $^3J_{PC}$ = 7 Hz, 1C; *m*-py), 156.9 ppm (dt, $^1J_{PC}$ = 210 Hz, $^2J_{FC}$ = 50 Hz, 1C; *i*-py), resonance for the *ortho*-position of the pyridyl-group was not observed. **HRMS (ESI-QTOF+):** m/z 316.1065 (Calcd. for $[M]^+$: 316.1067).

Synthesis of [(*o*-MeNC$_5$H$_4$)PFPh$_2$][O$_3$SCF$_3$]$_2$ (4a). $Me_3SiO_3SCF_3$ (0.12 mL, 0.646 mmol, 1.0 eq.) was added, dropwise, to a solution of **3** (0.301 g, 0.646 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). After stirring for 24 h at ambient temperature, a white solid settled out of the solution. The solvent volume was reduced to 1 mL *in vacuo*, 5 mL *n*-pentane was added, and the solution was cooled to -50 °C. The supernatant was decanted, and the solid was washed with *n*-pentane (3 x 5 mL). After drying *in vacuo*, a white powder was isolated (0.310 g, 81%, Anal. Calcd for $C_{20}H_{17}F_7NO_6PS_2$: C, 40.34; H, 2.88; N, 2.35%. Found: C, 40.32; H, 2.72; N, 2.87%). Single crystals of **4a** suitable for X-ray diffraction were obtained from slow diffusion of pentane into a concentrated CH_2Cl_2 solution at -35 °C. **^{1}H NMR** (CD_3CN, 400 MHz, Me_4Si): δ 4.4, (d, $^4J_{PH}$ = 3 Hz, 3H; N-CH_3), 8.0 (m, 4H; *o*-Ph), 8.1 (dd, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 15 Hz, 4H; *m*-Ph), 8.3 (m, 2H; *p*-Ph), 8.4 (m, 1H; *m*-py), 8.6 (m, 1H; *o*-py), 8.8 (m, 1H; *p*-py), 9.3 ppm (m, 1H; *m*-py). **^{19}F NMR** (CD_3CN, 377 MHz, $CFCl_3$): δ -79.3 (s, 6F; O_3SCF_3), -123.9 ppm (d, $^1J_{PF}$ = 1035 Hz, 1F; PF). **^{31}P{^{1}H} NMR** (CD_3CN, 162 MHz, H_3PO_4): δ 88.8 ppm (d, $^1J_{PF}$ = 1035 Hz, 1P). **^{13}C{^{1}H} NMR** (CD_3CN, 125 MHz, Me_4Si): δ 51.2 (dd, $^3J_{PC}$ = 5 Hz, $^4J_{FC}$ = 4 Hz, 1C; N-CH_3), 113.2 (dd, $^1J_{PC}$ = 112 Hz, $^2J_{FC}$ = 13 Hz, 2C; *i*-Ph), 122.0 (d, $^1J_{PC}$ = 320 Hz, 1C; *i*-py), 132.3 (d, $^2J_{PC}$ = 16 Hz, 4C; *o*-Ph), 136.3 (d, $^4J_{PC}$ = 2 Hz, 2C; *p*-Ph), 136.6 (dd, $^3J_{PC}$ = 14 Hz, $^4J_{FC}$ = 1 Hz, 4C; *m*-Ph), 141.4 (dd, $^4J_{PC}$ = 3 Hz, $^5J_{FC}$ = 2 Hz, 1C; *p*-py), 141.5 (dd, $^2J_{PC}$ = 18 Hz, $^3J_{FC}$ = 2 Hz, 1C; *o*-py), 147.8 (d, $^3J_{PC}$ = 11 Hz, 1C; *m*-py), 155.5 ppm (d, $^3J_{PC}$ = 5 Hz, 1C; *m*-py), resonance of the O_3SCF_3-group was not observed. **HRMS (ESI-QTOF+):** m/z 294.1042 (Calcd. for $[(o\text{-}MeNC_5H_4)PPh_2O]^+$: 294.1048).

Synthesis of [(*o*-MeNC$_5$H$_4$)PFPh$_2$][B(C$_6$F$_5$)$_4$]$_2$ (4b). A solution of freshly prepared $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (1.019 g, 1.04 mmol, 1.9 eq.) in C_6D_5Br (3 mL) was added to a suspension of **3** (0.255 g, 0.55 mmol, 1.0 eq.) in toluene (5 mL). The reaction mixture was stirred at ambient temperature for 20 min, resulting in a bright yellow solution. The solution was left for 12 h at ambient temperature, after which time yellow crystals settled out of solution. The supernatant was decanted and the resulting solid was washed with *n*-pentane (3 x 3 mL) and dried *in vacuo* to afford a pale yellow powder. (0.650 g, 72%. Anal. Calcd for $C_{66}H_{17}B_2F_{41}NP$: C, 47.89; H, 1.04; N, 0.85%. Found: C, 47.45; H, 1.30; N, 0.85%). **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 4.5, (d, $^4J_{PH}$ = 3 Hz, 3H; N-CH_3), 7.8 (dd, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 15 Hz, 4H; *m*-Ph), 8.0 (dd, $^3J_{HH}$ = 15 Hz, $^4J_{HH}$ = 5 Hz, 4H; *o*-Ph), 8.27 (m, 1H; *m*-py), 8.33 (m, 2H; *p*-Ph), 8.7 (m, 1H; *o*-py), 8.9 (m, 1H; *p*-py), 9.1 ppm (m, 1H; *m*-py). **^{11}B{^{1}H} NMR** (CD_2Cl_2, 128 MHz BF_3•OEt_2): δ -16.7 ppm (s). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -124.2 (d, $^1J_{PF}$ = 1035 Hz, 1F; PF), -133.0 (m(br), 16F; B(*o*-$C_6F_5)_4$), -162.0 (t, $^3J_{FF}$ = 20 Hz, 8F; B(*p*-$C_6F_5)_4$), -167.2 ppm (m(br), 16F, B(*m*-$C_6F_5)_4$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 Hz, H_3PO_4): δ 88.9 ppm (d, $^1J_{PF}$ = 1035 Hz, 1P). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125 MHz, Me_4Si): δ 51.2 (m, 1C; N-CH_3), 109.9 (dd, $^1J_{PC}$ = 111 Hz, $^2J_{FC}$ = 13 Hz, 2C; *i*-Ph), 133.3 (d, $^2J_{PC}$ = 16 Hz, 4C; *o*-Ph), 134.6 (dd, $^3J_{PC}$ = 14 Hz, $^4J_{FC}$ = 1 Hz, 4C; *m*-Ph), 136.4 (d(br), $^1J_{FC}$ = 245 Hz, 16C, B(*o/m*-$C_6F_5)_4$), 136.7 (d, $^4J_{PC}$ = 2 Hz, 1C; *p*-py), 138.7 (d(br), $^1J_{FC}$ = 249 Hz, 8C; B(*p*-$C_6F_5)_4$), 140.4 (dd, $^2J_{PC}$ = 18 Hz, $^3J_{FC}$ = 2 Hz, 1C; *o*-py), 143.0 (d, $^4J_{PC}$ = 2 Hz, 2C; *p*-Ph), 148.5 (d(br), $^1J_{FC}$ = 240 Hz, 16C; B(*o/m*-$C_6F_5)_4$), 148.8 (d, $^3J_{PC}$ = 10 Hz, 1C; *m*-py), 154.0 ppm (d, $^3J_{PC}$ = 5 Hz, 1C; *m*-py), resonances of the *ipso*-positions of the $B(C_6F_5)_4$ and pyridyl-group were not observed. **HRMS (ESI-QTOF):** m/z 294.1062 (Calcd. for $[(o\text{-}MeNC_5H_4)PPh_2O]+$: 294.1048).

Synthesis of [(*o*-MeNC$_5$H$_4$)P(CH$_3$)Ph$_2$][O$_3$SCF$_3$]$_2$ (5a). MeO_3SCF_3 (1.6 mL, 14.2 mmol, 3.9 eq.) was added, dropwise, to a solution of 2-pyridyldiphenylphosphine (0.968 g, 3.68 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at ambient temperature for 3 days, after which time a white solid had settled out of solution. The supernatant was decanted, and a mixture of CH_2Cl_2 and *n*-pentane (1 : 4 ratio) was added. After agitation for one minute, the supernatant was decanted, and the solid was washed with *n*-pentane (3 x 5 mL). The solid

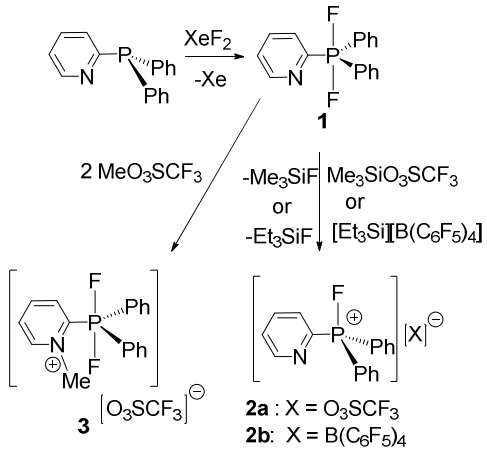
was dried *in vacuo* and a white powder was isolated. (1.76 g, 81%. Anal. Calcd for $C_{21}H_{20}F_6NO_6PS_2$: C, 42.64; H, 3.41; N, 2.37. Found: C, 42.37; H, 3.16; N, 2.25%). **^{1}H NMR** (CD_3CN, 400 MHz, Me_4Si): δ 3.4, (d, $^2J_{PH}$ = 13 Hz, 3H; P-CH_3), 4.4 (s, 3H; N-CH_3), 7.9 (m, 8H; Ph), 8.00 (m, 1H; *m*-py), 8.05 (m, 2H; *p*-Ph), 8.4 (m, 1H; *o*-py), 8.6 (m, 1H; *p*-py), 9.1 ppm (m, 1H; *m*-py). **^{19}F NMR** (CD_3CN, 377 MHz, $CFCl_3$): δ -78.9 (s, 6F; O_3SCF_3). **^{31}P{^{1}H} NMR** (CD_3CN, 162 MHz, H_3PO_4): δ 26.0 (s). **^{13}C{^{1}H} NMR** (CD_3CN, 125 MHz, Me_4Si): δ 9.6 (d, $^1J_{PC}$ = 55 Hz, 1C; P-CH_3), 51.0 (d, $^3J_{PC}$ = 4 Hz, 1C; N-CH_3), 115.7 (d, $^1J_{PC}$ = 90 Hz, 2C; *i*-Ph), 122.0 (d, $^1J_{PC}$ = 321 Hz, 1C; *i*-py), 132.2 (d, $^2J_{PC}$ = 14 Hz, 4C; *o*-Ph), 134.2 (d, $^4J_{PC}$ = 2 Hz, 1C; *p*-py), 135.0 (d, $^3J_{PC}$ = 12 Hz, 4C; *m*-Ph), 138.0 (d, $^3J_{PC}$ = 3 Hz, 2C; *p*-Ph), 139.7 (d, $^2J_{PC}$ = 14 Hz, 1C; *o*-py), 147.8 (d, $^3J_{PC}$ = 9 Hz, 1C; *m*-py), 154.6 ppm (d, $^3J_{PC}$ = 4 Hz, 1C; *m*-py), resonace of the O_3SCF_3-group was not observed. **HRMS (ESI-QTOF+)**: m/z 146.9 (Calcd. for $[M]^{2+}$: 146.6).

Synthesis of [(o-MeNC$_5$H$_4$)P(CH$_3$)Ph$_2$][B(C$_6$F$_5$)$_4$]$_2$ (5b). A solution of freshly prepared $[Et_3Si][B(C_6F_5)_4]$*2(C_7H_8) (2.20 g, 2.25 mmol, 1.9 eq.) in C_6D_5Br (0.5 mL) was added to a suspension of **5a** (698 mg, 1.18 mmol, 1.0 eq.) in toluene (2 mL). The reaction mixture was stirred at ambient temperature for 10 min, affording a bright yellow solution. 5 mL of *n*-pentane was added to induce precipitation. The supernatant was decanted, and the solid was washed with *n*-pentane (3 x 3 mL) and dried *in vacuo* to afford a pale yellow powder (1.12 g, 57%. Anal. Calcd for $C_{67}H_{20}B_2F_{40}NP$: C, 48.73; H, 1.22; N, 0.85. Found: C, 49.26; H, 1.39; N, 0.79). **^{1}H NMR** (CD_2Cl_2, 400 MHz, Me_4Si): δ 3.1 (d, $^2J_{PH}$ = 13 Hz, 3H; P-CH_3), 4.3 (s, 3H; N-CH_3), 7.7 (dd, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 15 Hz, 4H; *m*-Ph), 7.9 (dd, $^3J_{HH}$ = 15 Hz, $^4J_{HH}$ = 5 Hz, 4H; *o*-Ph), 8.1(m, 1H; *m*-py), 8.2 (m, 2H; *p*-Ph), 8.6 (m, 1H; *o*-py), 8.8 (m, 1H; *p*-py), 9.0 ppm (m, 1H; *m*-py). **^{11}B {^{1}H} NMR** (CD_2Cl_2, 128 MHz BF_3•OEt_2): δ -16.7 ppm (s). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -133.0 (m(br), 16F; B(*o*-C_6F_5)$_4$) -163.0 (t, $^3J_{FF}$ = 20 Hz, 8F; B(*p*-C_6F_5)$_4$), -167.2 ppm (m(br), 16F; B(*m*-C_6F_5)$_4$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 Hz, H_3PO_4): δ 25.3 ppm (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125 MHz, Me_4Si): δ 9.8 (d, $^1J_{PC}$ = 56 Hz, 1C; P-CH_3), 50.6 (d, $^3J_{PC}$ = 4 Hz, 1C; N-CH_3), 111.2 (d, $^1J_{PC}$ = 90 Hz, 2C; *i*-Ph), 133.0 (d, $^3J_{PC}$ = 11 Hz, 4C; *m*-Ph), 133.2 (d, $^2J_{PC}$ = 14 Hz, 4C; *o*-Ph), 134.9 (d, $^4J_{PC}$ = 2 Hz, 1C; *p*-py), 136.6 (d(br), $^1J_{FC}$ = 246 Hz, 16C, B(*o/m*-C_6F_5)$_4$), 138.8 (d(br), $^1J_{FC}$ = 246 Hz, 8C; B(*p*-C_6F_5)$_4$), 138.9 (d, $^2J_{PC}$ = 13 Hz, 1C; *o*-py), 139.8 (d, $^3J_{PC}$ = 3 Hz, 2C; *p*-Ph), 148.4 (d(br), $^1J_{FC}$ = 244 Hz, 16C; B(*o/m*-C_6F_5)$_4$), 148.8 (d, $^3J_{PC}$ = 8 Hz, 1C; *m*-py), 153.2 ppm (d, $^3J_{PC}$ = 3 Hz, 1C; *m*-py), resonances for the *ipso*-position of the B(C_6F_5)$_4$ and pyridyl-groups were not observed.

X-ray data collection, reduction, solution and refinement: Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets 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 absorption corrections were applied using SADABS. The structures were solved using XS and refined by full-matrix leas squares on F^2 using XL as implemented in the SHELXTL suite of programs. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

Results and Discussion

A CH_2Cl_2 solution of commercially available 2-pyridyldiphenylphosphine was oxidized using XeF_2 as the oxidant to the corresponding difluorophosphorane (*o*-NC_5H_4)PF_2Ph_2 (**1**) following a modified literature protocol (Scheme 1).[22, 30] Almost complete conversion was observed after stirring the reaction mixture for two hours at ambient temperature. Difluorophosphorane **1** was isolated in high yield (94%) and fully characterized by multinuclear NMR spectroscopy and elemental analysis. The ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2) shows a diagnostic triplet resonance at δ = -52.7 ppm ($^1J_{PF}$ = 670 Hz), indicative of a pentacoordinate difluorophosphorane.[28] The ^{19}F NMR spectrum (CD_2Cl_2) reveals the corresponding doublet resonance at δ = -36.4 ppm ($^1J_{PF}$ = 670 Hz). When mixed with difluorophosphorane **1**, $Me_3SiO_3SCF_3$ or $[Et_3Si][B(C_6F_5)_4]$*2(C_7H_8) facilitated fluoride abstraction, generating fluorophosphonium cations [(*o*-NC_5H_4)$PFPh_2$][X] (X = O_3SCF_3 **2a**, B(C_6F_5)$_4$ **2b**). These reactions are accompanied by the formation of Me_3SiF and Et_3SiF, respectively. The formed phosphonium ion salts **2a, b** precipitate from the reaction mixture after addition of *n*-pentane and were isolated by filtration in 92% (**2a**) and 97% (**2b**) yield, respectively (Scheme 1).

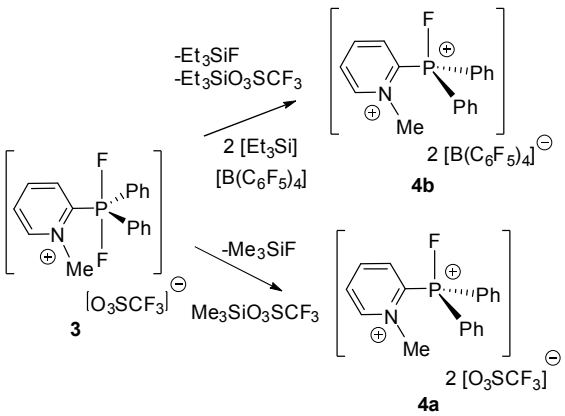


Scheme 1. Synthetic route to pyridinium-phosphonium cations **2a,b** and cationic difluorophosphorane **3**.

Compounds **2a** and **2b** were fully characterized by multinuclear NMR spectroscopy and elemental analysis. For **2a**, the ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2) exhibits a doublet resonance at δ = 80.1 ppm ($^1J_{PF}$ = 1004 Hz) with the corresponding doublet in the ^{19}F NMR spectrum (CD_2Cl_2) at δ = -136.8 ppm. The ^{19}F resonance for the O_3SCF_3 ion appears at δ = -79.0 ppm (s), which seems to support the presence of free O_3SCF_3.[35] Similarly, for **2b**, the ^{31}P{^{1}H} NMR spectrum (C_6D_5Br) displays a doublet at δ = 78.2 ppm ($^1J_{PF}$ = 1004 Hz). In the ^{19}F NMR spectrum, the resonance attributed to the phosphorus-

bound fluoride appears at δ = -137.3 ppm (d, $^1J_{PF}$ = 1004 Hz), and the resonances corresponding to the $B(C_6F_5)_4$ anion appear at δ = -133.1, -163.5 and -167.4 ppm. Compared to the triphenylfluorophosphonium analogue, $[Ph_3PF][B(C_6F_5)_4]$,[28] the $^{31}P\{^1H\}$ NMR resonance of **2b** is shifted upfield (Δδ = 16.6 ppm), and the ^{19}F NMR P-F resonance is shifted downfield (Δδ = 9.1 ppm).

The difluorophosphorane **1** was methylated with MeO_3SCF_3 affording the corresponding pyridinium-phosphorane salt $[(o\text{-}MeNC_5H_4)PF_2Ph_2][O_3SCF_3]$ **3** (Scheme 1). After stirring for 1.5 h at ambient temperature and extracting the product with *n*-pentane to remove the excess MeO_3SCF_3, the cationic difluorophosphorane **3** was isolated in high yield (98%) and fully characterized by multinuclear NMR spectroscopy, elemental analysis and X-ray crystallography. In the ^1H NMR spectrum (CD_2Cl_2), a diagnostic singlet resonance appears at δ = 4.4 ppm, which corresponds to the N-bound CH_3 protons. The $^{31}P\{^1H\}$ NMR spectrum contains a triplet resonance at δ = -55.64 ppm ($^1J_{PF}$ = 706 Hz). Compared to difluorophosphorane **1**, the coupling constant ($^1J_{PF}$) for species **3** has increased, consistent with a strong P-F interaction presumably arising from the presence of the electron withdrawing pyridinium substituent. In the ^{19}F NMR spectrum (CD_2Cl_2), the doublet resonance corresponding to the P-bound fluoride atoms is shifted upfield relative to difluorophosphorane **1** and appears at δ = -40.9 ppm ($^1J_{PF}$ = 706 Hz), and the resonance corresponding to O_3SCF_3 is observed at δ = -79.0 ppm (s). The molecular structure of cationic difluorophosphorane **3** was obtained by X-ray diffraction and shows a distorted trigonal bipyramidal geometry around phosphorus (Fig. 1). The fluoride substituents occupy the apical positions with a F-P-F angle of 171.8(4)°, which is comparable to the value reported for the related cationic difluorophosphorane $[(SIMes)PF_2Ph_2][B(C_6F_5)_4]$ (168.8(2)°).[30] While cationic pyridinium-phosphines have been employed as ligands in transition metal chemistry by Alcarazo and coworkers,[36] compound **3** is, to the best of our knowledge, the first example of a cationic, pyridinium-phophorane.



Scheme 2. Syntheses of pyridinium-fluorophosphonium dications **4a** and **4b**.

Fluoride abstraction to give the corresponding pyridinium-fluorophosphonium dications $[(o\text{-}MeNC_5H_4)PFPh_2][X]_2$ (X = O_3SCF_3 **4a**, $B(C_6F_5)_4$ **4b**) was achieved with either $Me_3SiO_3SCF_3$ or $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$ (Scheme 2). In the case of **4a**, equimolar amounts of cationic difluorophosphorane **3** and $Me_3SiO_3SCF_3$ were stirred at ambient temperature for 24 h. After removing the volatile Me_3SiF side product *in vacuo,* dication **4a** was isolated in 81% yield and fully characterized by multinuclear NMR spectroscopy, elemental analysis and X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum (CD_3CN) of dication **4a** contains a doublet resonance at δ = 88.8 ppm ($^1J_{PF}$ = 1035 Hz), which is shifted downfield relative to fluorophosphonium monocations, **2a** and **2b** (Δδ = 8.7 ppm (**2a**); 10.6 ppm (**2b**)). This downfield shift highlights the influence of the additional positive charge on the phosphorus atom. The $^{31}P\{^1H\}$ resonance of **4a** is also downfield compared to the related fluorophosphonium dication $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$ (Δδ = 10.7 ppm).[30] Moreover, the P-F fluoride resonance appears in the ^{19}F NMR spectrum (CD_3CN) at δ = -123.9 ppm as a doublet ($^1J_{PF}$ = 1035 Hz), and the O_3SCF_3 signal is observed at δ = -79.3 ppm (s), seemingly indicative of free O_3SCF_3.[35] Interestingly, the signal corresponding to the N-bound CH_3 protons appears as a doublet at δ = 4.4 ppm ($^4J_{PH}$ = 3 Hz), whereas no P-H coupling was observed in the ^1H NMR spectrum for cationic difluorophosphorane **3**. The molecular structure of dication **4a** was obtained by X-ray diffraction and shows a distorted tetrahedral geometry at the P centre (Fig. 2). Comparison of the metric parameters of dication **4a** to cationic difluorophosphorane **3** supports the notion of enhanced Lewis acidity resulting from the presence of the second positive charge, as the P-F bond distance has decreased from 1.676(8) Å (**3**) to 1.539(1) Å (**4a**) and is comparable to the distance for the related fluorophosphonium dication $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$ (1.532(2) Å).[30] Relative to species **3**, the P-C bond distances for dication **4a** have slightly decreased, whereas the N-C bond lengths for the (N-CH_3) moiety are comparable (**3**: 1.485(2) Å; **4a**: 1.479(2) Å). It is noteworthy that none of the oxygen atoms in the O_3SCF_3 anion are within the sum of the Van der Waal radii of the P centre in the solid state. In addition, even upon cooling to -40 °C NMR experiments showed no evidence of an interaction of the O_3SCF_3 anion with the P-center in solution.

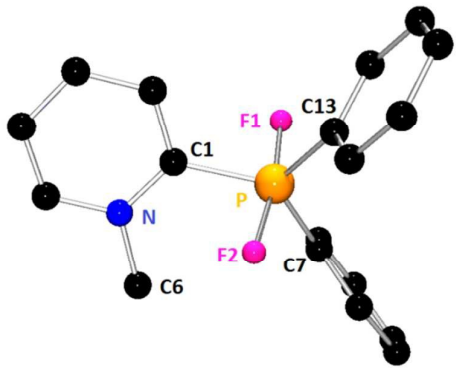


Figure 1. POV-ray depiction of the molecular structure of the cation of **3**. P: orange, F: pink, C: black, N: blue. Hydrogen atoms, O_3SCF_3 anion and CH_2Cl_2 in the asymmetric unit have

been omitted for clarity. Selected bond distances (Å) and angles (°): P-F1 1.676(8), P-F2 1.67(1), P-C1 1.854(1), P-C7 1.811(1), P-C13 1.812(1), N-C6 1.485(2); F1-P-F2 171.8(4), C7-P-C1 127(1), C13-P-C1 115(1), C7-P-C13 117(1).

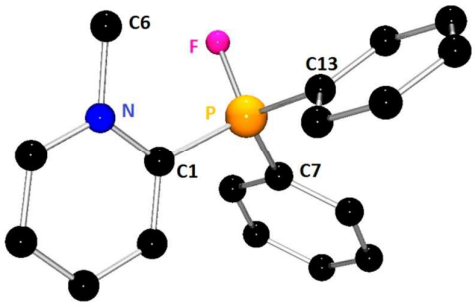
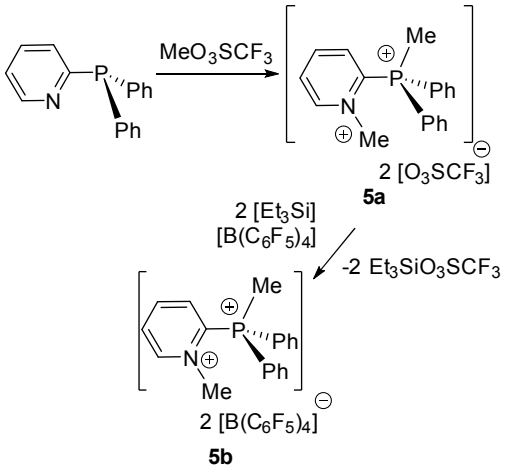


Figure 2. POV-ray depiction of molecular structure of fluorophosphonium dication **4a**. P: orange, F: pink, C: black, N: blue. Hydrogen atoms and O_3SCF_3 anion have been omitted for clarity. Selected bond distances (Å) and angles (°): P-F 1.539(1), P-C1 1.814(1), P-C7 1.759(1), P-C13 1.760(1), N-C6 1.479(2); F-P-C1 107(1), C7-P-C1 108.7(1), C13-P-C1 110 (1).

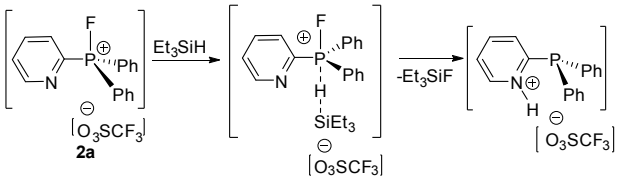


Scheme 3. Syntheses of pyridinium-methylphosphonium dications **5a** and **5b**.

The reaction of 2-pyridyldiphenylphosphine with an excess amount of MeO_3SCF_3 in CH_2Cl_2 afforded the pyridinium-methylphosphonium dication salt $[(o\text{-}MeNC_5H_4)P(CH_3)Ph_2][O_3SCF_3]_2$ **5a** after stirring at ambient temperature for 72 h. Removal of the excess MeO_3SCF_3 with *n*-pentane washings led to the isolation of dication **5a** in 81% yield (Scheme 3). The ^1H NMR spectrum (CD_3CN) contains a doublet resonance at δ = 3.4 ppm ($^1J_{PH}$ = 13 Hz) and a singlet at δ = 4.4 ppm, corresponding to the P- and N-bound CH_3 protons, respectively. The $^{31}P\{^1H\}$ NMR spectrum (CD_3CN) contains a singlet resonance at δ = 26.1 ppm, which is shifted upfield relative to the fluorophosphonium dications **4a** and **4b**, presumably due to the decreased electronegativity of the P-bound substituent and thus a less pronounced deshielding effect around phosphorus. A similar trend was observed for the dication $[(SIMes)PClPh_2][B(C_6F_5)_4]_2$, relative to its P-F counterpart.[27] In the ^{19}F NMR spectrum, the O_3SCF_3 signal appears at δ = -78.9 ppm (s), which is similar to the values observed for phosphonium cation **2a** and fluorophosphonium dication **4a**. Furthermore, when dication **5a** was mixed with two equivalents of $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$, stirred at ambient temperature for 10 minutes and washed with *n*-pentane to remove the $Et_3SiO_3SCF_3$ side product, the corresponding dicationic salt $[(o\text{-}MeNC_5H_4)P(CH_3)Ph_2][B(C_6F_5)_4]_2$ **5b** was isolated in 57% yield (Scheme 3). For dication **5b**, the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) contains a singlet at δ = 25.3 ppm, which is comparable to the reported value for **5a**. In the ^{19}F NMR spectrum (CD_2Cl_2), the O_3SCF_3 resonance disappears and new signals corresponding to the $B(C_6F_5)_4$ anion appear at δ = -133.0, -163.0 and -167.2 ppm. Similar to fluorophosphonium dications **4a** and **4b**, **5a** was insoluble in most organic solvents, while **5b** was soluble in most polar organic solvents, like CH_2Cl_2. It is noteworthy that $[(C_6F_5)_3PF][B(C_6F_5)_4]$[22] also exhibits limited solubility in CH_2Cl_2.

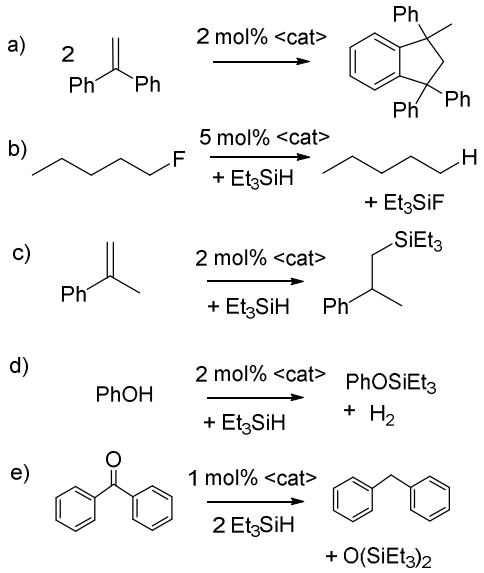
With these EPCs in hand, assement of Lewis acidity was undertaken using the Gutmann-Beckett test.[37-38] For each of **2a, 2b**, **4a, 4b, 5a** and **5b** multiple products were observed by $^{31}P\{^1H\}$ NMR spectroscopy upon addition of Et_3PO. Previous cases of fluoride-oxide exchange has been reported for the related phosphonium dication $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$.[30] Thus, this prompted evaluation of effective Lewis acidity of these pyridinium-phosphonium cations on the basis of their viability as catalysts for several transformations (*vide infra*).

Prior to catalytic tests, the stability of the new EPCs in the presence of Et_3SiH were probed. While the phosphonium dications **4a**, **4b**, **5a** and **5b** were stable in the presence of Et_3SiH, addition of equimolar amounts of cation **2a** or **2b** to solutions of Et_3SiH at room temperature resulted in the formation of a new product, as evidenced by the $^{31}P\{^1H\}$ NMR spectroscopy. After 24 h at ambient temperature, disappearance of the starting material and the formation of a new singlet at δ = -5.3 ppm was seen. For the cation **2a**, the ^{19}F NMR spectrum (CD_2Cl_2) of the crude mixture, shows a singlet resonance at δ = -79.0 ppm and a multiplet at δ = -175.9 ppm corresponding to the O_3SCF_3 anion and Et_3SiF,[40] respectively. Independent synthesis confirmed the cation to be $[(o\text{-}HNC_5H_4)PPh_2]^+$. One possible route involves the activation of the Si-H bond in Et_3SiH. This prompts fluoride abstraction by the Si-moiety affording Et_3SiF and protonation of the N atom of the pyridyl substituent giving cation $[(o\text{-}HNC_5H_4)PPh_2]^+$. Whether this proceeds via a transient hydridofluorophosphorane or a hypervalent silane species,[23, 24, 30, 31] has not been unambiguously determined (Scheme 4).



Scheme 4. Possible reaction pathway of fluorophosphonium cation **2a** with Et_3SiH.

The catalytic activity of these pyridinium-phosphonium cations was probed in a Friedel-Crafts type reaction, and in hydrodefluorination, hydrosilylation, dehydrocoupling, and hydrodeoxygenation reactions, excluding **2a** and **2b** from the reactions which use Et_3SiH (Scheme 5). For the Friedel-Crafts dimerization of 1,1-diphenylethylene (Scheme 5a), 2 mol% EPC was used. No dimerized product was observed for the monocations **2a** and **2b**, or the O_3SCF_3 dications (**4a**, **5a**), even after 10 h. On the other hand, the $B(C_6F_5)_4$ salts **4b** and **5b** rapidly catalysed the reaction, giving 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene in >99% (<30 min.) and 35% (2.5 h) conversion, respectively (determined from the ^1H NMR spectra; Table 1). Compared to the fluorophosphonium dication $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$,[30] **4b** demonstrated similar reactivity. The inactivity of the fluorophosphonium monocations highlights the influence of the second positive charge on the Lewis acidity. Although the dication **5b** was notably less active, it is promising nonetheless that substitution of the P-F fluoride for the less electron withdrawing methyl substituent did not inhibit catalysis. Moreover, the inability of the monocations **2a** and **2b** to effect the formation of any dimerized product supports the need for electron withdrawing groups to enhance Lewis acidity of monocationic phosphonium species.



Scheme 5. Phosphonium-based catalysis: a) Friedel-Crafts dimerization of 1,1-diphenylethylene. b) Hydrodefluorination of 1-fluoropentane. c) Hydrosilylation of α-methylstyrene. d) Dehydrocoupling of phenol with Et_3SiH. e) Hydrodeoxygenation of benzophenone.

Table 1. Friedel-Crafts Dimerization of 1,1-diphenylethylene

Catalyst	Reaction Time	Conversion (%)
2a	10 h	0
2b	10 h	0
4a	10 h	0
4b	<30 min	>99
5a	10 h	0
5b	2.5 h	35

In subsequent catalysis tests, hydrodefluorination of 1-fluoropentane,[22, 30, 31] hydrosilylation of α-methylstyrene, dehydrocoupling of phenol with Et_3SiH and hydrodeoxygenation of benzophenone were probed (Scheme 5b-d). In all cases, **4a** and **5a** were inactive. In the case of the hydrodefluorination of 1-fluoropentane 5 mol% of **4b** or **5b** in the present of Et_3SiH led to 92% and 13% conversion to pentane, respectively after 1 h (Table 2). Given the inherent challenge of this C-F bond-cleaving reaction,[22] it is not surprising that the less Lewis acidic dication **5b** is less active than the fluorophosphonium dication **4b**, which demonstrates comparable catalytic activity to $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$.[30-31] In the case of the hydrosilylation reaction, in the presence of 2 mol% **4b** or **5b** and Et_3SiH, heating the reaction mixture to 45 °C for 4 h gave >99 and 78% conversions to the corresponding hydrosilylated product, respectively (Table 2). Moreover, when 2 mol% of the catalysts **4b** or **5b** was added to Et_3SiH and phenol, >99 and 95% conversions to triethyl(phenoxy)silane and H_2 were obtained after heating to 50 °C for 48 h (Scheme 5d).[25, 31] Finally, in the case of the hydrodeoxygenation of benzophenone with Et_3SiH,[27] 1 mol% of the catalyst **4b** or **5b** effected >99% conversion to diphenylmethane after 2 h at ambient temperature. This is indeed significantly faster than previously reported for carbene-based phosphonium dications.[27] While no definitive evidence indicates an interaction between the P centre and the O_3SCF_3 ion, these catalytic data suggest that the more sterically encumbered, non-coordinating $B(C_6F_5)_4$ anion is required for catalysis.

Table 2. Conversions (%) for EPC-catalysed Transformations

Catalytic Reaction	4a	4b	5a	5b
Hydrodefluorination[a]	0	92	0	13
Hydrosilylation[b]	0	>99	0	78
Dehydrocoupling[c]	0	>99	0	95
Hydrodeoxygenation[d]	0	>99	0	>99

[a] 5 mol% catalyst, 1 h, 25 °C. [b] 2 mol% catalyst, 4 h, 45 °C. [c] 2 mol% catalyst, 48 h, 50 °C. [d] 1 mol% catalyst, 2 h, 25 °C.

Conclusions

Reaction of 2-pyridyldiphenylphosphine with XeF_2 and either $Me_3SiO_3SCF_3$ or $[Et_3Si][B(C_6F_5)_4]$ cleanly affords the corresponding fluorophosphonium salts. Methylation of the difluorophosphorane and subsequent fluoride abstraction gives pyridinium-fluorophosphonium dications, while methylation of the parent phosphine affords methyl-substituted phosphonium dications. These highly electrophilic phosphonium cations were used as catalysts in the Friedel-Crafts type dimerization of 1,1-diphenylethylene, hydrodefluorination of 1-fluoropentane, hydrosilylation of α-methylstyrene, dehydrocoupling of phenol with Et_3SiH and the hydrodeoxygenation of benzophenone. The fluorophosphonium monocations were unstable in the presence of Et_3SiH and were found to be weaker Lewis acids relative to their dicationic counterparts. Interestingly, no conversion in the aforementioned catalytic transformations was observed with the O_3SCF_3 salts of the dications, whereas the $B(C_6F_5)_4$ salts were active catalysts. The

fluorophosphonium dication **4b** proved to be significantly more Lewis acidic relative to the methylphosphonium dication **5b** and demonstrated comparable catalytic activity to previously reported phosphonium dications. Moreover, the facile syntheses and utility of the present pyridinium-phosphonium cations contributes to the ongoing development of more tunable and stable P-based Lewis acids. The study of phosphonium cations in metal-free catalysis and FLP chemistry is the subject of ongoing studies in our laboratory.

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