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ARTICLE TYPE

Electrophilic Phosphonium Cations (EPCs) with Perchlorinated-Aryl Substituents: Towards Air-Stable Phosphorus-based Lewis Acid Catalysts

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The series of phosphines incorporating (C_6Cl_5) substituents, $Ph_2P(C_6Cl_5)$ **1**, $PhP(C_6Cl_5)_2$ **2**, $P(C_6Cl_5)_3$ **3** and $(C_6F_5)P(C_6Cl_5)_2$ **4** were prepared. In the case of **1**, **2** and **4**, these were converted to the corresponding aryl-difluorophosphoranes **5-7** via reaction with XeF_2, whereas reaction of **3** with XeF_2 afforded only an inseparable mixture of products. The compounds **5-7** were converted to the fluorophosphonium cations **8-10**, whereas the reaction of **3** with Selectfluor afforded $(C_6Cl_5)_2POF$ and $(C_6Cl_5)_2$. The fluorophosphonium salts showed evidence of improved air stability as well as Lewis acid catalytic activity in hydrodefluorination, hydrosilylation, deoxygenation and dehydrocoupling chemistry.

Introduction

Our initial work which precipitated the concept of frustrated Lewis pairs (FLPs) is now ten years old.[1] In the intervening period, this area has seen dramatic growth.[2] More recently, applications of the concept to a broadening range of chemical systems has been reported. For example, systems that activate H_2 in the enzyme hydrogenase[3] have been described as FLP-like, and heterogeneous catalysts for CO_2 reduction[4] have been similarly described. Despite the ubiquity of Lewis acids of varying strengths within main group chemistry, it is only recently that this broader range of Lewis acids has been exploited for FLP chemistry.[5] We, and subsequently others, have reported the use of borenium cations in FLP catalysis.[6] Most recently, Krempner has described a very nice study in which strong bases are paired with weak Lewis acids to perform FLP chemistry.[7] The use of Lewis acids based on elements other than B, including Al, Si and C have also emerged and been reviewed.[5a]

Among the variety of Lewis acids under examination, we have focused attention on electrophilic phosphonium cations (EPCs). We initially exploited electron deficient substituents as an obvious approach to generate Lewis acidic phosphonium cations.[8] Subsequently, we found that the introduction of additional positively charged centers enhanced Lewis acidity (Figure 1).[9] Indeed this latter observation proved to be reminiscent of the strategy developed by Gabbai in his design of fluoride ion sensors.[10] We have used such Lewis acidic phosphonium cations in a variety of catalytic transformations. These include hydrodefluorination of fluoroalkanes, the hydrosilylation of ketones, imines, nitriles and olefins; dehydrocoupling of amines, thiols, or alcohols with silane; transfer-hydrogenation reactions; FLP hydrogenations of olefins and the activation of C-F bonds in Friedel-Crafts chemistry.[8, 9b, 9c, 11]

A general feature of these EPCs, specifically fluorophosphonium cations such as $[(C_6F_5)_3PF]^+$ is the sensitivity to moisture, which leads to catalyst degradation. While these catalysts are effective under rigorously dry conditions, it would clearly be favourable to develop analogs that exhibit similar Lewis acidic reactivity, but enhanced tolerance to moisture. It is interesting to note that similar moisture tolerance issues occur with the electrophilic boron based Lewis acid $B(C_6F_5)_3$. We noted the very creative approach developed by Ashley and coworkers[12] who investigated the family of closely related boranes that incorporated perchlorophenyl substituents. While these boranes retained comparable Lewis acidity, the presence of the perchlorophenyl substituents offered additional steric protection to the boron centre and thus provided a significant increase in air-stability. A further related study on the impact of perchlorophenyl substituents in borane has recently been authored by Wildgoose and coworkers.[13] Herein, we apply this strategy to fluorophosphonium cations and probe the impact of these substituents on air-stability and catalytic reactivity.

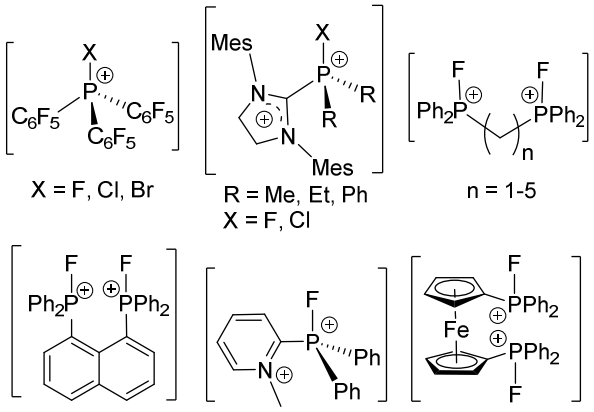

Figure 1. Examples of Electrophilic Phosphonium Cations.

Experimental Section

General Considerations All manipulations were performed in an MBraun MB Unilab glovebox or using standard Schlenk

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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, Et_2O, toluene 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, Apollo Scientific, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. $[Et_3Si][B(C_6F_5)_4]\cdot(C_7H_8)$ was prepared by the reported procedure.[14] NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian NMR system 400 MHz spectrometer, Agilent DD2-500 MHz spectrometer, or Agilent DD2-600 MHz spectrometer. ^{1}H NMR data, referenced to external Me_4Si, are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), normalized integrals. $^{13}C\{^1H\}$ NMR chemical shifts (δ) 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 $Ph_2P(C_6Cl_5)$ 1, $PhP(C_6Cl_5)_2$ 2, $P(C_6Cl_5)_3$ 3, $(C_6F_5)P(C_6Cl_5)_2$ 4: These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 100 mL Schlenk flask was charged with C_6Cl_6 (318 mg, 1.12 mmol), Et_2O (30 mL) and a magnetic stir bar, generating a white slurry. The reaction flask was cooled to –15 °C in a dry ice/acetone bath. A hexane solution of 2.5 M *n*-BuLi (0.44 mL, 1.12 mmol) was added dropwise to the stirring solution, which gradually turned the slurry to a clear, light yellow solution. The solution was then cooled to –78 °C, before a solution of Ph_2PCl (247 mg, 1.12 mmol) in Et_2O (3 mL) was added to the reaction flask in a dropwise fashion. The stirred solution was warmed to room temperature overnight. The solvent was removed *in vacuo* leaving an off-white solid. The product was dissolved in CH_2Cl_2 (6 mL) and filtered through Celite. The solvent was reduced and the solution was cooled to -35 °C to produce a white precipitate, which was collected by filtration. The white filtrate was then washed with *n*-pentane (2 x 2 mL) to yield **1** (340 mg, 70%) as a white solid. The recrystallization of **1** and **4** from vapour diffusion of *n*-pentane into a solution of the compound in dichloromethane yielded x-ray quality crystals.

1: Yield: (338 mg, 70%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.33 – 7.39 (m, 4H, *m*-C_6H_5), 7.08–7.03 (m, 6H, *o*-, *p*-C_6H_5) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 139.7 (d, $^2J_{PC}$ = 18 Hz, *o*-C_6Cl_5), 136.4 (s, *p*-C_6Cl_5), 136.0 (d, $^1J_{PC}$ = 24 Hz, *i*-C_6Cl_5), 134.3 (d, $^1J_{PC}$ = 15 Hz, *i*-C_6H_5), 133.3 (s, *m*-C_6Cl_5), 132.9 (d, $^2J_{PC}$ = 21 Hz, *o*-C_6H_5), 129.1 (s, *p*-C_6H_5), 129.0 (d, $^3J_{PC}$ = 6 Hz, *m*-C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 10.7 (s) ppm. Anal. Calcd. for $PC_{18}H_{10}Cl_5$: C: 49.76, H: 2.32. Found: C: 49.82%, H: 1.99%. HRMS (DART Ionization) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{10}Cl_5P$: 432.90410, Found: 432.90360.

2: Yield: (421 mg, 36%) as a pale yellow solid. ^{1}H NMR (500 MHz, C_6D_6): δ 7.44 (apparent triplet, $^3J_{PH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, 2H, *m*-C_6H_5), 6.98 – 7.07 (m, 4H, *o*-, *p*-C_6H_5) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 137.1 (d, $^2J_{PC}$ = 19 Hz, *o*-C_6Cl_5), 136.0 (d, $^1J_{PC}$ = 36 Hz, *i*-C_6Cl_5), 135.3 (d, $^4J_{PC}$ = 1 Hz, *p*-C_6Cl_5), 133.4 (d, $^3J_{PC}$ = 1 Hz, *m*-C_6H_5), 131.8 (d, $^1J_{PC}$ = 15 Hz, *i*-C_6H_5), 130.8 (s, *p*-C_6H_5), 128.9 (d, $^2J_{PC}$ = 9 Hz, *o*-C_6H_5), 128.5 (d, $^3J_{PC}$ = 14 Hz, *m*-C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ 15.1 (s) ppm. Anal. Calcd. for $PC_{18}H_5Cl_{10}$: C: 35.63, H: 0.83. Found: C: 35.29%, H: 0.92%. HRMS (DART Ionization) m/z: $[M+H]^+$ Calcd. for $C_{18}H_5Cl_{10}P$: 602.70924, Found: 602.70831.

3: Yield: (147 mg, 21%) as a white solid. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 19.1 (s) ppm. Anal. Calcd. for $PC_{18}Cl_{18}$: C: 27.76. Found: C: % 25.87. HRMS (EI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{18}HCl_{15}P$: 778.50553, Found: 778.50594.

4: Yield: (261 mg, 42% yield) as a white powder. ^{13}C NMR (125 MHz, C_6D_6): δ 147.9 (br d, $^1J_{FC}$ = 245 Hz, *o*-C_6F_5), 143.2 (br d, $^1J_{FC}$ = 258 Hz, *p*-C_6F_5), 137.9 (br d, $^1J_{FC}$ = 248 Hz, *m*-C_6F_5), 137.1 (d, $^2J_{PC}$ = 21 Hz, *o*-C_6Cl_5), 136.4 (s, *p*-C_6Cl_5), 133.6 (s, *m*-C_6Cl_5), 132.4 (d, $^1J_{PC}$ = 34 Hz, *i*-C_6Cl_5), 108.6 (br s, *i*-C_6F_5) ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ -129.2 to -129.6 (m, 2F, *o*-C_6F_5), -147.5 (tt, $^3J_{FF}$ = 22 Hz, $^5J_{FF}$ = 5 Hz, 1F, *p*-C_6F_5), -159.6 to -159.9 (m, 2F, *m*-C_6F_5) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ -17.8 (t, $^3J_{PF}$ = 40 Hz) ppm. Anal. Calcd. for $PC_{18}F_5Cl_{10}$: C: 31.03. Found: C: 31.19%. HRMS (DART Ionization) m/z: $[M+H]^+$ Calcd. for $C_{18}F_5Cl_{10}P$: 692.66213, Found: 692.66280.

Synthesis of $Ph_2PF_2(C_6Cl_5)$ 5, $PhPF_2(C_6Cl_5)_2$ 6, $(C_6F_5)PF_2(C_6Cl_5)_2$ 7: These compounds were prepared in a similar fashion and thus only one preparation is detailed. In a cold well, a 20 mL vial was charged with **1** (257 mg, 0.59 mmol), CH_2Cl_2 (4 mL) and a magnetic stir bar, forming a light yellow solution. To the stirring solution, a solution of XeF_2 (100 mg, 0.59 mmol) in CH_2Cl_2 (3 mL) was quickly added. The effervescent solution lightened as it was left to stir for 2 hr. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate. The precipitate was collected by filtration and washed with *n*-pentane (2 x 2 mL) yielding a white solid. The CH_2Cl_2 was removed *in vacuo* yielding **5** (230 mg, 83%) as a yellow solid. Recrystallization of **5** from vapour diffusion of *n*-pentane into a solution of the compound in dichloromethane yielded x-ray quality crystals.

5: Yield: (321 mg, 98 %). ^{1}H NMR (500 MHz, C_6D_6): δ 8.17 – 8.10 (m, 4H, *m*-C_6H_5), 7.08 – 7.01 (m, 6H, *o*-, *p*-C_6H_5) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 140.1 (dt, $^1J_{PC}$ = 217 Hz, $^2J_{FC}$ = 42 Hz, *i*-C_6Cl_5), 137.5 (dt, $^1J_{PC}$ = 181 Hz, $^2J_{FC}$ = 24 Hz, *i*-C_6H_5), 135.0 (dt, $^2J_{PC}$ = 13 Hz, $^3J_{FC}$ = 10 Hz, *o*-C_6H_5), 134.5 (dt, $^2J_{PC}$ = 3 Hz, $^3J_{FC}$ = 2 Hz, *o*-C_6Cl_5), 133.5 (d, $^4J_{PC}$ = 17 Hz, *p*-C_6Cl_5), 132.6 (dt, $^3J_{PC}$ = 3 Hz, $^4J_{FC}$ = 3 Hz, *m*-C_6Cl_5), 131.7 (dt, $^4J_{PC}$ = 4 Hz, $^5J_{FC}$ = 1 Hz, *p*-C_6H_5), 128.6 (dt, $^3J_{PC}$ = 13 Hz, $^4J_{PC}$ = 10 Hz, *m*-C_6H_5) ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ -41.8 (d, $^1J_{PF}$ = 716 Hz, PF_2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ -50.7 (t, $^1J_{PF}$ = 715 Hz) ppm. Anal. Calcd. for $PC_{18}H_{10}Cl_5F_2$: C: 45.76, H: 2.13. Found: C: 45.24%, H: 2.00%.

6: Yield: (123 mg, 76%) as an orange solid. ^{1}H NMR (500 MHz, C_6D_6): δ 8.11 – 8.04 (m, 2H, *m*-C_6H_5), 7.16 – 7.08 (m, 3H, *o*-, *p*-C_6H_5) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 137.7 (dt, $^1J_{PC}$ = 210 Hz, $^2J_{FC}$ = 32 Hz, *i*-C_6Cl_5), 136.7–136.6 (m, *o*-C_6Cl_5), 135.8 (dt, $^2J_{PC}$ = 14 Hz, $^3J_{FC}$ = 10 Hz, *o*-C_6H_5), 135.4 (dt, $^1J_{PC}$ = 187 Hz, $^2J_{FC}$ = 23 Hz, *i*-C_6H_5), 134.3 (d, $^4J_{PC}$ = 18 Hz, *p*-C_6Cl_5), 134.0 – 133.8 (m, *m*-C_6Cl_5), 133.0 (br d, $^4J_{PC}$ = 4 Hz, *p*-C_6H_5), 129.3 (dm, $^3J_{PC}$ = 18 Hz, *m*-C_6H_5) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ -28.9 (d, $^1J_{PF}$ = 747 Hz, PF_2) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ -44.9 (t, $^1J_{PF}$ = 747 Hz) ppm. Anal. Calcd. for $PC_{18}H_5Cl_{10}F_2$: C: 33.53, H: 0.78. Found: C: 34.16%, H: 0.86%.

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7: white solid (192 mg, 80% yield). ^{13}C NMR (125 MHz, C_6D_5Br): δ 146.5 (br d, $^1J_{FC}$ = 254 Hz, *o*-C_6F_5), 143.9 (br d, $^1J_{FC}$ = 259 Hz, *p*-C_6F_5), 137.9 (br dm, $^1J_{FC}$ = 255 Hz, *m*-C_6F_5), 136.91 (d, $^4J_{PC}$ = 4 Hz, *p*-C_6Cl_5), 135.0 (br d, $^2J_{PC}$ = 264 Hz, *o*-C_6Cl_5), 134.5 (dt, $^1J_{PC}$ = 217 Hz, $^2J_{FC}$ = 29 Hz, *i*-C_6Cl_5), 134.5 (dm, $^3J_{PC}$ = 18 Hz, *m*-C_6Cl_5), 113.0 (br dm, $^1J_{PC}$ = 201 Hz, *i*-C_6F_5) ppm. ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ -10.9 (dm, $^1J_{PF}$ = 756 Hz, PF_2), -129.2 to -129.6 (m, 2F, *o*-C_6F_5), -145.9 (t, $^3J_{FF}$ = 22 Hz, 1F, *p*-C_6F_5), -158.5 to -158.7 (m, 2F, *m*-C_6F_5) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_5Br): δ -41.2 (t, $^1J_{PF}$ = 757 Hz) ppm. Anal. Calcd. for $PC_{18}Cl_{10}F_7$: C: 29.43. Found: C: 28.52%.

Synthesis of [$Ph_2PF(C_6Cl_5)$][$B(C_6F_5)_4$] 8, [$PhPF(C_6Cl_5)_2$][$B(C_6F_5)_4$] 9, [$(C_6F_5)PF(C_6Cl_5)_2$][$B(C_6F_5)_4$] 10: These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 20 mL vial was charged with [Et_3Si][$B(C_6F_5)_4$] (682 mg, 0.77 mmol), toluene (10 mL) and a magnetic stir bar, forming a white slurry. To the stirring slurry, a solution of **5** (382 mg, 0.81 mmol) in toluene (5 mL) was added. The solution was allowed to stir overnight at room temperature, resulting in a dark orange solution. When the reaction mixture was allowed to settle, a dark orange oil collected at the bottom of the vial leaving a clear supernatant. After decanting the toluene from the oil, additional toluene (2 x 3 mL) containing a few drops of CH_2Cl_2 was added to wash the oil. After decanting the toluene washes, the oil was washed with *n*-pentane (3 x 4 mL) before removing the solid *in vacuo* resulting in **8** (697 mg, 80 %) as a fluffy white solid

8: Yield: (697 mg, 80 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 – 8.04 (m, 1H, *p*-C_6H_5), 7.88 – 7.78 (m, 4H, *o*-, *m*-C_6H_5) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3 (br d, $^1J_{FC}$ = 241 Hz, B(*o*-C_6F_5)), 145.3 (d, $^4J_{PC}$ = 3 Hz, P(*p*-C_6Cl_5)), 139.5 (dd, $^4J_{PC}$ = 2 Hz, $^5J_{FC}$ = 2 Hz, P(*p*-C_6H_5)), 138.3 (br d, $^1J_{FC}$ = 238 Hz, B(*p*-C_6F_5)), 137.7 (dd, $^2J_{PC}$ = 6 Hz, $^3J_{FC}$ = 1 Hz, P(*o*-C_6Cl_5)), 137.1 (d, $^3J_{PC}$ = 12 Hz, P(*m*-C_6Cl_5)), 136.3 (br d, $^1J_{FC}$ = 235 Hz, B(*m*-C_6F_5)), 133.5 (dd, $^2J_{PC}$ = 14 Hz, $^3J_{FC}$ = 1 Hz, P(*o*-C_6H_5)), 131.5 (d, $^3J_{PC}$ = 15 Hz, P(*m*-C_6H_5)), 123.8 (br s, B(*i*-C_6F_5)), 116.1 (dd, $^1J_{PC}$ = 112 Hz, $^2J_{FC}$ = 14 Hz, P(*i*-C_6H_5)), 115.9 (dd, $^1J_{PC}$ = 121 Hz, $^2J_{FC}$ = 11 Hz, P(*i*-C_6Cl_5)) ppm. ^{11}B NMR (128 MHz, C_6D_5Br): -16.5 (s) ppm. ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ -116.0 (d, $^1J_{PF}$ = 1010 Hz, PF_2), -132.0 (m/br, 8F, B(*o*-C_6F_5)), -162.3 (t, $^3J_{FF}$ = 21 Hz, 4F, B(*p*-C_6F_5)), -166.2 (m/br, 8F, B(*m*-C_6F_5)) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_5Br): δ 89.5 (d, $^1J_{PF}$ = 1009 Hz) ppm. Anal. Calcd. for $PC_{42}H_{10}Cl_5F_{21}B$: C: 44.54, H: 0.89. Found: C: 45.15%, H: 0.94%. HRMS (DART Ionization) m/z: $[M]^+$ Calcd. for $C_{18}H_{10}Cl_5PF$: 450.89468, Found 450.89445.

9: Yield: (320 mg, 90 %) as an off white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 – 8.08 (m, 1H, *p*-C_6H_5), 7.98 – 7.76 (m, 4H, *o*-, *m*-C_6H_5) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3 (br d, $^1J_{FC}$ = 240 Hz, B(*o*-C_6F_5)), 145.5 (dm, $^4J_{PC}$ = 3 Hz, P(*p*-C_6Cl_5)), 140.5 (m, P(*p*-C_6H_5)), 138.3 (br d, $^1J_{FC}$ = 239 Hz, B(*p*-C_6F_5)), 137.2 (d, $^3J_{PC}$ = 13 Hz, P(*m*-C_6Cl_5)), 136.7 (d, $^2J_{PC}$ = 6 Hz, P(*o*-C_6Cl_5)), 136.3 (br d, $^1J_{FC}$ = 239 Hz, B(*m*-C_6F_5)), 133.1 (d, $^2J_{PC}$ = 14 Hz, P(*o*-C_6H_5)), 132.2 (d, $^3J_{PC}$ = 17 Hz, P(*m*-C_6H_5)), 124.1 (br s, B(*i*-C_6F_5)), 118.3 (dd, $^1J_{PC}$ = 131 Hz, $^2J_{FC}$ = 11 Hz, P(*i*-C_6H_5)), 116.0 (dd, $^1J_{PC}$ = 114 Hz, $^2J_{FC}$ = 13 Hz, P(*i*-C_6Cl_5)) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): -16.7 (s) ppm. ^{19}F{^{1}H} NMR (470 MHz, C_6H_5Br): δ -125.6 (d, $^1J_{PF}$ = 1009 Hz, PF_2), -138.9 (m/br, 8F, B(*o*-C_6F_5)), -169.2 (m/br, 4F, B(*p*-C_6F_5)), -173.1 (m/br, 8F, B(*m*-C_6F_5)) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 84.4 (d, $^1J_{PF}$ = 1009 Hz) ppm. Anal. Calcd. for $PC_{42}H_5Cl_{10}F_{21}B$: C: 38.66. H: 0.39. Found: C: 42.17%, H: 0.87%. HRMS (DART Ionization) m/z: $[M]^+$ Calcd. for $C_{18}H_5Cl_{10}PF$: 620.69982, Found 620.69896.

10: (229 mg, 74% yield) as an off-white solid. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6 (br d, $^1J_{FC}$ = 277 Hz, P(*o*-C_6F_5)), 148.3 (br d, $^1J_{FC}$ = 241 Hz, B(*o*-C_6F_5)), 147.1 (d, $^4J_{PC}$ = 3 Hz, P(*p*-C_6Cl_5)), 139.4 (br d, $^1J_{FC}$ = 269 Hz, P(*p*-C_6F_5)), 138.3 (br d, $^1J_{FC}$ = 241 Hz, B(*p*-C_6F_5)), 137.7 (d, $^3J_{PC}$ = 15 Hz, P(*m*-C_6Cl_5)), 136.7 (d, $^2J_{PC}$ = 6 Hz, P(*o*-C_6Cl_5)), 136.4 (br d, $^1J_{FC}$ = 235 Hz, B(*m*-C_6F_5)), 134.9 (br d, $^1J_{FC}$ = 260 Hz, P(*m*-C_6F_5)), 124.0 (br s, B(*i*-C_6F_5)), 116.3 (dd, $^1J_{PC}$ = 144 Hz, $^2J_{FC}$ = 10 Hz, P(*i*-C_6Cl_5)), 95.8 (br d, $^1J_{PC}$ = 137 Hz, P(*i*-C_6F_5)) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): -16.6 (s) ppm. ^{19}F{^{1}H} NMR (470 MHz, C_6H_5Br): δ -117.0 (dd, $^1J_{PF}$ = 1030 Hz, $^3J_{FF}$ = 26 Hz, 1F, PF), -123.4 (br s, P(*o*-C_6F_5)), -124.7 (m, 1F, P(*p*-C_6F_5)), -126.8 (m, 1F, P(*o*-C_6F_5)), -132.2 (m/br, 8F, B(*o*-C_6F_5)), -150.4 (br s, P(*m*-C_6F_5)), -162.4 (t, $^3J_{FF}$ = 21 Hz, 4F, B(*p*-C_6F_5)), -166.4 (m/br, 8F, B(*p*-C_6F_5)) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_5Br): δ 71.0 (d, $^1J_{PF}$ = 1030 Hz) ppm. Anal. Calcd. for $PC_{42}Cl_{10}F_{26}B$: C: 36.17. Found: C: 37.21% HRMS (DART Ionization) *m/z*: $[M]^+$ Calcd. for $C_{18}F_6Cl_{10}P$: 710.65271, Found 710.65339.

Synthesis of $FPO(C_6Cl_5)_2$ 11: A 20 mL vial was charged with **4** (78 mg, 0.10 mmol), MeCN (3 mL) and a magnetic stir bar. A solution of 1-chloromethyl-4-fluoro-1,4-diazonia-bicyclo-[2.2.2]octane bis(tetrafluoroborate) in MeCN was added. The solution briefly turns dark purple as a black precipitate is formed before returning to a pale green colour. The supernatant is decanted and the solvent is removed *in vacuo* yielding **11** (24 mg, 43 %) as a yellow solid. ^{19}F NMR (376 MHz, CH_2Cl_2): δ –54.3 (d, $^1J_{PF}$ = 1065 Hz). ^{31}P{^{1}H} NMR (162 MHz, CH_2Cl_2): δ 21.2 (d, $^1J_{PF}$ = 1065 Hz). HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{12}Cl_{10}FPO$: 564.65753, Found: 564.65713.

X-ray Diffraction Studies: Crystals were coated in paratone oil and mounted in a cryo-loop. Data were collected on a Bruker APEX2 X-ray diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryo-stream cooler for both, initial indexing and full data collection. Data were collected using Bruker APEX-2 software and processed using SHELX and Olex2 an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved by direct methods within the SHELXTL package[15] and refined with Olex2.[16]

Results and Discussion

A series of mixed phenyl/pentachlorophenyl substituted phosphines were synthesized via a modified literature procedure[17]. Lithiation of C_6Cl_6 in Et_2O followed by the addition of Ph_2PCl, $PhPCl_2$, or PBr_3 yields $Ph_2P(C_6Cl_5)$ **1**, $PhP(C_6Cl_5)_2$ **2**, or $P(C_6Cl_5)_3$ **3**, respectively, in moderate yields (Scheme 1). The ^{1}H NMR data for **1** and **2** shows the expected phenyl proton resonances while the ^{31}P NMR data for **1**, **2** and **3** show singlets at 10.7, 15.1 and 19.1 ppm respectively. This trend of downfield shifting due to increasing perchlorophenyl substitution stands in contrast to the analogous series of pentafluorophenyl-substituted phosphines. The present contrasting observation appears to result from the greater steric bulk of the *ortho*-chlorine atoms in comparison to fluorine substituents, thus increasing the distortion of the phosphorus coordination sphere towards planarity at phosphorus. Mass spectral and elemental analysis data for compounds **1-3** were also consistent with formulations. In addition, a solid-state structure of **1** was obtained by X-ray diffraction (Figure 2).

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In addition, $Br_2P(C_6F_5)$ was synthesized by literature procedure[18] and reacted with two equivalents of LiC_6Cl_5 in Et_2O at -78 °C. Following workup, was isolated as a white powder (Scheme 1). The ^{19}F NMR data for **4** displayed 3 resonances, consistent with the presence of a pentafluorophenyl group, while the ^{31}P NMR spectrum exhibited a triplet at -17.8 ppm. These data are consistent with the formulation of **4** as $(C_6F_5)P(C_6Cl_5)_2$ and this confirmed by a solid state structure obtained by single crystal X-ray diffraction studies (Figure 3).

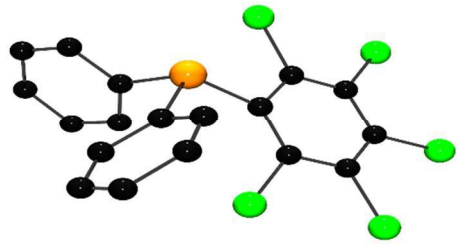


Figure 2. POV-ray depiction of **1**; C: black, P: orange, Cl: green, H-atoms were omitted for clarity.

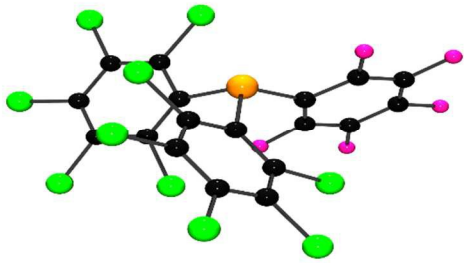
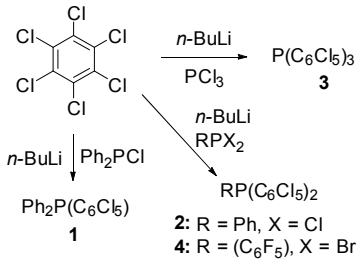


Figure 3. POV-ray depiction of **4**; C: black, P: orange, Cl: green, F: pink.



Scheme 1. Synthesis of **1**-**4**.

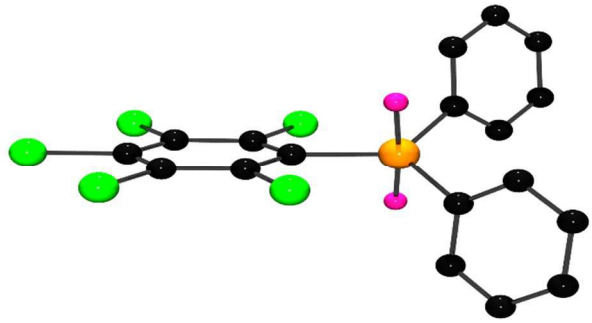


Figure 4. POV-ray depiction of **5**; C: black, P: orange, Cl: green, F: pink, hydrogen atoms have been omitted for clarity.

Treatment of **1** with an equimolar amount of XeF_2 in CH_2Cl_2 cleanly generates **5** as a white powder upon workup, in excellent yield. The ^{19}F NMR data for **5** displayed a doublet at -41.8 ppm with a $^1J_{PF}$ coupling constant of 716 Hz. Correspondingly, the ^{31}P NMR spectrum of **5** was seen as a triplet at -50.7 ppm, consistent with the presence of two chemically equivalent fluorine atoms on phosphorous. Collectively these data inferred the formulation of **5** as the difluorophosphorane species $Ph_2PF_2(C_6Cl_5)$. Additionally, the solid-state structure of **5** was confirmed by X-ray crystallography (Figure 4). In a similar fashion treatment of **2** with XeF_2 yields the corresponding species $PhPF_2(C_6Cl_5)_2$ **6** as a white powder in moderate yield. The ^{19}F and ^{31}P NMR data for **6** are analogous to that of **5** (Scheme 2).

Treatment of **3** with XeF_2 yielded an inseparable mixture of two products that exhibited ^{31}P NMR signals. A minor product displayed NMR features consistent with those seen for **5** and **6**, suggesting the formation of the difluorophosphorane, $PF_2(C_6Cl_5)_3$. However, the major product displayed two resonances in the ^{19}F NMR spectrum: a doublet of doublets and a doublet of triplets in a 2:1 ratio, while the corresponding ^{31}P NMR data showed a doublet of triplets. These data are consistent with the formation of $PF_3(C_6Cl_5)_2$. The inability to isolate $PF_2(C_6Cl_5)_3$ is attributed to the steric congestion prompting degradation. Indeed, despite multiple trials with varied conditions all efforts to separate the two products were unsuccessful. The formation of the major product suggests the loss of a (C_6Cl_5) ring from the starting phosphine. This view was supported by the isolation of crystals suitable for X-ray diffraction from the reaction mixture. These crystals were subsequently confirmed to be decachlorobiphenyl, $C_{12}Cl_{10}$ (Figure 5). The presence of this by-product suggests that the oxidation of **3** proceeds via a radical mechanism at least to some degree and that loss of the radical (C_6Cl_5) leads to radical coupling.

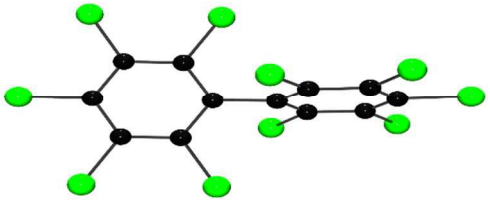


Figure 5. POV-ray depiction of decachlorobiphenyl; C: black Cl: green.

In contrast, reaction of **4** with XeF_2 in CH_2Cl_2 generates a light yellow solution. Upon reducing the solvent volume and cooling compound **7** could be obtained as a white powder in excellent yield. The ^{19}F NMR spectrum of **7** displays a distinctive doublet in addition to (C_6F_5) resonances. A triplet is observed by ^{31}P NMR at -41.2 ppm and these data lead to the formulation of **7** as the difluorophosphorane $(C_6F_5)PF_2(C_6Cl_5)_2$ (Scheme 2).

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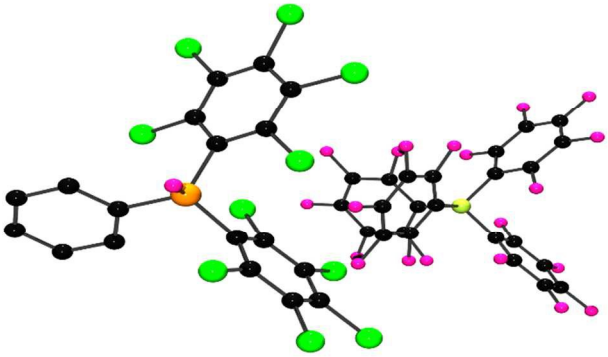
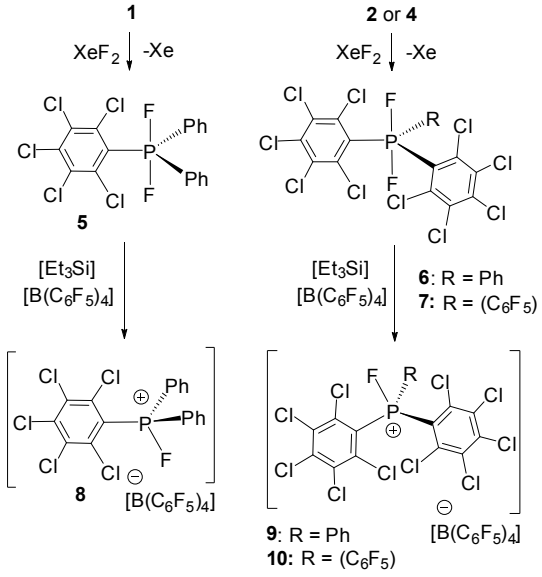


Figure 6. POV-ray depiction of **9**; C: black, P: orange, Cl: green, B: yellow-green, F: pink, hydrogen atoms have been omitted for clarity.

With the difluorophosphoranes **5-7** in hand, the compound **5** was added to a stirring slurry of $[Et_3Si][B(C_6F_5)_4]$ in toluene, affording a dark orange solution over the course of 1 h. A dark amber coloured oil collected at the bottom of the flask, leaving a clear supernatant. Separation of the oil by decantation of the supernatant and subsequent washing of the oil with toluene and pentane afforded **8** as a powdery white solid in excellent yield. The ^{19}F NMR data for **8** display a doublet with P-F coupling of 1009 Hz and a set of three resonances consistent with the presence of the perfluorophenyl groups of the counteranion $[B(C_6F_5)_4]^-$. The corresponding ^{31}P NMR spectrum exhibits a doublet centred at 89.5 ppm. Collectively these data lead to the formulation of **8** as $[Ph_2PF(C_6Cl_5)][B(C_6F_5)_4]$ (Scheme 2).

Similarly, the reaction of $[Et_3Si][B(C_6F_5)_4]$ with **6** yields **9** as an off-white powder with analogous NMR parameters leading to the formulation of **9** as $[PhPF(C_6Cl_5)_2][B(C_6F_5)_4]$. In this case the corresponding formulation was confirmed via X-ray crystallography (Figure 6).

Subsequent treatment of **7** with one equivalent of $[SiEt_3][B(C_6F_5)_4]$ in toluene yielded a dark amber oily suspension. After workup, **10** was obtained as an off-white solid. The ^{19}F NMR spectrum of **10** displays three resonances attributable to a $B(C_6F_5)_4^-$ anion, a doublet consistent with a P-F moiety and four resonances attributed to a pentafluorophenyl substituent. Variable temperature ^{19}F NMR studies reveal coalescence of the *ortho*-fluorine signals and sharpening of the *meta*-fluorine peaks at higher temperatures. The inequivalence of the fluorine atoms of the (C_6F_5) ring infer hindered rotation about the P-C bond, presumably a result of the enforced pseudo-tetrahedral geometry about P in the cation and the steric demands of the (C_6Cl_5) substituents. The ^{31}P NMR spectrum of **10** displays a doublet, with the expected coupling to fluorine. These data are consistent with the identity of **10** as $[(C_6F_5)PF(C_6Cl_5)_2][B(C_6F_5)_4]$ (Scheme 2).



Scheme 2. Synthesis of **5**-**10**.

As the difluorophosphorane $PF_2(C_6Cl_5)_3$ was not obtained, an alternate synthetic protocol targeting the fluorophosphonium cation was undertaken. The perchlorinated phosphine **3** was reacted with Selectfluor in a solution of MeCN. This leads to the generation and subsequent isolation of a species **11** as a yellow solid. NMR data revealed a single doublet in both ^{19}F and ^{31}P spectra, with the expected P-F coupling of 1066 Hz. No peak was found in the ^{19}F NMR spectrum attributable to a counteranion. Mass spectral data for CH_2Cl_2 extract showed a $[M]^+$ ion of 564.65713 m/z consistent with the formulation of **11** as $FOP(C_6Cl_5)_2$. In addition, crystals of decachlorobiphenyl were also isolated from this reaction suggesting complex redox chemistry although the source of oxygen in the phosphineoxide remains unknown.

With the fluorophosphonium cations **8-10** in hand, the stability of these compounds to atmospheric mositure was qualitatively evaluated. Samples of each species were prepared in bromobenzene, exposed to air for successively longer intervals and the solution was monitored by ^{19}F and ^{31}P NMR spectroscopies. Compound **8** proved to be somewhat robust to air, showing the onset of oxidation after 21 h. In contrast, the solution of compound **9** was found to be significantly more robust exhibiting no evidence of degradation after 48 h of exposure to air. Indeed, solid samples of **9** could be manipulated in the air and solutions prepared using unpurified reagent-grade bromobenzene as purchased with no observed evidence of degradation of **9**. A bromobenzene solution of **10** was less stable than **9** showing minor formation of HC_6F_5 by ^{19}F NMR spectroscopy after 4 h. As a point of comparison, the analogous treatment of the perfluorinated fluorophosphonium cation salt $[PF(C_6F_5)_3][B(C_6F_5)_4]$ led to evidence of degradation after 1 minute of exposure to air, with full decomposition occurring within 1 h. These observations suggest the presence of the perchlorophenyl substituents does enhance the stability of related fluorophosphonium cations, presumably a result of the steric protection of the P-F fragment. This view is consistent with data reported by Ashley[12] who used perchlorophenyl substituents to generate air-stable boranes.

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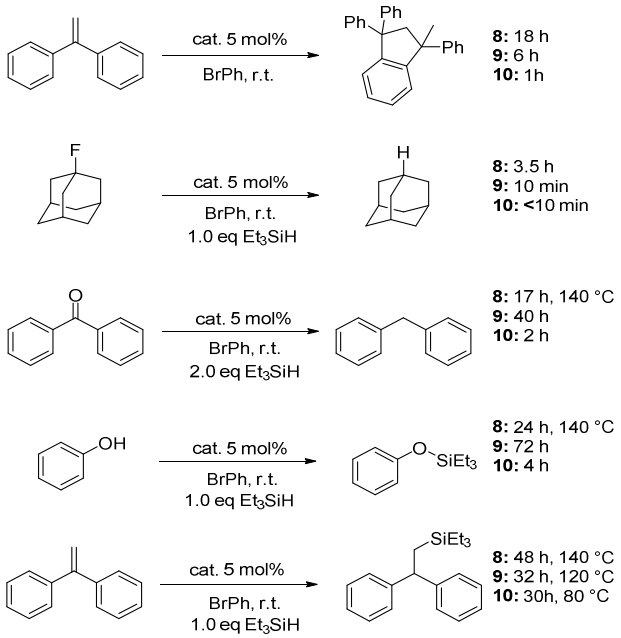

Scheme 3. Lewis acid catalyzed reactions.

The utility of **8**-**10** as Lewis acid catalysts was also evaluated in a series of reactions that are readily mediated by $[PF(C_6F_5)_3][B(C_6F_5)_4]$ (Scheme 4). Using 5 mol% of compound **8** as a catalyst, the dimerization of 1,1-diphenylethylene was complete in 18 h at room temperature. Similarly, 5 mol% of **8** catalyzed the complete hydrodefluorination of 1-fluoroadamantane in the presence of Et_3SiH in 3.5 h. In addition, the dehydrocoupling of phenol and Et_3SiH was completed in 24 h at 140 °C affording $PhOSiEt_3$. As well, 5 mol% of **8** mediated the deoxygenation of benzophenone to give complete conversion to Ph_2CH_2 in 17 h at 140 °C. Additionally, 5 mol% of **8** was able to catalyze the hydrosilylation of α-methylstyrene with Et_3SiH in 48 h at 140 °C.

Compound **9** was found to be a more active catalyst than **8** in analogous testing, again using 5 mol% catalyst loadings. The dimerization of 1,1-diphenylethylene reached completion within 6 h. The hydrodefluorination of 1-fluoroadamantane in the presence of Et_3SiH was complete in 10 minutes, benzophenone was fully deoxygenated in 40 h, while the dehydrocoupling of phenol and Et_3SiH was complete in 72 h at room temperature. Compound **9** also catalyzed the hydrosilylation of α-methylstyrene within 32 h at 120 °C.

Compound **10** was also screened as a catalyst under similar conditions using 5 mol% catalyst loadings. As expected, the presence of the (C_6F_5) substituent in **10** enhances its activity in Lewis acid catalysis. Indeed, it proved to be much more reactive than **8** and **9**. Using **10**, the cyclodimerization of 1,1-diphenylethylene was complete in 1 h while the hydrodefluorination of 1-fluoroadamantane in the presence of Et_3SiH and 5 mol% **10** is complete in under 10 minutes. The deoxygenation of benzophenone is complete in 2 h while the dehydrocoupling of Et_3SiH and phenol is complete in 4 h. The enhanced Lewis acidity of **10** was further demonstrated by its action as a much more competent catalyst for the hydrosilylation of α-methylstyrene with Et_3SiH, completing the reaction in 30 h at 80 °C.

Conclusions

This report has provided synthetic protocols for the syntheses of several phosphines that incorporate perchlorinated phenyl substituents, and the conversion of these species to the corresponding difluorophosphoranes and fluorophosphonium cations. These compounds exhibit improved stability in the air and prove to be effective catalysts in a series of prototypical reactions of fluorophosphonium cations. This stability is attributed to the steric protection associated with the perchlorinated aryl substituents. This strategy provides some improvement in air-stability of the fluorophosphonium cation, suggesting that steric protection of the P-F bond is a viable approach. Nonetheless, the steric protection comes at the cost of lower reactivity. We are continuing to explore other strategies targeting the syntheses of active, air-stable phosphonium Lewis acid catalysts. The results of these endeavours will be reported in due course.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data have been deposited in CCDC#: 1471988-1471992. Experimental details and spectral data have been deposited. See DOI: 10.1039/b000000x/

‡These authors have contributed equally to this publication.

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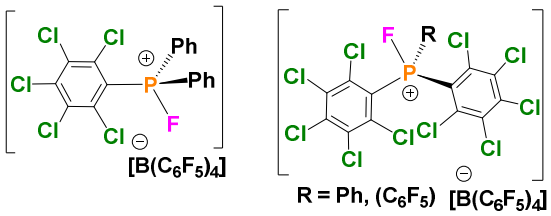
TOC Graphic



Lewis acid Catalysts