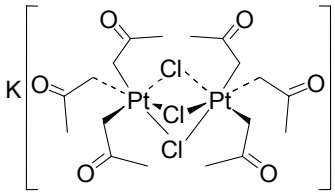
Supplementary Material (ESI) for Chemical Communications

Supplementary Information

An unprecedented process involving normal and redox transmetallation reactions between Hg and Pt affording the unexpected $K[Pt^{IV}_2\{CH_2C(O)Me\}_6(\mu\text{–}Cl)_3]$ complex: the key role of X-ray powder diffraction in unravelling its nature and structure

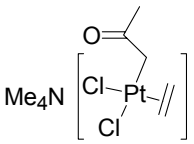
José Vicente,* Aurelia Arcas, Jesús M. Fernández-Hernández, Angelo Sironi, and Norberto Masciocchi

Experimental details for the preparation of



1

and



2'

^{1}H NMR spectrum of the 1:1 reaction mixture after 15 min in d^6-acetone

Synthesis of $K[Pt_2\{CH_2C(O)Me\}_6(\mu\text{–}Cl)_3]$ (1). To a solution of Zeise's salt, $K[PtCl_3(CH_2{=}CH_2)]$ (250 mg, 0.678 mmol), in acetone (10 mL), $[Hg\{CH_2C(O)Me\}_2]$ (430 mg, 1.366 mmol) was added. The reaction mixture was stirred for 20 h at room temperature and the solvent was removed. The grey solid obtained was washed with CH_2Cl_2 (3 x 5 mL) and the residue was suspended in MeCN (10 mL) and refluxed for 40 min. The hot suspension was filtered through Celite and the yellow filtrate was concentrated until a solid precipitated. Addition of Et_2O (5 mL) gave more precipitate. The suspension was filtered off and the solid was recrystallized from MeCN/Et_2O to give **1** as a colourless microcrystalline solid. Yield: 102 mg, 0.253 mmol, 74%. Mp : 200 °C (dec). Λ_M (acetone, 5 x 10^{-4} M): 106 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=O) 1689, ν(Pt-Cl) 245. ^{1}H NMR (400 MHz, *d_6*-acetone): δ 3.20 (s, 2 H, CH_2, $^2J_{HPt}$ = 103 Hz), 2.12 (s, 3 H, Me). ^{13}C-APT NMR (50.30 MHz, *d_6*-acetone): δ 210 (s, CO), 32.9 (s, Me), 25.8. (s, CH_2, $^1J_{CPt}$ = 657 Hz). ^{95}Pt{^{1}H} (86.18 MHz, *d_6*-acetone, ref. $Na_2[PtCl_6]$): δ -1743 (s). Crystals for the X-ray diffraction study were grown by slow diffusion of Et_2O into an MeCN solution of **1**. ESI-MS(-): 839 $[M\text{-}K^+]^-$; 437 $[Pt(CH_2C(O)Me)_3Cl_2]^-$. Anal. Calcd for $C_{18}H_{30}Cl_3KO_6Pt_2$: C, 24.62; H, 3.44. Found: C, 24.62; H, 3.44.

Synthesis of $Me_4N[Pt\{CH_2C(O)Me\}Cl_2(CH_2{=}CH_2)]$ (2'). To a solution of $K[PtCl_3(CH_2{=}CH_2)]$ (610 mg, 1.65 mmol), in acetone (17 mL), Me_4NCl (340 mg, 3.1 mmol) and $[Hg\{CH_2C(O)Me\}_2]$ (280 mg, 0.889 mmol) were successively added. The reaction mixture was stirred at room temperature for 6.5 h and the solvent was removed. The grey residue obtained was suspended in CH_2Cl_2 (10 mL) and the suspension was filtered through Celite. The yellow filtrate was concentrated (*ca.* 2 mL) and addition of Et_2O (3 x 5 mL) gave a suspension, which was filtered, and the solid was air-dried to

give **2'** as a pale yellow solid. Yield: 580 mg, 1.36 mmol, 83%. Mp: 72°C. Λ_M (acetone, 5 x 10^{-4} M): 114 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=O) 1647, ν(C–N), Me_4N) 947, ν(Pt-Cl) 311, 276. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.94 (bs, 4 H, CH_2=CH_2, $^2J_{HPt}$ = 67.8 Hz), 3.44 (s, 12 H, NMe_4), 2.43 (s, 2 H, Pt*CH*$_2$, $^2J_{HPt}$ = 106.8 Hz), 2.23 (s, 3 H, *Me*C(O)). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$): δ 213.4 (s, CO, $^2J_{CPt}$ = 46 Hz), 64.91. (s, CH_2=CH_2, $^1J_{CPt}$ = 230 Hz), 56.4 (t {1:1:1}, Me_4N, $^1J_{NC}$ = 4 Hz), 31.0 (s, *Me*C(O)), 22.1 (s, Pt*CH*$_2$, $^1J_{CPt}$ = 619 Hz). (400 MHz, acetona-d_6): 3.73 (bs, etileno, $^2J_{HPt}$ = 66.7 Hz), 3.45 (s, 12 H, NMe_4), 2.34 (s, 2 H, MeC(O)*CH*$_2$, $^2J_{HPt}$ = 106.5 Hz), 2.10 (s, 3 H, *Me*C(O)CH_2) ^{195}Pt{^{1}H} (86.18 MHz, $CDCl_3$, ref. $Na_2[PtCl_6]$): -3378.6 (s). Anal. Calcd for $C_9H_{21}Cl_2O_1Pt$: C, 25.42; H, 4.98; N, 3.29. Found: C, 25.49; H, 4.95; N, 3.16.

^{1}H NMR spectrum of the 1:1 reaction mixture after 15 min in d^6-acetone