Supporting data for:

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

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Synthesis of 1,3-xyylene-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 (e) 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, C4,6 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, C1,3 C6R2H4), 133.02 (d, 3J_PC 8.80 Hz,
Cm PPh3), 131.69 (d, 4JPC 2.93 Hz, Cp PPh3), 128.22 (d, 1JPC 99.28 Hz, Cipso PPh3), 128.89 (d, 2JPC 11.74 Hz, Co PPh3), 127.83 (Ar-C C6R2H4), 126.44 (Ar-C C6R2H4), 125.01 (Ar-C C6R2H4), 49.30 (d, 2JPC 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, 3JH-H 7.12 Hz, Ho (PPh3)), 7.55 (m, 6H, 3JH-H 7.63 Hz, Hp (PPh3)), 7.45 (m, 12H, 3JH-H 7.63 Hz, Hm (PPh3)), 6.71 (t, 1H, 3JH-H 7.45 Hz, C5H (C6R2H4)), 6.48 (d, 2H, 3JH-H 7.45 Hz, C4,6H (C6R2H4)), 4.22 (d, 4H, 3JH-P 4.82 Hz, Ar-C\(\text{H}_2\)-N)

13C (CD2Cl2; δ ppm) 151.98 (d, 3JPC = 20.54 Hz, C1,3 (C6R2H4)), 134.30 (d, 3JPC = 10.27 Hz, Cm (PPh3)), 132.07 (s, C4 (PPh3)), 129.28 (d, 1JPC 100.5 Hz, Cipso (PPh3)), 128.21 (d, 2JPC = 12.50 Hz, Co (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 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)(CH2NH2PPh2)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 to120 °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
decaned 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\(_2\)Cl\(_2\); \( \delta \) ppm) 7.91 (m, 10H, H\(_o\) PPh\(_3\), PPh\(_2\)), 7.62 (m, 3H, \( ^3J_{HH} \) 7.12 Hz, H\(_p\) PPh\(_3\)), 7.54 (m, 6H, \( ^3J_{HH} \) 7.12 Hz, H\(_m\) PPh\(_3\)), 7.45 (m, 2H, \( ^3J_{HH} \) 7.12 Hz, H\(_p\) PPh\(_3\)), 7.38 (m, 4H, \( ^3J_{HH} \) 7.12 Hz, H\(_m\) PPh\(_2\)), 6.86 (t, 1H, \( ^3J_{HH} \) 7.12 Hz, C\(_3\)H (C\(_6\)H\(_4\)R\(_2\))), 6.79 (m, 2H, C\(_{4,6}\)H (C\(_6\)H\(_4\)R\(_2\))), 4.27 (m, 2H, CH\(_2\)=N), 3.89 (m, 2H, CH\(_2\)-NH), 1.72 (broad, 1H, NH)

\( ^{13}C \) (CD\(_2\)Cl\(_2\); \( \delta \) ppm) 148.89 (dd, \( ^3J_{PC} \) 20.47 Hz, \( ^4J_{PC} \) 2.32Hz, CR (C\(_6\)H\(_4\)R\(_2\))), 139.01 (d, \( ^3J_{PC} \) 8.30 Hz, CR (C\(_6\)H\(_4\)R\(_2\))), 134.78 (d, \( ^1J_{PC} \) 45.11 Hz, C\(_{ipso}\) (PPh\(_2\))), 134.40 (d, \( ^2J_{PC} \) 11.77 Hz, C\(_o\) (PPh\(_3\))), 134.06 (d, \( ^3J_{PC} \) 10.30 Hz, C\(_o\) (PPh\(_2\))), 131.14 (d, \( ^4J_{PC} \) 2.94 Hz, C\(_p\) (PPh\(_3\))), 130.98 (d, \( ^4J_{PC} \) Hz, C\(_p\) (PPh\(_2\))), 129.51 (s, (C\(_6\)H\(_4\)R\(_2\))), 128.45 (d, \( ^1J_{PC} \) 87.11 Hz, C\(_{ipso}\) (PPh\(_3\))), 128.54 (d, \( ^3J_{PC} \) 12.50 Hz, C\(_m\) (PPh\(_3\))), 128.13 (d, \( ^3J_{PC} \) 10.30 Hz, C\(_m\) (PPh\(_2\))), 124.42 (s, C\(_5\) (C\(_6\)H\(_4\)R\(_2\))), 123.81 (s, (C\(_6\)H\(_4\)R\(_2\))), 120.36 (d, \( ^2J_{PC} \) 3.14 Hz, C\(_2\) (C\(_6\)H\(_4\)R\(_2\))), 57.71 (s, CH\(_2\)=N), 51.91 (d, \( ^3J_{PC} \) 7.84 Hz, CH\(_2\)-NH)

\( ^{31}P\{^1H\} \) NMR (CD\(_2\)Cl\(_2\); \( \delta \) ppm) 74.11 (d, \( ^3J_{PP} \) = 15.10 Hz, PPh\(_2\)), 29.47 (d, \( ^3J_{PP} \) = 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-C\(_6\)H\(_3\)(CH\(_2\)N=PPh\(_3\))(CHN=PPh\(_3\))PdCl][B(C\(_6\)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 vile. 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 prepar by recrystallization from a solution of DCM and cyclohexane.

\( ^1H \) NMR (CD\(_2\)Cl\(_2\); \( \delta \) ppm) 8.23 (d, 1H, \( ^3J_{HP} \) 21.52 Hz, CH-N=P), 7.81 (m, 14H, PPh\(_3\)), 7.64 (m, 10H, PPh\(_3\)), 7.50 (m, 6H, PPh\(_3\)), 7.42 (dd, 1H, CH (C\(_6\)H\(_4\)R\(_2\))), 7.12 (m, 2H, CH (C\(_6\)H\(_4\)R\(_2\))), 4.37 (m, 2H, CH\(_2\)-NH)

\( ^{11}B \) (CD\(_2\)Cl\(_2\); \( \delta \) ppm) -16.66 (s)

\( ^{13}C \) (CD\(_2\)Cl\(_2\); \( \delta \) ppm) 189.56 (m, CH=N), 153.76 (d, \( ^3J_{PC} \) = 20.71 Hz, C\(_R\) (C\(_6\)R\(_2\)H\(_4\))), 148.17 (dm, \( ^1J_{CF} \) 236.51 Hz, o-C\(_6\)F\(_5\)), 138.22 (dm, \( ^1J_{CF} \) 251.77 Hz, p-C\(_6\)F\(_5\)), 136.29 (dm, \( ^1J_{CF} \) 245.32 Hz, m-C\(_6\)F\(_5\)), 136.15 (d, \( ^4J_{PC} \) = 3.27 Hz, C\(_p\) (PPh\(_3\))), 134.82 (d, \( ^3J_{PC} \) = 10.90 Hz, C\(_p\) (PPh\(_2\))))
Hz, Cn (PPh3)), 134.16 (d, 3JPC = 9.81 Hz, Cn (PPh3)), 133.14 (d, 4JPC = 3.27 Hz, Cp (PPh3)), 130.12 (d, 2JPC = 13.08 Hz, Co (PPh3)), 128.79 (d, 2JPC = 11.99 Hz, Co (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, F0 (C6F5)), -162.80 (t, 3JFF 19.07 Hz, Fp (C6F5)), -166.65 (broad t, 3JFF 19.07 Hz, Fm (C6F5))

31P {1H} NMR (CD2Cl2; δ ppm) 45.09 (d, 4JPP 1.59 Hz, CHN=PPh3), 34.61 (d, 4JPP 1.59 Hz, CH2N=PPh2)


**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 vile. 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, 3JHP 24.07 Hz, 4JHP 5.68 Hz, CH-N=P), 7.91 (m, 10H, 3JHH 7.63 Hz, Hm PPh3), [Ho PPh2 buried]], 7.85 (m, 1H, CH (C6H4R2)), 7.73 (m, 6H, 3JHH 7.63 Hz, Hm (PPh3)), 7.68 (m, 2H, Hp PPh3)7.57 (m, 4H, Hm PPh2), 7.47 (m, 4H, 3JHH 7.63 Hz, Hp PPh3), 7.38 (broad d, 1H, 3JHH 7.63 Hz, CH (C6H4R2)), 7.27 (t, 1H, 3JHH 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, 2JPC 2.93 Hz, CH2-NH), 148.12 (dd, 3JPC 19.81 Hz, 4JPC 2.20 Hz, C1 (C6H4R2)), 148.54 (dm, 1JCF 239.89 Hz, o-C6F5), 138.86 (d, 3JPC 8.80 Hz, C2 (C6H4R2)), 138.63 (dm, 1JCF 244.29 Hz, p-C6F5), 136.71 (dm, 1JCF 242.82 Hz, m-C6F5), 136.66 (d, 1JPC 37.41 Hz, Cipso (PPh2)), 136.38 (d, 4JPC 2.94 Hz, Cp (PPh3)), 134.83 (d, 3JPC 10.27 Hz, Cm (PPh3)), 133.80 (d, 2JPC 13.20 Hz, Co (PPh2)), 132.62 (d, 4JPC 2.20 Hz, Cp (PPh2)), 130.86 (d, 1JPC 65.29 Hz, Cipso (PPh3)), 130.43 (d, 2JPC 13.20 Hz, Cm (PPh3)), 129.04 (d, 3JPC 12.47 Hz, Cipso (PPh3)), 126.75 (s, (C6H4R2)), 118.53 (s, (C6H4R2)), 50.75 (d, 2JPC 4.40 Hz, CH2-NH)
$^{19}$F{¹H}(CD₂Cl₂; δ ppm) -132.18 (broad s, F₀(C₆F₅)), -162.74 (t, $^3$J₉F 19.07 Hz, Fₚ(C₆F₅)), -166.59 (broad t, $^3$J₉F 19.07 Hz, Fₘ(C₆F₅))

$^{31}$P{¹H} NMR (CD₂Cl₂; δ ppm) 77.93 (d, $^3$J₉P 7.95 Hz, PPh₂), 44.20 (d, $^3$J₉P 7.95 Hz, PPh₃)

Anal. Calc. for C₆₂H₃₂N₂P₂PdClBF₂₀: C, 53.18; H, 2.31; N, 2.00. Found: C, 53.48; H, 2.74; N, 2.05.