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Stepwise Ethene and/or Methylacrylate/CO Insertions into the Pd-C Bond of Cationic Pd(II) Complexes Stabilized by a *(P,O)* Chelate

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EXPERIMENTAL DETAILS

Ligand*P,O* = $Ph_2PNHC(O)Me$

$[Pd(Me)(P,O)(NCMe)]PF_6$ **1**

$[Pd\{C(O)Me\}(P,O)(NCMe)]PF_6$ **2**

$[Pd\{CH_2CH_2C(O)CH_3\}(P,O)]$ **3**

$[Pd\{CH[C(O)OMe]CH_2C(O)CH_3\}(P,O)]PF_6$ **4**

$[Pd\{C(O)CH_2CH_2C(O)Me\}(P,O)]PF_6$ **5**

$[Pd\{CH_2CH_2C(O)CH_2CH_2C(O)Me\}(P,O)]PF_6$ **6**

$[Pd\{CH[C(O)OMe]CH_2C(O)CH_2CH_2C(O)Me\}(P,O)]PF_6$ **7**

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A) Synthesis and characterization of the complexes

1: Solid [PdCl(Me)(COD)] (COD = 1,5-cyclooctadiene) (1.086 g, 4.098 mmol) was added to a MeCN (300 mL) solution of $Ph_2PNHC(O)Me$ (1.004 g, 4.098 mmol), followed by addition of $TlPF_6$ (1.432 g, 4.098 mmol). The solution was stirred for 30 min, filtered and the solvent was evaporated. The residue was washed with diethylether (25 mL) and dried *in vacuo* to afford $[Pd(Me)(P,O)(NCMe)]PF_6$ **1** as a white solid (2.030 g, 90% yield). IR (CH_2Cl_2): ν_{CO} = 1614s cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2): δ = 0.76 (d, $^3J(P,H)$ = 1.8 Hz, 3H, Pd-CH_3), 2.22 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 7.42-7.66 (m, 10H, aromatic), 8.40 (broad, 1H, NH); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ = −4.0 (s, Pd-CH_3), 3.0 (s, CH_3CN), 22.4 (s, NC(O)CH_3), 119.4 (s, C_N), 128.0-133.4 (aromatic), 182.9 (d, $^{2+3}J(P,C)$ = 5 Hz, CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 79.3; elemental analysis calcd for $C_{17}H_{20}F_6N_2OP_2Pd$ (%): C 37.08, H 3.66, N 5.09; found: C 36.86, H 3.61, N 4.83.

2: CO was bubbled through a solution of **1** (0.500 g, 0.908 mmol) in CH_2Cl_2 (70 mL) at room temperature for 1 h. After filtration and removal of the volatiles under vacuum, the residue was washed with pentane (20 mL) and dried *in vacuo*, affording [Pd{C(O)Me}(*P,O*)(NCMe)]PF_6 **2** as a yellow powder (0.464 g, 88% yield). This complex can be stored for weeks in a Schlenk flask under an atmosphere of N_2 and no decomposition was observed in CH_2Cl_2 after 1 week. IR (CH_2Cl_2):n_{CO} = 1716s, 1618s cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): $d = 2.30$ (d, ^4J(P,H) = 1.5 Hz, 3H, Pd-C(O)CH_3), 2.32 (s, 3H, CH_3CN), 2.35 (d, ^4J(PH) = 1.2 Hz, 3H, NC(O)CH_3), 7.64-7.85 (m, 10H, aromatic), 10.00 (broad, 1H, NH); $^{13}C\{^1H\}$ NMR (50 MHz, CD_3CN): $d = 23.3$ (s, NC(O)*C*H_3), 37.0 (d, ^3J(P,C) = 26 Hz, PdC(O)*C*H_3), 128.7-134.0 (aromatic), 182.5 (d, ^{2+3}J(P,C) = 4 Hz, N*C*(O)CH_3), 217.0 (d, ^2J(P,C) = 4 Hz, Pd*C*(O)CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): d = 58.9; elemental analysis calcd for $C_{18}H_{20}F_6N_2O_2P_2Pd$ (%): C 37.36, H 3.48, N 4.84; found: C 37.31, H 3.72, N 4.76.

3: C_2H_4 was bubbled through a solution of **2** (0.245 g, 0.422 mmol) in CH_2Cl_2 (30 mL) at room temperature for 1.5 h. The work-up was similar to that described for **2**, affording complex $\overline{[Pd\{CH_2CH_2C(O)CH_3\}(P,O)]}$ **3** as an orange powder (0.180 g, 75% yield). Yellow crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/pentane. IR (CH_2Cl_2):n_{CO} = 1635m, 1611m cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): $d = 2.11$ (t, ^3J(H,H) = 6.1 Hz, 2H, $PdCH_2$), 2.44 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 3.24 (t, ^3J(H,H) = 6.1 Hz, 2H, $PdCH_2CH_2$), 7.59-7.91 (m, 10H, aromatic), 10.37 (broad, 1H, NH); ^1H NMR (200 MHz,

CD_2Cl_2): $\delta = 1.99$ (dt, ^3J(H,H) = 6.1 Hz, ^3J(P,H) = 1.9 Hz, 2H, $PdCH_2$), 2.33 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.03 (t, ^3J(H,H) = 6.1 Hz, 2H, $PdCH_2CH_2$), 7.22-7.72 (m, 10H, aromatic), 8.92 (broad, 1H, NH). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $\delta = 18.1$ (s, $PdCH_2$), 22.3 (d, ^3J(P,C) = 4.2 Hz, $NC(O)CH_3$), 28.2 (d, ^4J(P,C) = 2.2 Hz, $CH_2C(O)CH_3$), 51.03 (s, $PdCH_2CH_2$), 129.7-133.6 (aromatic), 183.8 (d, ^{2+3}J(P,C) = 4.9 Hz), $NC(O)CH_3$), 234.4 (d, ^3J(P,C) = 1.9 Hz, $CH_2C(O)CH_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ = 77.4; elemental analysis calcd for $C_{18}H_{21}F_6NO_2P_2Pd$ (%): C 38.22, H 3.74, N 2.48; found : C 38.33, H 3.89, N 2.51.

4: To a solution of **2** (0.545 g, 0.940 mmol) in CH_2Cl_2 (70 mL) was added 1.64 equiv of methyl acrylate (139.0 µL, 1.542 mmol). The solution was stirred for 4 h at ambient to give a yellow solution. After filtration and removal of the volatiles under vacuum the yellow residue was washed with pentane (2 x 20 mL) and dried *in vacuo* affording $[Pd\{CH[C(O)OMe]CH_2C(O)CH_3\}(P,O)]PF_6$ **4** (0.490 g, 83% yield). IR (CH_2Cl_2): ν_{CO} = 1692m, 1632m, 1601m cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 2.36$ (s, 3H, $NC(O)CH_3$), 2.57 (s, 3H, $CH_2C(O)CH_3$), 2.95 (s, 3H, OCH_3), 3.02–3.07 (m, 3H, Pd-C*H*-CH_2), 7.54-7.91 (m, 10H, aromatic), 9.86 (broad, 1H, NH); ^1H NMR (500 MHz, acetone-d_6): 2-D NMR experiments (COSY, HMBC, HSQC) and simulation with gNMR were used to determine the chemical shifts and coupling constant of the complex spin systems formed by the $CHCH_2$ protons and to distinguish the different methylene groups; $\delta = 2.45$ (d, ^4J(P,H) = 0.6 Hz, 3H, $NC(O)CH_3$), 2.61 (s, 3H, $CH_2C(O)CH_3$), 2.91 (s, 3H, OCH_3), ABCX (X = P) system for Pd-CH_b-CH_aH_c: 3.16 (ddd, $^2J(H_c,H_a)$ = 19.3 Hz, $^3J(H_a,H_b)$ = 2.4 Hz,

^4J(P,H) = 0.6 Hz, 1H, H_a), 3.22 (ddd, $^3J(H_c,H_b)$ = 6. Hz, $^3J(H_a,H_b)$ = 2.4 Hz, ^3J(P,H) = 2.3 Hz, 1H, H_b), 3.44 (dd, $^2J(H_c,H_a)$ = 19.3 Hz, $^3J(H_c,H_b)$ = 6.1 Hz, 1H, H_c), 7.67-8.08 (m, 10H, aromatic), 9.20 (broad, 1H, NH); $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): d = 22.0 (d, ^3J(P,C) = 4.1 Hz, NC(O)CH_3), 28.3 (s, $CH_2C(O)CH_3$), 33.2 (s, PdCH), 51.3 (s, C(O)OCH_3), 51.8 (PdCHCH_2), 130.3-134.8 (aromatic), 176.5 (C(O)OCH_3), 185.8 (d, ^2J(P,C) = 4.2 Hz, NC(O)CH_3), 235.8 (d, ^3J(P,C) = 2.5 Hz, $CH_2C(O)CH_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ = 81.9; elemental analysis calcd for $C_{20}H_{23}F_6NO_4P_2Pd$ (%): C 38.51, H 3.72, N 2.25; found: C 38.34, H 3.85, N 2.37.

5: Complex $[Pd\{C(O)CH_2CH_2C(O)Me\}(P,O)]PF_6$ **5** was obtained as a yellow powder, from **3** (1.800 g, 3.186 mmol) in CH_2Cl_2 (100 mL) and CO, in a similar manner to **2** (1.509 g, 79% yield). IR (CH_2Cl_2):n_{CO} = 1708s, 1657m, 1616m cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): $d = 2.39$ (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.81 (t, ^3J(H,H) = 6.0 Hz, 2H, PdC(O)CH_2), 2.96 (t, ^3J(H,H) = 6.0 Hz, 2H, CH_2C(O)CH_3), 7.63-7.88 (m, 10H, aromatic), 9.96 (broad, 1H, NH); ^{1}H NMR (500 MHz, CD_2Cl_2): $d = 2.30$ (d, ^4J(P,H) = 1 Hz, 3H, NHC(O)CH_3), 2.48 (s, 3H, $CH_2C(O)CH_3$), 2.66 (t, ^3J(H,H) = 6.0 Hz, 2H, PdC(O)CH_2), 2.84 (t, ^3J(H,H) = 6.0 Hz, 2H, CH_2C(O)CH_3), 7.45-7.75 (m, 10H, aromatic), 8.65 (broad, 1H, NH); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $d = 23.1$ (d, ^3J(P,C) = 4.2 Hz, NC(O)CH_3), 31.1 (d, ^4J(P,C) = 1.9 Hz, $CH_2C(O)CH_3$), 38.0 (s, $CH_2C(O)CH_3$), 39.2 (d, ^3J(P,C) = 24.6 Hz, PdC(O)CH_2), 129.6-133.6 (aromatic), 183.5 (d, ^{2+3}J(P,C) = 5.4 Hz, NC(O)CH_3), 214.3 (d, ^2J(P,C) = 8.8 Hz, PdC(O)), 219.6 (s, Pd(O)CCH$_2$); $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): d = 63.0; elemental analysis calcd for

$C_{19}H_{21}F_6NO_3P_2Pd \cdot 0.25\ Et_2O$ (%): C 39.24, H 3.87, N 2.29; found: C 38.89, H 4.03, N 2.27.

6: Complex $[Pd\{CH_2CH_2C(O)CH_2CH_2C(O)Me\}(P,O)]PF_6$ **6** was obtained as a yellow powder, from **5** (0.050 g, 0.084 mmol) in CH_2Cl_2 (15 mL) and C_2H_4, in a similar manner to **3** and after 1 h reaction time (0.036 g, 69% yield). IR (CH_2Cl_2): ν_{CO} = 1715m, 1630m, 1613s cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): $\delta = 2.11$ (dt, $^3J(H,H)$ = 6.0 Hz, $^3J(P,H)$ = 2.1 Hz, 2H, $PdCH_2$), 2.18 (s, 3H, $CH_2C(O)CH_3$), 2.44 (d, $^4J(P,H)$ = 0.6 Hz, 3H, $NHC(O)CH_3$), 3.00 (m, 4H, $CH_2CH_2C(O)CH_3$), 3.24 (dt, $^3J(H,H)$ = 6.0, $^4J(P,H)$ = 2.1 Hz, 2H, $PdCH_2CH_2$), 7.63-7.87 (m, 10H, aromatic), 9.92 (broad, 1H, NH); ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 1.76$ (dt, $^3J(H,H)$ = 6.0, $^3J(P,H)$ = 2.0 Hz, 2H, $PdCH_2$), 1.92 (s, 3H, $CH_2C(O)CH_3$), 2.08 (d, $^4J(P,H)$ = 0.5 Hz, 3H, $NHC(O)CH_3$), 2.65 (m, 4H, $CH_2CH_2C(O)CH_3$), 2.84 (dt, $^3J(H,H)$ = 6.0, $^4J(P,H)$ = 0.5 Hz, 2H, $PdCH_2CH_2$), 7.55-7.67 (m, 10H, aromatic), 8.81 (broad, 1H, NH); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $\delta = 18.4$ (s, $PdCH_2CH_2$), 22.3 (d, $^3J(P,C)$ = 4.2 Hz, $NC(O)CH_3$), 29.5 (s, $CH_2C(O)CH_3$), 34.5 (s) and 38.3 (s, $C(O)CH_2CH_2C(O)$), 50.4 (s, $PdCH_2$), 128.3-133.6 (aromatic), 183.8 (d, $^2J(P,C)$ = 4.8 Hz, $NC(O)CH_3$), 206.6 (s, $CH_2C(O)CH_3$), 235.0 (s, $CH_2C(O)CH_2$); $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ = 77.5; elemental analysis calcd for $C_{21}H_{25}F_6NO_3P_2Pd$ (%): C 40.57, H 4.05, N 2.25; found: C 40.36, H 4.09, N 2.15.

7: Complex $[Pd\{CH[C(O)OMe]CH_2C(O)CH_2CH_2C(O)Me\}(P,O)]PF_6$ **7** was prepared from **5** (0.780 g, 1.311 mmol) and 1.2 equiv of methyl acrylate (141 µL, 1.573 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was stirred at ambient temperature for 16 h, under an

atmosphere of CO. The solution was then filtered, and the volatiles were removed under vacuum to leave a yellow powder (0.670 g, 75% yield). IR (CH_2Cl_2):n_{CO} = 1714s, 1700s, 1631m, 1601s cm^{-1};. ^1H NMR (500 MHz, acetone-d_6): 2-D NMR experiments (COSY, HMBC, HSQC) and simulation with gNMR were used to determine the chemical shifts and coupling constants of the complex spin systems formed by the $CHCH_2$ and CH_2CH_2 protons and to distinguish the different methylene groups; d = 2.19 (s, 3H, $CH_2C(O)CH_3$), 2.44 (s, 3H, $NC(O)CH_3$), 2.92 (s, 3H, OMe), ABCD spin system for $C(O)CH_cH_dCH_aH_bC(O)CH_3$: 2.96 (ddd, $^2J(H_a,H_b)$ = 20.3 Hz, $^3J(H_a,H_c)$ = 7.0 Hz, $^3J(H_a,H_d)$ = 5.2 Hz, 1H, H_a), 3.00 (ddd, $^2J(H_a,H_b)$ = 20.3 Hz, $^3J(H_b,H_c)$ = 4.7 Hz, $^3J(H_b,H_d)$ = 7.7 Hz, 1H, H_b), 3.10 (ddd, $^3J(H_c,H_a)$ = 7.0 Hz, $^3J(H_c,H_b)$ = 4.7 Hz, $^2J(H_c,H_d)$ = 18.5 Hz, 1H, H_c), 3.20 (ddd, $^2J(H_d,H_c)$ = 18.5 Hz, $^3J(H_d,H_b)$ = 7.7 Hz, $^3J(H_d,H_a)$ = 5.2 Hz, 1H, H_d), ABCX (X = P) spin system for Pd-CH_b-CH_aH_c: 3.20 (ddd, $^2J(H_c,H_a)$ = 19.0 Hz, $^3J(H_a,H_b)$ = 2.6 Hz, 1H, H_a), 3.24 (ddd, $^3J(H_c,H_b)$ = 6.0 Hz, $^3J(H_a,H_b)$ = 2.6, $^3J(P,H)$ = 2.0 Hz, 1H, H_b), 3.42 (dd, $^3J(H_c,H_a)$ = 6.0 Hz, $^2J(H_c,H_b)$ = 19.0 Hz, 1H, H_c), 7.67-8.09 (m, 10H, aromatic), 10.54 (broad, 1H, NH); $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): d = 21.7 (d, $^3J(P,C)$ = 4.8 Hz, $NC(O)CH_3$), 29.6 (s, $CH_2C(O)CH_3$), 33.0 (s, PdCH), 35.4 (d, $^4J(P,C)$ = 1.9 Hz, $CH_2CH_2C(O)CH_3$), 37.7 (s, $CH_2C(O)CH_3$), 50.9 (s, $PdCHCH_2$), 51.2 (s, $C(O)OCH_3$), 128.3-133.6 (aromatic), 176.2 (s, $C(O)OCH_3$), 185.6 (d, $^{2+3}J(P,C)$ = 3.8 Hz, $NC(O)CH_3$), 210.0 (s, $CH_2C(O)CH_3$), 236.3 (d, $^3J(P,C)$ = 1.9 Hz, $CH_2C(O)CH_2$); $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): d = 81.6; FAB-MS: m/z: 534 (27%) $[M^+]$; elemental analysis calcd for $C_{23}H_{27}F_6NO_5P_2Pd$ (%): C 40.64, H 4.00, N 2.06; found: C 41.04, H 4.16 , N 2.04 .

B) X-ray data for complex (3)

Crystal structure data for $[Pd\{CH_2CH_2C(O)CH_3\}(P,O)]$ **3**: $C_{18}H_{21}F_6NO_2P_2Pd$; M = 565.71, monoclinic, $P1\ 2_1/n\ 1$, a = 8.6887(2), b = 18.822(1), c = 13.0904(6) Å, b = 100.983(3)°, V = 2101.6(3) Å^3, Z = 4, D_C = 1.79 gcm^{-3}, m = 1.103 mm^{-1}, $F(000)$ = 1128, $l(Mo_{K\alpha})$ = 0.71073 Å, T = 173 K. Red crystal, dimensions 0.20 ∞ 0.15 ∞ 0.15 mm^3. A total of 12017 reflections were collected on Kappa CCD diffractometer (phi scans, 2°<q<29°). The structure was solved using direct methods and refined against |F|. Absorption corrections were computed from the psi scans of four reflections. For all computations the Nonius MoLEN package was used: R = 0.041, Rw = 0.059, GOF = 1.049, maximum residual electron density 0.801 eÅ^{-3} for 4413 reflections having I>3σ(I). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced as fixed contributors (($d_{C\text{-}H}$ = 0.95 Å, B_H = 1.3B_{equiv}(C)Å^2).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-136484. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2^1EZ, UK (fax: (+44)^1223-336-033; e-mail: deposit<?@>ccdc.cam.ac.uk).

Table 1: X-ray experimental data for **3**

Formula	: $C_{18}H_{21}F_6NO_2P_2Pd$
Molecular weight	: 565.71
Crystal system	: monoclinic
Space group	: P 1 2_1/n 1
a(Å)	: 8.6887(2)
b(Å)	: 18.822(1)
c(Å)	: 13.0904(6)
β(deg)	: 100.983(3)
V($Å^3$)	: 2101.6(3)
Z	: 4
Color	: colorless
Crystal dim(mm)	: 0.20 x 0.15 x 0.15
Dcalc(gcm^{-3})	: 1.79
F(000)	: 1128
μ(mm^{-1})	: 1.103
Temperature(K)	: 173
Wavelength(Å)	: 0.71073
Radiation	: MoKα graphite monochromated
Diffractometer	: KappaCCD
Scan mode	: phi scans
hkl limits	: 0,9/0,28/-19,19
Theta limits(deg)	: 2.5/32.61
Number of data meas.	: 12017
Number of data with I > 3 σ(I)	: 4413
Weighting scheme	: $4Fo^2/(s^2(Fo^2) + 0.0064\ Fo^4)$
Number of variables	: 271
R	: 0.041
Rw	: 0.059
GOF	: 1.049
Largest peak in final difference ($eÅ^{-3}$)	: 0.801