Supporting Information

Pendant Phosphorus Lewis Acid:
Route to A Palladium-Benzoyl Derived Phorsphorane

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Materials and Methods

All manipulations were performed in a Vacuum Atmospheres glovebox or using standard Schlenk techniques under an inert atmosphere of anhydrous N\textsubscript{2}. Dry, oxygen-free solvents (CH\textsubscript{2}Cl\textsubscript{2}, n-pentane, toluene) were prepared using an Innovative Technologies solvent purification system. Deuterated solvents dichloromethane (CD\textsubscript{2}Cl\textsubscript{2}) and benzene (C\textsubscript{6}D\textsubscript{6}) were dried and stored over 3 Å molecular sieves prior to use. Commercial reagents were used as received without further purification. Combustion analyses were performed at the University of Toronto by employing a PerkinElmer CHN analyzer. IR spectra were recorded on a Bruker ALPHA spectrometer equipped with an ATR sampling unit. All glassware was oven-dried at temperatures above 180°C and cooled under vacuum prior to use. NMR spectra were measured on a Bruker AVANCE 400 MHz, Agilent DD2 600 MHz, or Agilent DD2 500 MHz spectrometer at 25°C. Assignments of hydrogen and carbon resonances in the \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectra were performed via indirect deduction from the cross-peaks in 2D correlation experiments (HMBC, HSQC, HH-COSY) when necessary. \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} data are referenced to external Me\textsubscript{4}Si. \textsuperscript{31}P\{\textsuperscript{1}H\} and \textsuperscript{19}F spectra are externally referenced to 85% H\textsubscript{3}PO\textsubscript{4} and CFCl\textsubscript{3} samples, respectively. Chemical shifts (\(\delta\)) are reported in ppm, multiplicity is reported as follows \((s = \text{singlet}, d = \text{doublet}, t = \text{triplet}, m = \text{multiplet})\) and coupling constants \((J)\) are reported in Hz.
Synthesis and Characterization

1.1 Preparation and Characterization of (2-BrC₆H₄)PF₂Ph₂ (2)

A solution of XeF₂ (0.373 g, 2.20 mmol, 1.0 eqv.) in CH₂Cl₂ (5 ml) was added dropwise to a solution of (2-bromophenyl)diphenylphosphine (0.753 g, 2.21 mmol, 1.0 eqv.) in CH₂Cl₂ (10 ml) at -35 °C. The resulting clear, colourless reaction mixture was stirred for 1 h and gradually warmed to ambient temperature. The solvent was removed in vacuo and the residue was washed with n-pentane (2 x 10 ml). After removing the supernatant, all volatiles were removed in vacuo to yield compound 2 as a colorless, crystalline solid (0.806 g, 96%, Anal. Calcd for C₁₈H₁₄F₂PBr: C, 57.02; H, 3.72%. Found: C, 57.05; H, 3.72%).

¹H NMR (700 MHz, 298 K, C₆D₆): δ¹H 8.24 (m, 4H; H₈), 7.49 (ddd, ³J_PH = 18.9 Hz, ³J_HH = 8 Hz, ⁴J_HH = 2 Hz, 1H; H₉), 7.30 (ddd, ³J_PH = 8 Hz, ³J_HH = 7 Hz, ⁴J_HH = 1 Hz, 1H; H₃), 7.12 (m, 6H; H₉, H₁₀), 6.75 (m, 1H; H₅), 6.62 (m, 1H; H₄).

¹³C{¹H} NMR (176 MHz, 298 K, C₆D₆): δ¹³C 141.5 (dt, ¹J_PC = 202 Hz, ²J_FC = 36 Hz; C₁), 136.3 (dt, ¹J_PC = 180 Hz, ²J_FC = 26 Hz; C₇), 135.9 (dt, ³J_PC = 13, ⁴J_FC = 10 Hz; C₈), 134.2 (d, ³J_PC = 26 Hz; C₃), 132.3 (dt, ²J_PC = 12 Hz, ³J_FC = 4 Hz; C₆), 131.9 (dt, ³J_PC = 4 Hz, ⁴J_FC = 1 Hz; C₁₀), 130.8 (m; C₄), 128.7 (dt, ²J_PC = 17 Hz, ³J_FC = 2 Hz; C₉), 126.7 (d, ³J_PC = 17 Hz; C₅), 122.2 (dt, ²J_PC = 5 Hz, ³J_FC = 3 Hz; C₂).

¹⁹F NMR (377 MHz, 298 K, C₆D₆): δ -36.4 ppm (d, ¹J_PF = 674 Hz, 1F; PF₂).

³¹P{¹H} NMR (162 MHz, 298 K, C₆D₆): δ -48.0 ppm (t, ¹J_PF = 674 Hz, 1P; PF₂).
$^{1}$H NMR (700 MHz, 298 K, C$_6$D$_6$) spectrum of (2-BrC$_6$H$_4$)PF$_2$Ph$_2$ (2).

$^{13}$C[$^1$H] NMR (176 MHz, 298 K, C6D6) spectrum of (2-BrC$_6$H$_4$)PF$_2$Ph$_2$ (2).
In a 50 ml vial, solid Pd(PPh$_3$)$_4$ (1.306 g, 1.23 mmol, 1.0 eqv.) was suspended in toluene (20 ml). A solution of compound 2 (0.603 g, 1.59 mmol, 1.3 eqv.) in toluene (10 ml) was added. The vial was sealed and heated to 90 ºC for 45 h. The solvent was reduced in vacuo until precipitate was observed. N-pentane (20 ml) was added and the suspension was filtered. The resulting pale yellow solid was washed with n-pentane (3 x 10 ml) and dried in vacuo to yield the desired product (1.025 g, 90%, Anal. Calcd for C$_{54}$H$_{44}$BrF$_2$P$_3$Pd: C, 64.21; H, 4.39%. Found: C, 64.02; H, 4.27%). Single crystals of compound 3 suitable for X-ray diffraction were obtained from slow evaporation of n-pentane into a concentrated C$_6$H$_6$ solution at ambient temperature.

$^1$H NMR (400 MHz, 296 K, CD$_2$Cl$_2$): δ$^1$H 7.58 (ddm, $^3$J$_{PH}$ = 14.3 Hz, $^3$J$_{HH}$ = 8.4 Hz, 4H; H$_8$), 7.49 (tm, $^3$J$_{HH}$ = 7.4 Hz, 2H; H$_{10}$), 7.36 (br m, 12H, H$_{12}$), 7.31 (m, 4H, H$_6$), 7.22 (br m, 18H, H$_{13}$, H$_{14}$).
7.16 (m, 1H, H₆)², 7.04 (m, 1H, H₃), 6.75 (m, 1H, H₅), 6.44 (m, 1H, H₄). ¹ from gcosy, ¹ tentative assignment of o-,m-PPh₃

¹³C{¹H} NMR (126 MHz, 298 K, C₆D₆): δ¹³C 156.3 (d, ²JPC = 20.2 Hz, C₂), 145.8 (d, ¹JPC = 198 Hz, C₁), 139.1 (dt, ³JPC = 23.3, ⁴JFC = 5.3 Hz, C₃), 138.6 (dt, ¹JPC = 190 Hz ², ²JFC = 27.3 Hz, C₇), 136.2 (m, C₈), 136.0 (dt, ¹JPC = 23.3, ⁴JFC = 5.3 Hz, C₆), 135.3 (m, C₁₂), 131.9 (t, ¹JPC = 22.0 Hz, C₁₁), 131.6 (d, ⁴JPC = 3.5 Hz, C₁₀), 130.0 (C₁₄), 128.6 (dt, ³JPC = 16.4 Hz, ⁴JFC = 2.0 Hz, C₉), 128.0 (t, ³JPC = 5.0 Hz, C₁₃), 127.4 (d, ⁴JPC = 3.7 Hz, C₄), 122.70 (d, ³JPC = 17.9 Hz, C₆). ² from ghmbc, ³ from ghsqc, ¹ tentative assignment

¹⁹F NMR (377 MHz, 296 K, CD₂Cl₂): δ¹⁹F -38.8 (dt, ¹JPF = 680 Hz, JPF = 12 Hz, PF₂).

³¹P{¹H} NMR (162 MHz, 296 K, CD₂Cl₂): δ³¹P 18.6 (td, JPF = 12 Hz, JPP = 4 Hz, 2P; PPh₃), -55.3 (tt, ¹JPF = 680 Hz, JPP = 4 Hz, 1P, PF₂).

¹H NMR (400 MHz, 298 K, CD₂Cl₂) spectrum of (2-PF₂Ph₂)(C₆H₄)Pd(PPh₃)₂Br (3).

¹³C{¹H} NMR (126 MHz, 298 K, CD₂Cl₂) spectrum of (2-PF₂Ph₂)(C₆H₄)Pd(PPh₃)₂Br (3).
$^{19}$F NMR (377 MHz, 298 K, CD$_2$Cl$_2$) and $^{31}$P($^1$H) NMR (162 MHz, 298 K, CD$_2$Cl$_2$) spectra of (2-PF$_2$Ph)$_2$(C$_6$H$_4$)Pd(PPh$_3$)$_2$Br (3).

1.3 Preparation and Characterization of [(2-PFPh$_2$)(C$_6$H$_4$)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$]

At room temperature, trimethylsilyl trifluoromethanesulfonate (Me$_3$SiO$_3$SCF$_3$; 0.044 g, 0.20 mmol, 1 eqv.) was added dropwise to a suspension of compound 2 (0.200 g, 0.20 mmol, 1 eqv.) in toluene (10 ml), causing the solid to immediately dissolve. Within seconds, a new solid precipitate was formed. After stirring for 1 h at room temperature, the suspension was allowed to settle and the supernatant was decanted. The solid was washed with n-pentane (3 x 5 ml) and dried in vacuo, affording compound 4 as a pale yellow solid (0.201 g, 89%, Anal. Calcd for C$_{78}$H$_{44}$BBrF$_{21}$P$_3$Pd: C, 56.09; H, 2.66%. Found: C, 55.93; H, 2.75%). Single crystals of
compound 4 suitable for X-ray diffraction were obtained from slow diffusion of pentane into a concentrated CH\(_2\)Cl\(_2\) solution at ambient temperature.

\(^1\)H NMR (400 MHz, 296 K, CD\(_2\)Cl\(_2\)): δ\(^1\)H 7.76 (m, \(^3\)J\(_{HH}\) = 7.7 Hz, 2H, H\(_{10}\)), 7.52 (m, 1H, H\(_3\)), 7.48 (m, 6H, H\(_{14}\)), 7.47 (m, 4H, H\(_9\)), 7.31 (m, 12H, H\(_{13}\)), 7.20 (br, 12H, H\(_{12}\)), 7.13 (m, 1H, H\(_6\)), 7.09 (m, 4H, H\(_8\)), 7.04 (m, 1H, H\(_5\)), 7.01 (m, 1H, H\(_4\)).

\(^{13}\)C\{\(^1\)H\} NMR (126 MHz, 298 K, CD\(_2\)Cl\(_2\)): δ\(^{13}\)C 168.6 (C\(_2\)\(^a\)), 142.1 (C\(_3\)\(^b\)), 138.6 (d, \(^2\)J\(_{PC}\) ≈ 35 Hz, C\(_6\)), 137.5 (C\(_{10}\)), 135.0 (t, \(^2\)J\(_{PC}\) = 6.0 Hz, C\(_{12}\)), 133.8 (C\(_4\)), 133.4 (d, \(^2\)J\(_{PC}\) = 12.1 Hz, C\(_8\)), 131.1 (C\(_{14}\)), 130.7 (d, \(^2\)J\(_{PC}\) = 14.2 Hz, C\(_9\)), 130.4 (t, \(^1\)J\(_{PC}\) = 23.6 Hz, C\(_{11}\)), 128.8 (t, \(^3\)J\(_{PC}\) = 5.1 Hz, C\(_{13}\)), 124.7 (C\(_{15}\)), 121.3 (\(^1\)J\(_{PC}\) ≈ 100 Hz\(^a\), C\(_1\)), 118.1 (\(^1\)J\(_{PC}\) ≈ 100 Hz\(^a\), C\(_7\)).\(^a\) from ghmbc, \(^b\) from ghsqc.

Not observed: CF\(_3\)SO\(_3\).

\(^{19}\)F NMR (377 MHz, 296 K, CD\(_2\)Cl\(_2\)): δ\(^{19}\)F -78.9 (s, 3F; O\(_3\)SCF\(_3\)), -135.2 (dt, \(^1\)J\(_{PF}\) = 988 Hz, \(J_{PF} = 15\) Hz, 1F; PF).

\(^{31}\)P\{\(^1\)H\} NMR (162 MHz, 296 K, CD\(_2\)Cl\(_2\)): δ\(^{31}\)P 89.9 (d, \(^1\)J\(_{PF}\) = 988 Hz, 1P; PF), 20.6 (d, \(J_{PF} = 15\) Hz, 2P; PPh\(_3\)).

\(^1\)H NMR (400 MHz, 298 K, CD\(_2\)Cl\(_2\)) spectrum of ([Pd(PPh\(_3\))\(_2\)]Br[O\(_3\)SCF\(_3\)] (4).
$^{13}\text{C}^{1}\text{H}}$ NMR (126 MHz, 298 K, CD$_2$Cl$_2$) spectrum of ([2-PFPh$_2$](C$_6$H$_4$)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$] (4).

$^{19}\text{F}$ NMR (377 MHz, 298 K, CD$_2$Cl$_2$) and $^{31}\text{P}^{1}\text{H}}$ NMR (162 MHz, 298 K, CD$_2$Cl$_2$) spectra of

$^{[(2-PFPh$_2$)(C$_6$H$_4$)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$]}$ (4).
1.4 Preparation and Characterization of [(2-PFPh$_2$)(C$_6$H$_4$CO)Pd(PPh$_3$)$_2$Br] [O$_3$SCF$_3$] (5):

Solid compound 4 (0.228 g, 0.20 mmol) was dissolved in CH$_2$Cl$_2$ (10 ml) and transferred to a 25 ml bomb. The vessel was filled CO gas to 2 bar, sealed, and stirred at room temperature for 24 h, during which time the solution deepens in colour. After purging the vessel of excess CO in vacuo, the solution was reduced to 2 ml. N-pentane (10 ml) was added and the suspension was filtered. The resulting solid was washed with n-pentane (10 ml) and dried in vacuo. Washing with n-pentane and drying in vacuo was repeated twice to afford the desired product as a pale orange powder (0.218 g, 93%, Anal. Calcd for C$_{56}$H$_{44}$BrF$_4$O$_4$P$_3$: C, 57.57; H, 3.80%. Found: C, 57.14; H, 3.80%). Single crystals of compound 4 suitable for X-ray diffraction were obtained from slow diffusion of pentane into a concentrated CH$_2$Cl$_2$ solution at ambient temperature.

$^1$H NMR (400 MHz, 296 K, CD$_2$Cl$_2$): δ$^1$H 8.14 (dd, $^3$J$_{PH}$ = 11.6 Hz, $^3$J$_{HH}$ = 7.4 Hz, 1H; H$_8$), 7.96 (m, 4H; H$_3$), 7.88 (m, 1H; H$_5$), 7.75 (m, 1H; H$_6$), 7.51 (m, 1H, H$_4$)$^a$, 7.50 (m, 2H, H$_{10}$), 7.37 (m, 6H; H$_{14}$), 7.27 (m, 12H, H$_{12}$), 7.22 (m, 12H, H$_{13}$), 7.19 (m, 4H, H$_9$)$^a$. $^a$ from ghsqc

$^{13}$C($^1$H) NMR (126 MHz, 298 K, CD$_2$Cl$_2$): δ$^{13}$C 139.3 (m, C$_2$), 137.2 (d, $^3$J$_{PC}$ = 15.1 Hz, C$_5$), 136.7 (d, $^3$J$_{PC}$ = 12.4 Hz, C$_3$), 136.3 (d, $^4$J$_{PC}$ = 2.9 Hz, C$_4$), 135.0 (m, C$_6$), 134.5 (t, $^4$J$_{PC}$ = 6.3 Hz, C$_{12}$), 134.3 (d, $^4$J$_{PC}$ = 4.5 Hz, C$_{10}$), 133.9 (dd, $^2$J$_{PC}$ = 11.9, $^3$J$_{FC}$ = 7.1 Hz, C$_8$), 131.7 (C$_{14}$), 129.7 (d, $^3$J$_{PC}$ = 15.6 Hz, C$_9$), 129.1 (t, $^2$J$_{PC}$ = 25.1 Hz, C$_{12}$), 129.0 (t, $^3$J$_{PC}$ = 5.4 Hz, C$_{13}$), 126.5 (dd, $^1$J$_{PC}$ = 148.6 Hz, $^2$J$_{FC}$ = 19.8 Hz, C$_7$), 124.0 (dd, $^1$J$_{PC}$ = 151.4 Hz, $^2$J$_{FC}$ = 29.3 Hz, C$_1$). Not observed: C$_{11}$, C$_{15}$, CF$_3$SO$_3$. Repeat experimentation with $^{13}$CO$_{(g)}$ reveals δ$^{13}$C for C$_{15}$ = 261.7.

$^{19}$F NMR (377 MHz, 296 K, CD$_2$Cl$_2$): δ$^{19}$F -78.7 (s, 3F; O$_3$SCF$_3$), -82.85 (d, $^1$J$_{PF}$ = 773 Hz, 1F;
$^{31}\text{P(}^{1}\text{H})\text{ NMR}$ (162 MHz, 296 K, CD$_2$Cl$_2$): $\delta^{31}\text{P}$ 21.4 (s, 2P, PPh$_3$), -0.3 (d, $^{1}J_{\text{PF}}$ = 773 Hz, 1P, PF).

$^{1}\text{H NMR}$ (400 MHz, 298 K, CD$_2$Cl$_2$) spectrum of [(2-PFPh$_2$)(C$_{6}$H$_4$CO)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$] (5).

$^{13}\text{C(}^{1}\text{H})\text{ NMR}$ (126 MHz, 298 K, CD$_2$Cl$_2$) spectrum of [(2-PFPh$_2$)(C$_{6}$H$_4$CO)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$] (5).
$^{13}$C ($^{1}$H) NMR (126 MHz, 298 K, CD$_2$Cl$_2$) spectrum of ([2-PFPh$_2$)(C$_6$H$_4^{13}$CO)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$] (5).

$^{19}$F NMR (377 MHz, 298 K, CD$_2$Cl$_2$) and $^{31}$P ($^{1}$H) NMR (162 MHz, 298 K, CD$_2$Cl$_2$) spectra of [(2-PFPh$_2$)(C$_6$H$_4$CO)Pd(PPh$_3$)$_2$Br][O$_3$SCF$_3$] (5).
IR Spectra

1.5 IR Spectrum of \([(2-PFPh_2)(C_6H_4)Pd(PPh_3)_2Br][O_3SCF_3]\) (4)
1.6 IR Spectrum of \([(2\text{-PFPh}_2)(C_6H_4CO)\text{Pd}(\text{PPh}_3)_2\text{Br})[O_3\text{SCF}_3]\) (5)
1.7 IR Spectrum of [(2-PFPh₂)(C₆H₄₁₃CO)Pd(PPh₃)₂Br][O₃SCF₃] (5⁻¹³C₁₅)