Supplementary Material (ESI) for Chemical Communications

Chiral palladium bis(phosphite) *PCP*-pincer complexes *via* ligand C-H activation

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Electronic Supplementary Information

Synthesis of ligand 4b. A mixture of **6** (1.50 g, 6.76 mmol) and 4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (4.74 g, 13.5 mmol) in toluene (60 mL) at -40 ºC was treated drop-wise with NEt_3 (3.0 mL, 21.4 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight, then filtered and the solvent was removed under vacuum to give **4b** as a colourless solid (6.37 g, 94 %). ^{1}H NMR (300 MHz; $CDCl_3$): 1.30 (18H, s, ^{t}Bu), 7.02-7.22 (8H, m, ArH), 7.25-7.40 (6H, m, ArH), 7.52 (2H, d, *J* = 9 Hz, ArH), 7.49 (2H, d, *J* = 9 Hz, ArH), 7.74 (2H, d, *J* = 9 Hz, ArH), 7.78 (2H, d, *J* = 8 Hz, ArH), 7.82 (2H, d, *J* = 9 Hz, ArH), 7.86 (2H, d, *J* = 9 Hz, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 144.6 (s). Anal. calcd for $C_{54}H_{44}O_6P_2$: C, 76.23; H, 5.21. Found: C, 76.01; H, 5.54.

Synthesis of 7. A mixture of **6** (5.0 g, 22.5 mmol) and PCl_3 (15.0 mL, 172 mmol) in toluene (80 mL) at -40 ºC was treated drop-wise with NEt_3 (25.0 mL, 180 mmol) in toluene (20 mL). The reaction was allowed to warm to room temperature overnight. The

filtrate was collected under nitrogen, and the filtrate residue washed with toluene (2 x 20 mL). The solvent from the combined filtrate and washing was removed under vacuum to give a white solid. Toluene (2 x 20 mL) was added to this solid and then removed under vacuum to ensure the full removal of PCl_3 to give **7** as a white solid (8.70 g, 91 %) and used without further purification. ^{1}H NMR (300 MHz; $CDCl_3$): 1.30 (18H, s, ^{t}Bu), 7.31 (1H, s, ArH), 7.79 (1H, s, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 183.6 (s).

Synthesis of Ligand 4c. A mixture of NEt_3 (6.0 mL, 43.0 mmol) and **7** (2.00 g, 4.72 mmol) in toluene (60 mL) at -40 ºC was treated drop-wise with (2R,3R)-(-)-2,3-butanediol (0.86 mL, 9.42 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight, then filtered and the filtrate residue washed with toluene (2 x 20 mL). The solvent from the filtrate was removed under vacuum to give **4c** as a white solid. (3.10 g, 72.5 %). ^{1}H NMR (300 MHz; $CDCl_3$): 1.28 (18H, s, ^{t}Bu), 1.32 (6H, d, J = 9 Hz, CH_3), 1.40 (6H, d, J = 5 Hz, CH_3), 3.80 (2H, dq, J = 6 & 5 Hz, OCH), 4.17 (2H, dq, J = 9 & 6 Hz, OCH), 6.79 (1H, s, ArH), 7.18 (1H, s, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 135.4 (s); ^{13}C NMR (75 MHz; $CDCl_3$) 18.45, 19.60 (s, CH_3), 30.55 (s, CH_3 ^{t}Bu), 34.92 (s, C ^{t}Bu), 78.47, 81.13 (s, OCH), 112.52 (t, J = 16 Hz, CH), 125.92, 134.43, 149.47.

Synthesis of ligand 4d. A mixture of NEt_3 (3.0 mL, 21.5 mmol) and **7** (1.00 g, 2.36 mmol) in toluene (60 mL) at -40 ºC was treated drop-wise with (D)-mannitoldiol (1.24 g, 4.72 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight, then filtered and the filtrate residue washed with toluene (2 x 20 mL). The solvent from the solution was removed under vacuum to give **4d** as a very hygroscopic white solid (2.61 g, 69 %). ^{1}H NMR (300 MHz; $CDCl_3$): 1.25 (6H, s, CH_3), 1.26 (18H, s, ^{t}Bu), 1.33 (6H, s, CH_3), 1.39 (6H, s, CH_3), 1.42 (6H, s, CH_3), 3.98-4.19 (12H, m, OCH & OCH_2), 4.19-4.27 (2H, m, OCH), 4.47-4.50 (2H, m, OCH), 6.56 (1H, s, ArH), 7.21 (1H, s, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 136.7 (s); ^{13}C NMR (75 MHz; $CDCl_3$): 25.36, 25.68, 26.89, 27.22 (s, CH_3), 30.09 (s, CH_3 ^{t}Bu), 34.93 (s, C ^{t}Bu), 66.18 (s, $C(Me)_2$), 66.58, 67.17 (s, CH_2), 67.69 (s, $C(Me)_2$), 76.38, 76.89, 80.13, 81.37 (s, OCH), 110.49, 113.11 (t, J = 15 Hz, Ar CH), 129.44, 135.50.

Synthesis of complex 5a. Method A. A mixture of ligand **4a** (0.30 g, 0.4 mmol) and $[PdCl_2(NCPh)_2]$ (0.15 g, 0.4 mmol) in 1,2-dichloroethane (20 mL) was heated to reflux during which time a white suspension was formed. The mixture was maintained at reflux until a clear yellow solution was obtained (approx. 6 days). The solvent was removed under vacuum, the residue was re-dissolved in THF and filtered through celite. The solvent was removed under vacuum and trituration with pentane to give **5a** as a pale yellow powder (0.27 g, 77.5 %). Crystals suitable for X-ray analysis were grown from $CDCl_3$. ^{1}H NMR (300 MHz; $CDCl_3$): 6.80 (2H, d, *J* = 8 Hz, ArH), 7.21-7.68 (9H, m, ArH), 7.87-8.08 (16H, m, ArH); ^{31}P NMR ($CDCl_3$): 147.2 (s); MS (EI): *m/z* = 878 (M^+), 843 (M^+ - Cl), 738 (M^+ - PdCl).

Method B. Ligand **4a** (0.404 g, 0.547 mmol), $[PdCl_2(NCMe)_2]$ (0.142g, 0.546 mmol) and 1,2-dichloroethane (2.5 mL) where placed in microwave reaction vessel and heated in a CEM Discover 300 W microwave reactor at 150 ºC for 1h. Work-up as method A (91.5 %).

General method for the synthesis of complexes 5b - d: A mixture of the appropriate ligand **4** (0.08 mmol) and $[PdCl_2(NCMe)_2]$ (0.021 g, 0.08 mmol) in 1,2-dichloroethane (2 mL) was treated with NEt_3 (0.011 mL, 0.08 mmol) and then heated at 80 ˚C for 2h. The resultant mixture was filtered through celite, the solvent was removed under vacuum and the residue crystallised from CH_2Cl_2/Et_2O

Complex 5b: Grey solid (0.041 g, 51 %). ^{1}H NMR (300 MHz; $CDCl_3$): 1.17 (18H, s, ^{t}Bu), 7.24 (1H, s, ArH), 7.27 (2H, ddd, *J* = 8, 7 & 1 Hz, ArH), 7.34 (2H, d, *J* = 9 Hz, ArH), 7.35 (2H, ddd, *J* = 8, 7 & 1 Hz, ArH), 7.44 (2H, ddd, *J* = 8, 7 & 1 Hz, ArH), 7.46 (2H, d, *J* = 9 Hz, ArH), 7.48 (2H, d, *J* = 9 Hz, ArH), 7.53 (2H, ddd, *J* = 8, 7 & 1 Hz, ArH), 7.64 (2H, d, *J* = 9 Hz, ArH), 7.88 (2H, d, *J* = 8 Hz, ArH), 7.95 (2H, d, *J* = 9 Hz, ArH), 8.00 (2H, d, *J* = 8 Hz, ArH), 8.02 (2H, d, *J* = 9 Hz, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 147.3 (s); Anal. calcd for $C_{54}H_{43}ClO_6P_2Pd \cdot CDCl_3$: C, 59.40; H, 4.08. Found: C, 59.55; H, 3.85.

Complex 5c: Grey solid (0.021 g, 47.5 %); ^{1}H NMR (300 MHz; $CDCl_3$): 1.24 (18H, br s, ^{t}Bu), 1.48 (12H, br s, CH_3), 4.32 (4H, br s, CH), 7.02 (1H, s, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 147.6 (s); ^{13}C NMR (75 MHz; $CDCl_3$): 18.78, 19.18 (s, CH_3), 30.19 (s, CH_3 ^{t}Bu), 35.15 (s, C ^{t}Bu), 81.49, 82.89 (s, OCH), 125.23, 130.01, 146.51, 151.90.

Complex 5d: Grey solid (0.052 g, 68.5 %); ^{1}H NMR (300 MHz; $CDCl_3$): 1.24 (18H, s, ^{t}Bu), 1.30 (6H, s, CH_3), 1.34 (6H, s, CH_3), 1.39 (6H, s, CH_3), 1.41 (6H, s, CH_3), 3.92-3.96 (2H, m, OCH), 4.02-4.09 (4H, m, OCH), 4.13-4.18 (2H, m, OCH), 4.29-4.32 (2H, m, OCH), 4.43-4.46 (2H, m, OCH), 4.52-4.58 (4H, m, OCH), 7.04 (1H, s, ArH); ^{31}P NMR (121 MHz; $CDCl_3$): 151.2 (s); ^{13}C NMR (75 MHz; $CDCl_3$): 25.23, 25.36, 27.17, 27.43 (s, CH_3), 30.06 (s, CH_3 ^{t}Bu), 35.08 (s, C ^{t}Bu), 66.45 (s, $C(Me)_2$), 66.66, 66.92 (s, CH_2), 67.16 (s, $C(Me)_2$), 74.81, 74.94, 80.96, 81.42 (s, OCH), 125.51, 130.60, 146.75, 151.04; Anal. calcd for $C_{38}H_{59}ClO_{14}P_2Pd$: C, 48.36; H, 6.30. Found: C, 48.13; H, 6.61.

Synthesis of complex 8. Ligand **5b** (0.504 g, 0.592 mmol) and $[PdCl_2(NCMe)_2]$ (0154 g, 0.592 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred at room temperature for 1 h. The solution was concentrated under reduced pressure and ethanol (20 mL) added. The CH_2Cl_2 was removed under reduced pressure to induce precipitation of the product. The yellow crystalline solid was isolated by filtration and dried *in vacuo* to give **8** as a orange solid. (0.57 g, 93.5 %). Crystals suitable for X-ray analysis were grown from CH_2Cl_2:MeOH. ^{1}H NMR ($CDCl_3$; 300 MHz): 0.28 (s, 18H, ^{t}Bu), 1.23 (s, 18H, ^{t}Bu), 6.01 (d, 2H, J = 9 Hz, Ar-H), 7.03-7.12 (m, 12H, Ar-H), 7.24-7.38 (m, 8H, Ar-H), 7.43 (d, 2H, J = 6 Hz, Ar-H), 7.51 (d, 4H, J = 6 Hz, Ar-H), 7.52 (d, 2H, J = 6 Hz, Ar-H), 7.69 (d, 2H, J = 7 Hz, Ar-H), 7.73 (dd, 4H, J = 3 & 9 Hz, Ar-H), 7.79 (d, 2H, J = 9 Hz, Ar-H), 7.95 (d, 4H, J = 9 Hz, Ar-H), 8.13 (d, 2H, J = 6 Hz, Ar-H), 8.22 (d, 2H, J = 6 Hz, Ar-H), 8.38 (s, 4H, Ar-H), 8.44 (br s, 2H, Ar-H).^{31}P NMR ($CDCl_3$; 121.5 MHz): 102.29 (d, $^{2}J_{PP}$ = 46.2 Hz), 104.28 (d, $^{2}J_{PP}$ = 46.2 Hz). ^{13}C NMR ($CDCl_3$; 75.5 MHz): 28.61, 30.64 (s, CH_3 ^{t}Bu), 34.82, 35.27 (s, C ^{t}Bu), 111.59, 120.03, 122.09, 122.34, 124.08, 125.46, 126.01, 126.62 (d, J_{CP} = 10 Hz), 126.89, 127.15, 127.40, 127.71, 128.40 (d, J_{CP} = 11 Hz), 128.79,

129.21, 130.24, 131.60, 132.47, 132.44, 132.80, 133.14. Anal. calcd for $C_{108}H_{88}Cl_4O_{12}P_4Pd_2.(CH_2Cl_2)_{1.5}$: C, 60.26; H, 4.20. Found: C, 60.19; H, 4.64.

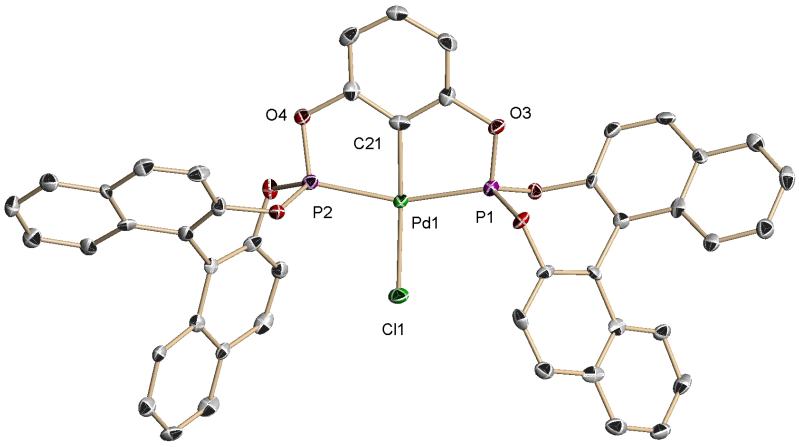

Figure S1. Molecular structure of complex **5a**. **S**elected bond lengths (Å) and angles (°): **5a.** Pd1-P1, 2.2615(19); Pd1-Pd2, 2.2445(18); Pd1-C21, 1.969(6); Pd1-Cl1, 2.3486(18); P1-O1, 1.613(5); P1-O2, 1.586(5); P1-O3, 1.597(5); P2-O4, 1.612(5); P2-O5, 1.587(5); P2-O6, 1.595(5); P1-Pd1-Cl1, 101.66(7); P2-Pd1-Cl1, 99.44(7); P2-Pd1-P1, 158.13(7); C21-Pd1-Cl1, 175.7(2); C21-Pd1-P1, 79.6(2); C21-Pd1-P2, 78.9(2); O2-P1-O1, 103.3(3);

O2-P1-O3, 105.3(3); O3-P1-O1, 97.8(3); O5-P2-O4, 97.9(3); O5-P2-O6, 103.0(2); O6-P2-O4, 106.6(3).