

Supporting data for:

Non-Innocent Reactivity of *bis*-Phosphinimine Pincer Ligands in Palladium Complexes

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Synthesis of 1,3-xylylene-bis(triphenylphosphinimine) (1)

Method 1

A slurry of sodium hydride in THF (1.11 g, 46.26 mmol; 25 mL) was combined with m-xylylenediamine (0.44 mL, 3.304 mmol) at room temperature and stirred. A slurry of triphenylphosphine dibromide in THF (2.79 g, 6.608 mmol; 50 mL) was then added giving a grey coloured slurry. The reaction mixture stirred for 2 days at which point the reaction mixture was off white with a white precipitate. The reaction mixture was filtered through a fine porosity filter frit giving a clear off-white solution. The solvent was removed in-vacuo yielding an off-white powder. The powder was washed with Et₂O and the colourless eluent was filtered off. The product was dried and obtained in a 83 % yield (1.79 g, 2.73 mmol)

Method 2

A solution of m-xylylenediamine in DCM (1 g, 7.34 mmol; 20mL) was combined with excess triethylamine () in a 250mL round-bottom schlenk flask and placed under a stream of nitrogen. The reaction mixture was cooled to 0°C and a solution of dibromotriphenylphosphorane in DCM (6.20 g, 14.68 mmol; 50 mL) was cannula transferred in while stirring the reaction mixture giving a clear colourless solution. The reaction was warmed to room temperature and stirred for 1 hour. The mixture was dried, and THF (75 mL) was added. The stirring slurry was then cooled to -30 °C and a solution of potassium hexamethylsilylamide in THF (5.86 g, 29.37 mmol; 50 mL) was added resulting in an off-white mixture. The reaction mixture was stirred over night before being filtered through celite over a medium porosity filter frit. The solution was dried in-vacuo giving a white solid that was re-dissolved in a minimal amount of DCM and precipitated by hexanes. The white fluffy solid was collected over a fine porosity filter frit and residual solvent was removed in-vacuo giving the desired product in 85 % yield (4.1 g, 6.24 mmol).

¹H NMR (CD₂Cl₂; δ ppm) 7.70 (m, 12H, H_o PPh₃), 7.55 (m, 6H, H_p PPh₃), 7.46 (m, 12H, H_m PPh₃), 7.25 (s, 1H, C₂H C₆R₂H₄), 7.20 (d, 2H, ³J_{H-H} 8.00 Hz, C_{4,6}H C₆R₂H₄), 7.11 (trip, 1H, ³J_{H-H} 8.00 Hz, C₅H C₆R₂H₄), 4.22 (d, 4H, ³J_{H-P} 15.66 Hz, Ar-CH₂-N)

¹³C (CD₂Cl₂; δ ppm) 145.92 (d, ³J_{PC} 16.18 Hz, C_{1,3} C₆R₂H₄), 133.02 (d, ³J_{PC} 8.80 Hz,

C_m PPh₃), 131.69 (d, ⁴J_{PC} 2.93 Hz, C_p PPh₃), 128.22 (d, ¹J_{PC} 99.28 Hz, C_{ipso} PPh₃), 128.89 (d, ²J_{PC} 11.74 Hz, C_o PPh₃), 127.83 (Ar-C C₆R₂H₄), 126.44 (Ar-C C₆R₂H₄), 125.01 (Ar-C C₆R₂H₄), 49.30 (d, ²J_{PC} 2.93 Hz, CH₂)

³¹P{¹H} NMR (CD₂Cl₂; δ ppm) 9.45 (s)

Anal. Calc. for C₄₄H₃₈N₂P₂: C, 80.46; H, 5.84; N, 4.27. Found: C 80.32; H, 5.56; N, 4.21.

Synthesis of 1,3-C₆H₃(CH₂N=PPh₃)₂PdCl (2)

A solution of ligand in DCM (100 mg, 0.152 mmol; 2 mL) was combined in 20 mL scintillation vial with a yellow solution of bis(benzonitrile)palladium dichloride in DCM (58 mg, 0.152 mmol; 2 mL) immediately giving a colour change to a red-brown solution. The reaction mixture was stirred for 2 days yielding an orange solution. The reaction mixture was run through a plug of alumina in a pipette. An additional 2 mL of DCM was washed through the alumina and the resultant yellow solution was dried. The above procedure was repeated once yielding a pale yellow solution. The reaction mixture was concentrated and a yellow powder precipitated with hexanes. The clear colorless solution was decanted off and the yellow powder dried *in vacuo*. The product was obtained in a 33 % yield (40 mg, 0.050 mmol).

¹H NMR (CD₂Cl₂; δ ppm) 7.88 (m, 12H, ³J_{H-H} 7.12 Hz, H_o (PPh₃)), 7.55 (m, 6H, ³J_{H-H} 7.63 Hz, H_p (PPh₃)), 7.45 (m, 12H, ³J_{H-H} 7.63 Hz, H_m (PPh₃)), 6.71 (t, 1H, ³J_{H-H} 7.45 Hz, C₅H (C₆R₂H₄)), 6.48 (d, 2H, ³J_{H-H} 7.45 Hz, C_{4,6}H (C₆R₂H₄)), 4.22 (d, 4H, ³J_{H-P} 4.82 Hz, Ar-CH₂-N)

¹³C (CD₂Cl₂; δ ppm) 151.98 (d, ³J_{PC} = 20.54 Hz, C_{1,3} (C₆R₂H₄)), 134.30 (d, ³J_{PC} = 10.27 Hz, C_m (PPh₃)), 132.07 (s, C_p (PPh₃)), 129.28 (d, ¹J_{PC} 100.5 Hz, C_{ipso} (PPh₃)), 128.21 (d, ²J_{PC} = 12.50 Hz, C_o (PPh₃)), 122.19 (s, Ar-C (C₆R₂H₄)), 119.17 (s, Ar-C (C₆R₂H₄)) 117.33 (s, Ar-C (C₆R₂H₄)), 61.90 (s, CH₂)

³¹P{¹H} NMR (CD₂Cl₂; δ ppm) 30.03 (s)

Anal. Calc. for: C, 66.16; H, 4.80; N, 3.51. Found: C, 65.67; H, 5.10; N, 3.84.

Synthesis of 1,3-C₆H₃(CH₂N=PPh₃)(CH₂NHPPH₂)PdCl (3)

A white slurry of ligand in THF (200 mg, 0.305 mmol; 15 mL) and a yellow slurry of CODPdCl₂ in THF (87 mg, 0.305 mmol; 5 mL) were combined in a 250 mL tube bomb (pressure vessel). The reaction mixture was placed in an oil bath at room temperature and warmed to 120 °C with stirring. The solids dissolved in solution and the reaction mixture was stirred for 12 hours. The reaction mixture was filtered through a short plug of alumina and a yellow solution was obtained. The solution was concentrated and precipitated with hexanes giving a bright yellow solid. The clear colourless eluent was

decanted and the residual solvent was removed in-vacuo. The yellow solid was obtained in a 72 % yield (158 mg, 0.219 mmol).

^1H NMR (CD_2Cl_2 ; δ ppm) 7.91 (m, 10H, H_o PPh_3 , PPh_2), 7.62 (m, 3H, $^3\text{J}_{\text{H-H}}$ 7.12 Hz, H_p PPh_3), 7.54 (m, 6H, $^3\text{J}_{\text{H-H}}$ 7.12 Hz, H_m PPh_3), 7.45 (m, 2H, $^3\text{J}_{\text{H-H}}$ 7.12 Hz, H_p PPh_2), 7.38 (m, 4H, $^3\text{J}_{\text{H-H}}$ 7.12 Hz, H_m PPh_2), 6.86 (t, 1H, $^3\text{J}_{\text{HH}}$ 7.12 Hz, C_5H ($\text{C}_6\text{H}_4\text{R}_2$)), 6.79 (m, 2H, $\text{C}_{4,6}\text{H}$ ($\text{C}_6\text{H}_4\text{R}_2$)), 4.27 (m, 2H, $\text{CH}_2=\text{N}$), 3.89 (m, 2H, CH_2-NH), 1.72 (broad, 1H, NH)

^{13}C (CD_2Cl_2 ; δ ppm) 148.89 (dd, $^3\text{J}_{\text{PC}}$ 20.47 Hz, $^4\text{J}_{\text{PC}}$ 2.32 Hz, C_R ($\text{C}_6\text{H}_4\text{R}_2$)), 139.01 (d, $^3\text{J}_{\text{PC}}$ 8.30 Hz, C_R ($\text{C}_6\text{H}_4\text{R}_2$)), 134.78 (d, $^1\text{J}_{\text{PC}}$ 45.11 Hz, C_{ipso} (PPh_2)), 134.40 (d, $^2\text{J}_{\text{PC}}$ 11.77 Hz, C_o (PPh_3)), 134.06 (d, $^3\text{J}_{\text{PC}}$ 10.30 Hz, C_o (PPh_2)), 131.14 (d, $^4\text{J}_{\text{PC}}$ 2.94 Hz, C_p (PPh_3)), 130.98 (d, $^4\text{J}_{\text{PC}}$ Hz, C_p (PPh_2)), 129.51 (s, ($\text{C}_6\text{H}_4\text{R}_2$)), 128.45 (d, $^1\text{J}_{\text{PC}}$ 87.11 Hz, C_{ipso} (PPh_3)), 128.54 (d, $^3\text{J}_{\text{PC}}$ 12.50 Hz, C_m (PPh_3)), 128.13 (d, $^3\text{J}_{\text{PC}}$ 10.30 Hz, C_m (PPh_2)), 124.42 (s, C_5 ($\text{C}_6\text{H}_4\text{R}_2$)), 123.81 (s, ($\text{C}_6\text{H}_4\text{R}_2$)), 120.36 (d, $^2\text{J}_{\text{PC}}$ 3.14 Hz, C_2 ($\text{C}_6\text{H}_4\text{R}_2$)), 57.71 (s, $\text{CH}_2=\text{N}$), 51.91 (d, $^2\text{J}_{\text{PC}}$ 7.84 Hz, CH_2-NH)

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ ppm) 74.11 (d, $^3\text{J}_{\text{PP}}$ = 15.10 Hz, PPh_2), 29.47 (d, $^3\text{J}_{\text{PP}}$ = 15.10 Hz, PPh_3)

Anal. Calc. for: C, 63.15; H, 4.75; N, 3.88. Found: C, 63.19; H, 5.04; N, 3.89.

Synthesis of [1,3- $\text{C}_6\text{H}_3(\text{CH}_2\text{N}=\text{PPh}_3)(\text{CHN}=\text{PPh}_3)\text{PdCl}][\text{B}(\text{C}_6\text{F}_5)_4]$ (4)

A clear yellow solution of NCNPdCl in DCM (70 mg, 0.097 mmol; 2 mL) was combined with a deep yellow solution of trityl borate in DCM (90 mg, 0.097 mmol; 3 mL) were combined in a scintillation vial. Immediately a colour change to very pale yellow was observed. The reaction mixture was stirred for 12 hours before being dried to a bright orange solid. The solid was re-dissolved in a minimal amount of diethyl ether before hexane was then added to the mixture giving a fluffy orange powder and a tacky orange solid. The powder was separated and the procedure repeated (x3) on the tacky solid. The powder slurries were combined and the excess solvent decanted off before the orange powder was dried. The remaining solid and powder were combined and the product was washed with hexanes (3 x 4 mL) and dried in vacuo. The product was obtained in a 88% yield (126 mg, 0.085 mmol). Sample for elemental analysis was prepared by recrystallization from a solution of DCM and cyclohexane.

^1H NMR (CD_2Cl_2 ; δ ppm) 8.23 (d, 1H, $^3\text{J}_{\text{HP}}$ 21.52 Hz, $\text{CH}-\text{N}=\text{P}$), 7.81 (m, 14H, PPh_3), 7.64 (m, 10H, PPh_3), 7.50 (m, 6H, PPh_3), 7.42 (dd, 1H, CH ($\text{C}_6\text{H}_4\text{R}_2$)), 7.12 (m, 2H, CH ($\text{C}_6\text{H}_4\text{R}_2$)), 4.37 (m, 2H, CH_2-NH)

^{11}B (CD_2Cl_2 ; δ ppm) -16.66 (s)

^{13}C (CD_2Cl_2 ; δ ppm) 189.56 (m, $\text{CH}=\text{N}$), 153.76 (d, $^3\text{J}_{\text{PC}}$ = 20.71 Hz, C_R ($\text{C}_6\text{R}_2\text{H}_4$)), 148.17 (dm, $^1\text{J}_{\text{CF}}$ 236.51 Hz, o- C_6F_5), 138.22 (dm, $^1\text{J}_{\text{CF}}$ 251.77 Hz, p- C_6F_5), 136.29 (dm, $^1\text{J}_{\text{CF}}$ 245.23 Hz, m- C_6F_5), 136.15 (d, $^4\text{J}_{\text{PC}}$ = 3.27 Hz, C_p (PPh_3)), 134.82 (d, $^3\text{J}_{\text{PC}}$ = 10.90

Hz, C_m (PPh₃)), 134.16 (d, ³J_{PC} = 9.81 Hz, C_m (PPh₃)), 133.14 (d, ⁴J_{PC} = 3.27 Hz, C_p (PPh₃)), 130.12 (d, ²J_{PC} = 13.08 Hz, C_o (PPh₃)), 128.79 (d, ²J_{PC} = 11.99 Hz, C_o (PPh₃)), 127.96 (s, Ar-C (C₆R₂H₄)), 126.95 (s, Ar-C (C₆R₂H₄)), 125.20 (s, Ar-C (C₆R₂H₄)), 119.75 (s, Ar-C (C₆R₂H₄)), 118.75 (s, Ar-C (C₆R₂H₄)), 63.50 (s, CH₂)

¹⁹F {¹H} (CD₂Cl₂; δ ppm) -132.17 (broad s, F_o(C₆F₅)), -162.80 (t, ³J_{FF} 19.07 Hz, F_p(C₆F₅)), -166.65 (broad t, ³J_{FF} 19.07 Hz, F_m(C₆F₅))

³¹P {¹H } NMR (CD₂Cl₂; δ ppm) 45.09 (d, ⁴J_{PP} 1.59 Hz, CHN=PPh₃), 34.61 (d, ⁴J_{PP} 1.59 Hz, CH₂N=PPh₃)

Anal. Calc. for C₇₄H₄₈N₂P₂PdClBF₂₀: C, 56.95; H, 3.10; N, 1.80. Found: C, 56.58; H, 3.14; N, 2.04.

Synthesis of [1,3-C₆H₃(CHN=PPh₃)(CH₂NHPPH₂)PdCl][B(C₆F₅)₄] (5)

A clear yellow solution of PCNPdCl in DCM (70 mg, 0.097 mmol; 2 mL) was combined with a deep yellow solution of trityl borate in DCM (90 mg, 0.097 mmol; 3 mL) were combined in a scintillation vial. Immediately a colour change to very pale yellow was observed. The reaction mixture was stirred for 12 hours before being dried to a bright yellow solid. The crude product was dissolved in a minimal amount of diethyl ether before hexane was then added to the mixture giving a fluffy yellow powder and a tacky yellow solid. The powder was separated and the procedure repeated (x3) on the tacky solid. The powder slurries were combined and the excess solvent decanted off before the yellow powder was dried. The powder and solid products were combined and washed with hexanes (3 x 4 mL) before being dried in vacuo. The product was obtained in a 93 % yield (126 mg, 0.090 mmol).

¹H NMR (CD₂Cl₂; δ ppm) 8.39 (dd, 1H, ³J_{HP} 24.07 Hz, ⁴J_{HP} 5.68 Hz, CH-N=P), 7.91 (m, 10H, ³J_{HH} 7.63 Hz, H_m PPh₃), [H_o PPh₂ buried], 7.85 (m, 1H, CH (C₆H₄R₂)), 7.73 (m, 6H, ³J_{HH} 7.63 Hz, H_m (PPh₃)), 7.68 (m, 2H, H_p PPh₂), 7.57 (m, 4H, H_m PPh₂), 7.47 (m, 4H, ³J_{HH} 7.63 Hz, H_p PPh₃), 7.38 (broad d, 1H, ³J_{HH} 7.63 Hz, CH (C₆H₄R₂)), 7.27 (t, 1H, ³J_{HH} 7.63 Hz, C₅H (C₆H₄R₂)), 4.15 (m, 2H, CH₂-NH), 2.22 (broad, 1H, NH)

¹¹B (CD₂Cl₂; δ ppm) -16.66 (s)

¹³C (CD₂Cl₂; δ ppm) 192.28 (m, CH=N), 163.02 (d, ²J_{PC} 2.93 Hz, CH₂-NH), 148.12 (dd, ³J_{PC} 19.81 Hz, ⁴J_{PC} 2.20 Hz, C₁ (C₆H₄R₂)), 148.54 (dm, ¹J_{CF} 239.89 Hz, o-C₆F₅), 138.86 (d, ²J_{PC} 8.80 Hz, C₂ (C₆H₄R₂)), 138.63 (dm, ¹J_{CF} 244.29 Hz, p-C₆F₅), 136.71 (dm, ¹J_{CF} 242.82 Hz, m-C₆F₅), 136.66 (d, ¹J_{PC} 37.41 Hz, C_{ipso} (PPh₂)), 136.38 (d, ⁴J_{PC} 2.94 Hz, C_p (PPh₃)), 134.83 (d, ³J_{PC} 10.27 Hz, C_m (PPh₃)), 133.80 (d, ²J_{PC} 13.20 Hz, C_o (PPh₂)), 132.62 (d, ⁴J_{PC} 2.20 Hz, C_p (PPh₂)), 130.86 (d, ¹J_{PC} 65.29 Hz, C_{ipso} (PPh₃)), 130.43 (d, ²J_{PC} 13.20 Hz, C_o (PPh₃)), 129.04 (d, ³J_{PC} 12.47 Hz, C_m (PPh₃)), 126.75 (s, (C₆H₄R₂)) 119.52 (s, (C₆H₄R₂)), 118.53 (s, (C₆H₄R₂)), 50.75 (d, ²J_{PC} 4.40 Hz, CH₂-NH)

$^{19}\text{F}\{^1\text{H}\}$ (CD_2Cl_2 ; δ ppm) -132.18 (broad s, $\text{F}_o(\text{C}_6\text{F}_5)$), -162.74 (t, $^3J_{\text{FF}}$ 19.07 Hz, $\text{F}_p(\text{C}_6\text{F}_5)$), -166.59 (broad t, $^3J_{\text{FF}}$ 19.07 Hz, $\text{F}_m(\text{C}_6\text{F}_5)$)

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ ppm) 77.93 (d, $^3J_{\text{PP}}$ 7.95 Hz, PPh_2), 44.20 (d, $^3J_{\text{PP}}$ 7.95 Hz, PPh_3)

Anal. Calc. for $\text{C}_{62}\text{H}_{32}\text{N}_2\text{P}_2\text{PdClBF}_{20}$: C, 53.18; H, 2.31; N, 2.00. Found: C, 53.48; H, 2.74; N, 2.05.