Supplementary Material (ESI) for Dalton Transactions

Monohapto-allyl Pd(II) complexes with bidentate hybrid P,N ligands†

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Complex [Pd(η^1-C_3H_5}Cl(NOP^{Me2}-*N,P*)] 1: the ligand NOP^{Me2} (0.370 g, 1.08 mmol) and [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.200 g, 0.055 mmol) were dissolved in CH_2Cl_2 (20 mL). The yellow solution was stirred for 1 h at room temperature, and the solvent was removed under vacuum. The residue was treated with pentane (30 mL), the off-white solid thus obtained was washed with pentane (2x20 mL) and dried under vacuum, to afford **1** (0.51 g, 89%). Spectroscopic data: IR (CH_2Cl_2): 1636 (s, ν(CN)) cm^{-1}. ^{1}H NMR (400.13 MHz, toluene-d_8, 233 K): δ 1.56 (s, 6H, NC(CH_3)$_2$), 1.59 (s, 6H, OC(CH_3)$_2$), 3.00 (br, 2H, Pd-CH_2), 3.23 (s, 2H, OCH_2), 4.21 (d, 1H , $^3J_{HH}$ = 16.4 Hz, =CH*H* trans to –CH=), 4.73 (d, 1H, $^3J_{HH}$ = 8.0 Hz, =C*H*H cis to –CH=), 6.89 (m, 1H, –CH=), 7.03-7.07 (m, 6H, aromatic H), 7.55-7.60 (m, 4H, aromatic H). ^{13}C{^{1}H} NMR (100 MHz, toluene-d_8, 233 K): δ 27.3 (s, NC(*C*H_3)$_2$), 27.7 (d, $^3J_{PC}$ = 5.0 Hz, OC(*C*H_3)$_2$), 29.5 (br, Pd-CH_2-), 70.0 (s, N*C*(CH_3)$_2$), 76.8 (s, O*C*(CH_3)$_2$), 80.9 (s, OCH_2), 105.9 (br, =CH_2), 127.3-128.1(overlapping d for toluene and *m*-aryl), 131.2 (s, *p*-aryl), 132.5 (d, $^2J_{PC}$=13.8 Hz, *o*-aryl), 134.5 (d, $^1J_{PC}$ = 54.7 Hz, *ipso*-aryl), 141.0 (br, CH=), 168.8 (d, $^3J_{PC}$ = 4.0 Hz, C=N). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 115.1(s). Anal. Found : C, 52.55; H, 5.45; N, 2.55. Calcd. for $C_{23}H_{29}ClNO_2PPd$: C, 52.77; H, 5.59; N, 2.68%.

Complex [Pd(η^3-C_3H_5}(NOP^{Me2}-*N,P*)]PF_6 4: the ligand NOP^{Me2} (0.220 g, 0.65 mmol) and [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.120 g, 0.32 mmol) were dissolved in CH_2Cl_2 (20 mL). The yellow solution was stirred for 1 h at room temperature, then solid NH_4PF_6 (0.110 g, 0.67 mmol) was added and the mixture was stirred for another 3 h and filtered. The filtrate was taken to dryness under vacuum and the residue was treated with pentane (30 mL), the off-white solid thus obtained was washed with pentane (2x20 mL) and dried under vacuum to afford **4** (0.320 g, 78%). Spectroscopic data: IR(CH_2Cl_2): 1630 (s, ν(CN)) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, rom temp.): δ 1.31 (s, 6H, NC(CH_3)$_2$), 1.71 (s, 3H, OC(CH_3)(C*H*$_3$)), 1.79 (s, 3H, OC(C*H*$_3$)(CH_3)), 2.89 (d, 1H, $^3J_{HH}$ = 12.3 Hz, allylic H *cis* to P), 3.69 (d, 1H, $^3J_{HH}$ = 6.9 Hz, allylic H *cis* to P), 3.92 (dd, 1H, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 14.1 Hz allylic H *trans* to P), AB spin system: δ_A 4.32 (d, 1H, $^2J_{HH}$ = 9 Hz, OCH*H*), δ_B 4.34 (d, 1H, $^2J_{HH}$ = 9Hz, OC*H*H), 5.13 (ddd, 1H, $^3J_{HH}$ = 6.4 Hz, $^3J_{PH}$ = 9.3 Hz, $^4J_{HH}$ = 1.8 Hz, allyl H *trans* to P), 5.86 (m, 1H, -CH=), 7.42-7.53 (m, 10H, aryl). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, room temp.): δ 27.5 (s, NC(*C*H$_3$)(CH_3)), 27.7 (d, $^3J_{PC}$ = 6.3 Hz, OC(CH_3)(*C*H$_3$)), 27.8 (s, NC(CH_3)(*C*H$_3$)), 28.3 (d, $^3J_{PC}$ = 6.3Hz, OC(*C*H$_3$)(CH_3)), 55.3 (d, $^3J_{PC}$ = 3.6 Hz, allylic CH_2 *cis* to P), 69.8 (s, N*C*(CH_3)$_2$), 79.2 (d, $^3J_{PC}$ = 2.5 Hz, O*C*(CH_3)$_2$), 79.9 (d, $^3J_{PC}$ = 32.6 Hz, allylic CH_2 *trans* to P), 80.6 (s, OCH_2), 120.9 (d, $^3J_{PC}$ = 6.9 Hz, allylic CH), 129.3 (d, $^3J_{PC}$ = 11.5 Hz, *m*-aryl), 131.0 (d, $^2J_{PC}$ = 15.4 Hz, *o*-aryl), 131.6 (d, $^2J_{PC}$ = 15.9 Hz, *o*-aryl), 132.4 (d, $^4J_{PC}$ = 2.4Hz, *p*-aryl), 132.6 (d, $^4J_{PC}$ = 2.3 Hz, *p*-aryl), 133.7 (d, $^1J_{PC}$ = 53.6 Hz, ipso-aryl), 134.4 (d, $^1J_{PC}$=51.6 Hz, *ipso*-aryl), 141.0 (br, CH=), 168.8 (d, $^3J_{PC}$ = 4.0 Hz, C=N). ^{31}P{^{1}H} NMR (121.5MHz, $CDCl_3$): δ 118.3 (s, OP), -143.0 (sept, PF_6). Anal. Found : C, 43.35; H, 4.50; N, 2.20. Calcd. for $C_{23}H_{29}F_6NO_2P_2Pd$: C, 43.59; H, 4.61; N, 2.21%.

Complex [Pd{C(O)C_3H_5}Cl(NOP^{Me2}-*N,P*)] 5: CO was bubbled through a solution of **1** (0.573 g, 1.09 mmol) in toluene (50 mL) at room temperature for 1 h. After filtration and removal of the volatiles under vacuum, the residue was washed with pentane (3x20 mL) and dried under vacuum, to afford **5** as a pale-yellow powder (0.550 g, 91% yield). Spectroscopic data: IR(CH_2Cl_2): 1688 (s, ν(CO)), 1638 (s, ν(CN)) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ 1.44 (s, 6H, NC(CH_3)$_2$), 1.99 (s, 6H, OC(CH_3)$_2$), 3.26 (dt, 2H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.2 Hz, C(O)CH_2), 3.87 (s, 2H, OCH_2), 4.57 (dd, 1H, $^3J_{HH}$ = 15.2 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 1.2 Hz, =CH*H trans* to –CH=), 4.86 (dm, 1H, $^3J_{HH}$ = 10.1 Hz, =C*H*H *cis* to –CH=), 5.68 (m, 1H, -CH=), 7.41-7.46 (m, 6H, aromatic H), 7.65-7.72 (m, 4H, aromatic H). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 27.3(s, NC(*C*H_3)$_2$), 28.1 (d, $^3J_{PC}$ = 5.2 Hz, OC(*C*H_3)$_2$), 56.6 (d, $^3J_{PC}$ = 21.6 Hz, C(O)*C*H_2), 70.0 (s, N*C*(CH$_3$)$_2$), 77.5 (s, O*C*(CH$_3$)$_2$), 81.3 (s, OCH_2), 117.0 (s, =CH_2), 128.7 (d, $^3J_{PC}$ = 11.3 Hz, *m*-aryl), 131.3 (d, $^2J_{PC}$ = 14.9 Hz, *o*-aryl), 131.5 (s, *p*-aryl), 131.9 (s, -CH=), 135.1 (d, $^1J_{PC}$ = 52.8 Hz, *ipso*-aryl), 169.7 (d, $^3J_{PC}$ = 2.9 Hz, C=N), 226.7 (d, $^2J_{PC}$ = 10.0 Hz, C=O). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 100.8(s). Anal. Found : C, 52.10; H, 5.30; N, 2.45. Calcd. for $C_{24}H_{29}ClNO_3PPd$: C, 52.19; H, 5.29; N, 2.54%.

Complex [Pd{C(O)C_3H_5}Cl(NOPON^{Me2}-*N,P*)] 6: CO was bubbled through a solution of **2** (0.500 g, 0.829 mmol) in toluene (40 mL) at room temperature for 1 h. After filtration and removal of the volatiles under vacuum, the residue was washed with pentane (2x20 mL) and dried under vacuum, to afford **6** as off-white powder(0.42g, 80% yield). Spectroscopic data: IR(CH_2Cl_2): 1692 (s, ν(CO)), 1661(m, ν(CN) of uncoordinated oxazoline), 1637 (s, ν(CN) of coordinated oxazoline) cm^{-1}. ^{1}H NMR (300.13 MHz, C_6D_6, room temp.): δ 1.11 (s, 6H, NC(C*H*$_3$)(CH$_3$)), 1.26 (br s, 6H, NC(CH$_3$)(C*H*$_3$)), 1.51 (s, 6H, OC(CH$_3$)(C*H*$_3$)), 1.72 (s, 6H, OC(C*H*$_3$)(CH$_3$)), AB spin system: δ$_A$ 3.40 (2H, OCH*H*), δ$_B$ 3.43 (2H, OC*H*H), 4.01 (d, 2H, $^3J_{HH}$ = 6.9 Hz, C(O)CH_2), 5.02 (d, 2H, $^3J_{HH}$ = 11.7 Hz, =CH_2), 6.34

(m, 1H, -CH=), 7.02-7.07 (m, 3H, aromatic H), 7.86-8.13 (m, 2H, aromatic H). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6): δ 27.3-28.0 (overlapping d and s, $OC(CH_3)_2$ and $NC(CH_3)_2$), 56.3 (d, $^{3}J_{PC}$ = 25.9 Hz, $C(O)CH_2$), 68.6 (br, $NC(CH_3)_2$), 79.4 (s, $OC(CH_3)_2$), 80.0 (s, OCH_2), 116.6 (s, $=CH_2$), 129.4 (d, $^{3}J_{PC}$ = 11.1 Hz, *m*-aryl), 130.8 (d, $^{2}J_{PC}$ = 15.3 Hz, *o*-aryl), 131.3 (s, *p*-aryl), 133.5 (s, -CH=), 137.7 (d, $^{1}J_{PC}$ = 42.3 Hz, *ipso*-aryl), 167.0 (br, C=N), 221.4 (d, $^{2}J_{PC}$ = 16.8 Hz, C=O). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ 118.4(s). Anal. Found: C, 49.15; H, 6.00; N, 4.35. Calcd. for $C_{26}H_{38}ClN_2O_5PPd$: C, 49.46; H, 6.07; N, 4.44%.