The First Family of Platinum(IV) Acetonyl Complexes. Mono-, Bis-, and Tris(acetonyl) Derivatives†

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[Hg{$CH_2C(O)Me$}$_2$] and K[$PtCl_3(C_2H_4)$] react (2:1 molar ratio) to give K[Pt_2{$CH_2C(O)Me$}$_6(\mu$-Cl)$_3$] (**1**·K) through the intermediate K[Pt{$CH_2C(O)Me$}$Cl_2(\eta^2$-CH_2═CH_2)] (**2**·K). The anionic complex **1** has been also obtained as the [K(18-C-6)]$^+$ salt (**1**·C) by reacting **1**·K with 18-crown-6, and **2** has been isolated as the Me_4N salt (**2**·NMe_4) by reacting [Hg{$CH_2C(O)Me$}$_2$] and K[$PtCl_3(C_2H_4)$] (1:2) in the presence of an excess of $(Me_4N)Cl$. The tris(acetonyl) Pt(IV) complexes *fac*-$(PPN)_2$[Pt{$CH_2C(O)Me$}$_3$-Cl_3] (**3**), *fac*-[Pt{$CH_2C(O)Me$}$_3$(Cl)L_2] (L = ^{t}BuNC (**4**), XyNC (**5**; Xy = $C_6H_3Me_2$-2,6)), and *fac*-[Pt-{$CH_2C(O)Me$}$_3$Cl(N∧N)] (N∧N = bpy (**6**), phen (**7**)) have been obtained by reacting **1**·K with (PPN)Cl, L, and N∧N, respectively, and *fac*-[Pt{$CH_2C(O)Me$}$_3$(CN^tBu)(bpy)]OTf (**8**) was obtained from **6**, TlTfO, and ^{t}BuNC. The mono(acetonyl) complex *mer*-[Pt{$CH_2C(O)Me$}Cl_3(bpy)] (**9**) and the bis(acetonyl) Pt-(IV) derivatives [*OC*-6-13]-[Pt{$CH_2C(O)Me$}$_2Cl_2$(bpy)] (**10**) and [*OC*-6-43]-[Pt{$CH_2C(O)Me$}$_2$(Me)I-(bpy)] (**11**) have been obtained by reacting [Pt{$CH_2C(O)Me$}Cl(bpy)] with $PhICl_2$ and by reacting [Pt{$CH_2C(O)Me$}$_2$(bpy)] with $PhICl_2$ and MeI, respectively. Room-temperature isomerization of **11** gives [*OC*-6-34]-[Pt{$CH_2C(O)Me$}$_2$(Me)I(bpy)] (**12**). The first mixed ketonylmetal complex, [*OC*-6-33]-[Pt-{$CH_2C(O)Me$}$_2${$CH_2C(O)Ph$}Br(bpy)] (**13**), has been obtained by reacting [Pt{$CH_2C(O)Me$}$_2$(bpy)] with $PhC(O)CH_2Br$. The crystal structures of **1**·C, **6**, **8**, and **9** have been determined.

Introduction

We are interested in the synthesis of ketonylmetal complexes, M−$CH_2C(O)R$ (R = hydrocarbyl),[1,2] because they are involved in important organic reactions.[3] The chemistry of ketonyl Pt-(IV) complexes is poorly developed, and none of the few reported complexes has been characterized by X-ray diffraction studies.[4] Only the monoketonyl complexes [Pt{$CH_2C(O)Ph$}-$Me_2(X)(N∧N)]^{n+}$ (N∧N = 2,9-dimethyl-1,10-phenanthroline; X = Br, I, n = 0; X = MeCN, n = 1), (NH_4)[Pt{$CH_2C(O)$-Me}$Cl_4(NH_3)$], and K_2[Pt{$CH_2C(O)Me$}Cl_5] have been obtained respectively by reacting [$PtMe_2L_2$] with $XCH_2C(O)Ph$,[5] by light irradiation of a $[PtCl_6]^{2-}$solution in acetone (no isolated yield was reported),[6] and by reacting $K_2[PtCl_4]$ with iodoacetone in water.[7,8]

We are involved in the study of the reactivity of organomercury complexes as transmetalating agents.[9−12] In this context, using [Hg{$CH_2C(O)Me$}$_2$] as the transmetalating agent, we have reported the synthesis of the simple (acetonyl)palladium(II) complex [Pd{$CH_2C(O)Me$}Cl]$_n$, which has allowed us to prepare a variety of mono(acetonyl)palladium(II) complexes and the first complexes containing the chelating $\kappa^2(C,O)$-C(NHR)═CHC(O)Me (R = ^{t}Bu, Xy) ligand, resulting from the insertion of isocyanide into the Pd−$CH_2C(O)Me$ bond and a subsequent β-ketoimine to β-ketoenamine tautomerization process.[11,13] Here we describe the reaction between [Hg{$CH_2C(O)Me$}$_2$] and K[$PtCl_3(C_2H_4)$] to give the tris(acetonyl)platinum(IV) complex

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$K[Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$, the crystal structure of which has been solved by X-ray powder diffraction. This process represents the first example of the use of a reagent in successive transmetalation and redox reactions, and the complex itself is the first fully characterized ketonyl Pt(IV) complex, the first diplatinum(IV) complex containing three bridging halo ligands, and the first tris(ketonyl)metal complex ever isolated. An intermediate Pt(II) acetonyl complex, $[Pt\{CH_2C(O)Me\}Cl_2(C_2H_4)]^-$, has been detected and isolated as the Me_4N salt. These results have been the subject of a preliminary communication.[10] In this paper we report (i) full details of the aforementioned reaction and the synthesis and single-crystal X-ray diffraction study of $[K(18\text{-}C\text{-}6)][Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$ (18-C-6 = 18-crown-6), whose data confirm those obtained for the anion in an X-ray powder diffraction study of $K[Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$, (ii) the synthesis of the first family of tris(ketonyl) Pt(IV) complexes, including neutral, anionic, and cationic derivatives, (iii) the synthesis, through oxidative addition reactions, of mono(acetonyl), the first bis(ketonyl), and additional members of the new family of tris(acetonyl) Pt(IV) complexes, and (iv) the first X-ray single-crystal structures of ketonyl Pt(IV) complexes.

Experimental Section

The reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Molar conductivities were measured on ca. 5×10^{-4} mol L^{-1} acetone solution with a Crison Micro CM2200 conductimeter. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets or KBr pellets. NMR spectra were recorded on Varian Unity 300, Bruker AC 200, Avance 300 and 400, and Bruker 600 spectrometers at room temperature. Chemical shifts are referenced to TMS (^1H, ^{13}C), H_3PO_4 (^{31}P), or Na_2PtCl_6 (^{195}Pt). When needed, NMR assignments were performed with the help of APT, DEPT, COSY, and one-dimensional NOE experiments and HETCOR techniques. $[Hg\{CH_2C(O)Me\}_2]$,[14] $K[PtCl_3(C_2H_4)]$,[15] $[Pt\{CH_2C(O)Me\}_2(bpy)]$, $[Pt\{CH_2C(O)Me\}Cl(bpy)]$,[2] and $PhICl_2$[16] were prepared according to literature methods.

Synthesis of $K[Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$ (1·K). To a solution of $K[PtCl_3(C_2H_4)]$ (250 mg, 0.68 mmol) in acetone (10 mL) was added $[Hg\{CH_2C(O)Me\}_2]$ (430 mg, 1.37 mmol). The resulting suspension was stirred for 20 h at room temperature and then concentrated to dryness. The resulting gray solid was washed with CH_2Cl_2 (3×5 mL) and refluxed for 40 min in MeCN (10 mL), and the hot suspension was filtered through Celite. The yellow filtrate was concentrated until a colorless solid started to precipitate. Et_2O (5 mL) was added, the suspension was filtered off, and the solid was recrystallized from MeCN/Et_2O to give **1** as a colorless microcrystalline solid. Yield: 102 mg, 74%. Mp: 200 °C dec. Λ_M (acetone, 5×10^{-4} mol L^{-1}): 106 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(CO) 1689, ν(PtCl) 245. ^1H NMR (400 MHz, d_6-acetone): δ 3.20 (s, 2 H, CH_2, $^2J_{HPt}$ = 103 Hz), 2.12 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (50.30 MHz, d_6-acetone): δ 210 (CO), 32.9 (Me), 25.8 (CH_2, $^1J_{CPt}$ = 657 Hz). $^{95}Pt\{^1H\}$ (85.88 MHz, d_6-acetone): δ −1743 (s). ESI-MS (−): *m/z* 839 $[M - K^+]^-$; 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 $[K(18\text{-}C\text{-}6)][Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$ (1·C). To a suspension of **1**·K (35 mg, 0.04 mmol) in acetone (2 mL) was added 18-C-6 (16 mg, 0.06 mmol). The resulting solution was filtered through Celite, and the filtrate was concentrated to dryness. The residue was stirred with Et_2O (10 mL) for 15 min at 0 °C, the suspension was filtered, and the solid was air-dried to give **1·C** as a colorless solid. Yield: 36 mg, 80%. Mp: 148 °C. Λ_M (acetone, 4.11×10^{-4} mol L^{-1}): 83 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(CO) 1682; ν(PtCl) 250, 232. ^1H NMR (300 MHz, d_6-acetone): δ 3.66 (s, 24 H, CH_2, 18-C-6), 3.19 (s, 12 H, CH_2, $^2J_{HPt}$ = 103 Hz), 2.12 (s, 18 H, Me). $^{13}C\{^1H\}$ NMR (200 MHz, d_6-acetone): δ 210.9 (CO, $^2J_{CPt}$ = 48 Hz), 71.8 (CH_2, 18-C-6), 33.9 (Me), 26.8 (CH_2 $^1J_{CPt}$ = 657 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): −1730 (s). Anal. Calcd for $C_{30}H_{54}Cl_3KO_{12}Pt_2$: C, 31.54; H, 4.76. Found: C, 31.81; H, 4.74. Single crystals of **1·C** were obtained by slow diffusion of Et_2O into an acetone solution of **1·C**.

Synthesis of *cis*-$(Me_4N)[Pt\{CH_2C(O)Me\}Cl_2(C_2H_4)]$ (2·NMe_4). To a solution of $K[PtCl_3(C_2H_4)]$ (610 mg, 1.65 mmol) in acetone (17 mL) were added $(Me_4N)Cl$ (340 mg, 3.1 mmol) and $[Hg\{CH_2C(O)Me\}_2]$ (280 mg, 0.89 mmol). The suspension was stirred for 6.5 h and then was concentrated to dryness. The residue was stirred in CH_2Cl_2 (10 mL), the suspension was filtered through Celite, and the filtrate was concentrated to ca. 2 mL. The addition of Et_2O (10 mL) gave a suspension, which was filtered, and the solid was air-dried to give **2·NMe_4** as a pale yellow solid. Yield: 580 mg, 83%. Mp: 72 °C. Λ_M (acetone, 5×10^{-4} mol L^{-1}): 114 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(CO) 1647, ν(CN) 947, ν(PtCl) 311, 264. ^1H NMR (400 MHz, d_6-acetone): δ 3.73 (br, C_2H_4, $^2J_{HPt}$ = 66.7 Hz), 3.45 (s, 12 H, NMe_4), 2.34 (s, 2 H, Pt*CH*$_2$, $^2J_{HPt}$ = 106.5 Hz), 2.10 (s, 3 H, *Me*CO). ^1H NMR (400 MHz, $CDCl_3$): δ 3.94 (br, 4 H, C_2H_4, $^2J_{HPt}$ = 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*CO). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 213.4 (s, CO, $^2J_{CPt}$ = 46 Hz), 64.91 (C_2H_4, $^1J_{CPt}$ = 230 Hz), 56.4 (t {1:1:1}, Me_4N, $^1J_{NC}$ = 4 Hz), 31.0 (s, *Me*CO), 22.1 (s, Pt*CH2*, $^1J_{CPt}$ = 619 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ -3378.6 (s). Anal. Calcd for $C_9H_{21}Cl_2OPt$: C, 25.42; H, 4.98; N, 3.29. Found: C, 25.49; H, 4.95; N, 3.16.

Synthesis of *fac*-$(PPN)_2[Pt\{CH_2C(O)Me\}_3Cl_3]$ (3). To a suspension of **1·K** (23.7 mg, 0.03 mmol) in CH_2Cl_2 (3 mL) was added (PPN)Cl (62 mg, 0.11 mmol). After 10 min of stirring, the suspension was filtered through Celite and the filtrate was concentrated (1 mL). Addition of Et_2O (10 mL) gave a suspension which was stirred for 1 h in a water/ice bath and filtered off. The colorless solid was washed with Et_2O (5 mL) and air-dried to give **3**. Yield: 70 mg, 84%. Mp: 158 °C. Λ_M (acetone, 3.87×10^{-4} mol L^{-1}): 208 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(CO) 1665, ν(PtCl) 265, 241(br). ^1H NMR (300 MHz, $CDCl_3$): δ 7.71−7.40 (m, 60 H, PPN), 3.30 (s, 6 H, CH_2, $^2J_{HPt}$ = 102 Hz), 2.19 (s, 9 H, Me). $^{13}C\{^1H\}$ NMR (50.30 MHz, $CDCl_3$): δ 211.9 (CO, $^2J_{CPt}$ = 48 Hz), 133.9 (m, PPN, C_p), 131.9 (m, PPN, C_m), 129.5 (m, PPN, C_o), 126.7 (dd, PPN, C_{ipso}, $^1J_{CP}$ = 108 Hz, $^3J_{CP}$ = 1.7 Hz), 32.9 (Me), 25.4 (CH_2, $^1J_{CPt}$ = 651 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 21.1. $^{195}Pt\{^1H\}$ NMR (86.50 MHz, $CDCl_3$): δ −1739. Anal. Calcd for $C_{81}H_{75}Cl_3N_2O_3P_4Pt$: C, 62.77; H, 4.88; N, 1.81. Found: C, 62.57; H, 4.90; N, 1.91.

Synthesis of *fac*-$[Pt\{CH_2C(O)Me\}_3Cl(CN^tBu)_2]$ (4). To a suspension of **1·K** (36 mg, 0.04 mmol) in acetone (3 mL) was added ^{t}BuNC (30 μL, 0.26 mmol). The reaction mixture was stirred for 5 h and filtered through Celite. The filtrate was concentrated to give a pale yellow oil that was washed with *n*-pentane (3 mL) and vacuum-dried for 24 h to give **4** as a pale yellow solid. Yield: 30 mg, 64%. Mp: 74−80 °C. IR (Nujol, cm^{-1}): ν(CN) 2242, 2227, ν(CO) 1681, ν(PtCl) 271. ^1H NMR (400 MHz, $CDCl_3$): δ 3.04 (d, 2 H, CH_2, $^2J_{HH}$ = 7.0 Hz, $^2J_{HPt}$ = 91.7 Hz), 2.98 (s, 2 H, CH_2 trans to Cl, $^2J_{HPt}$ = 89.8 Hz), 2.27 (s, 6 H, *Me*C(O) trans to ^{t}BuNC), 2.26 (d, 2 H, CH_2 trans to ^{t}BuNC, $^2J_{HH}$ = 7.0 Hz, $^2J_{HPt}$ = 67.5 Hz), 2.23 (s, 3 H, *Me*C(O), $^3J_{HPt}$ = 4.8 Hz), 1.57 (s, 18 H, C*Me*$_3$).

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$^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): δ 213.8 (CO trans to ^{t}BuNC, $^2J_{CPt}$= 33 Hz), 211.3 (CO, $^2J_{CPt}$ = 42 Hz), 117.1 (t {1:1:1}, CN, $^1J_{CN}$ = 18 Hz, $^1J_{CPt}$ = 816 Hz), 58.8 (*C*$(Me)_3$), 31.4 (*Me*C(O) trans to ^{t}BuNC), 31.1 (*Me*C(O) trans to Cl), 29.9 (CH_2 trans to ^{t}BuNC, $^1J_{CPt}$ = 463 Hz), 29.6 (C*Me*$_3$), 25.9 (CH_2 trans to Cl, $^1J_{CPt}$ = 548.0 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ -3343 (q, {1:2:3:2:1}, $^2J_{NPt}$ = 22 Hz). Anal. Calcd for $C_{19}H_{33}ClN_2O_3Pt$: C, 40.18; H, 5.86; N, 4.93. Found: C, 39.83; H, 5.87; N, 5.03.

Synthesis of *fac*-[Pt{$CH_2C(O)Me$}$_3$Cl(CNXy)$_2$] (5). To a suspension of **1·K** (33 mg, 0.04 mmol) in acetone (3 mL) was added XyNC (27 mg, 0.20 mmol). The reaction mixture was stirred for 5 h and filtered through Celite. The filtrate was concentrated to dryness to give a yellow oil which was washed with *n*-pentane (2 × 5 mL) and vacuum-dried for 24 h, to give **5** as a pale yellow oil. Yield: 40 mg, 81%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 2 H, CH, Xy), 7.12 (m, 4 H, CH, Xy), 3.25 (s, 2 H, CH_2 trans to Cl, $^2J_{HPt}$ = 85.3 Hz), 3.23 (d, 2 H, CH_2 trans to XyNC, $^2J_{HH}$ = 7.5 Hz, $^2J_{HPt}$ = 85.3 Hz), 2.52 (d, 2 H, CH_2 trans to XyNC, $^2J_{HH}$ = 7.5 Hz, $^2J_{HPt}$ = 68.7 Hz), 2.49 (s, 12 H, Me, Xy), 2.33 (s, 3 H, *Me*C(O), $^4J_{HPt}$ = 5.3 Hz), 2.26 (s, 6 H, *Me*C(O)). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 213.8 (CO, trans to XyNC, $^2J_{CPt}$ = 33 Hz), 211.4 (CO, trans to Cl, $^2J_{CPt}$ = 42 Hz), 136.5 (C, Xy), 130.5 (CH, Xy), 128.9 (t, {1:1:1}, XyN*C*), 128.1 (CH, Xy), 125.0 (br, C, Xy), 31.4 (*Me*C-(O) trans to XyNC), 30.8 (*Me*C(O) trans to Cl, $^3J_{CPt}$ = 8 Hz), 30.0 (CH_2 trans to XyNC, $^1J_{CPt}$ = 468 Hz), 26.8 (CH_2 trans to Cl, $^1J_{CPt}$ = 565 Hz), 18.4 (Me, Xy). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −3307 (br). Anal. Calcd for $C_{27}H_{33}ClN_2O_3Pt$: C, 48.83; H, 5.01; N, 4.22. Found: C, 48.70; H, 4.79; N, 4.13.

Synthesis of *fac*-[Pt{$CH_2C(O)Me$}$_3$Cl(bpy)] (6). Method a. To a suspension of **1·K** (40 mg, 0.05 mmol) in acetone (5 mL) was added bpy (28 mg, 0.18 mmol), and the mixture was stirred for 6 h and filtered. The filtrate was concentrated (0.5 mL), and addition of Et_2O (10 mL) gave a suspension, which was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give **6**. Yield: 43 mg, 85%.

Method b. To a suspension of [Pt{$CH_2C(O)Me$}$_2$(bpy)] (205 mg, 0.45 mmol) in acetone (40 mL) was added [HgCl{$CH_2C(O)$-Me}] (150 mg, 0.51 mmol), and the reaction mixture was refluxed for 24 h. The resulting suspension was filtered through Celite, the filtrate was concentrated (3 mL), and Et_2O (20 mL) was added. The suspension was filtered, and the solid was recrystallized from CH_2Cl_2/Et_2O to give **6** as a yellow solid. Yield: 130 mg, 50%.

Method c. To a solution of [Pt{$CH_2C(O)Me$}$_2$(bpy)] (93 mg, 0.20 mmol) in CH_2Cl_2 (7 mL) was added chloroacetone (0.5 mL, 6.20 mmol). The mixture was stirred at 90 °C for 62 h in a Carius tube and, after cooling, filtered through Celite. The filtrate was concentrated (2 mL), and addition of Et_2O (15 mL) gave a suspension that was filtered off, washed with Et_2O (5 mL), and air-dried to give complex **6** as a yellow solid. Yield: 80 mg, 73%. Mp: 192−195 °C. IR (Nujol, cm^{-1}): ν(CO) 1675, 1636; ν(PtCl) 273. ^1H NMR (400 MHz, $CDCl_3$): δ 9.60−9.55 (m, 2 H, bpy), 8.20 (m, 2 H, bpy), 8.10−8.06 (m, 2 H, bpy), 7.74−7.71 (m, 2 H, bpy), 3.62 (H_A, AB system, 2 H, CH_2 trans to bpy, $^2J_{H_AH_B}$ = 8.8 Hz, $^2J_{H_APt}$ = 93 Hz), 3.56 (H_B, AB system, 2 H, CH_2 trans to bpy, $^2J_{H_BH_A}$ = 8.8 Hz, $^2J_{H_BPt}$ = 97 Hz), 2.57 (s, 3 H, CH_2 trans to Cl, $^2J_{HPt}$ = 91.6 Hz), 2.27 (s, 3 H, Me trans to bpy), 1.31 (s, 3 H, Me trans to Cl). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 214.2 (Me*C*(*O*)CH_2, $^2J_{CPt}$ = 30 Hz), 210.0 (Me*C*(*O*)CH_2, $^2J_{CPt}$ = 45.2 Hz), 155.0 (C, bpy), 149.7 (CH, bpy, J_{CPt} = 15 Hz), 139.8 (CH, bpy), 127.3 (CH, bpy, J_{CPt} = 17 Hz), 123.7 (CH, bpy, J_{CPt} = 11 Hz), 33.7 (*Me*C(O) trans to bpy), 31.4 (*Me*C(O) trans to Cl), 24.6 (CH_2 trans to Cl, J_{CPt} = 585 Hz), 19.9 (CH_2 trans to bpy, $^1J_{CPt}$ = 581 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −2012 (s). Anal. Calcd for $C_{19}H_{23}ClN_2O_3Pt$: C, 40.90; H, 4.16; N, 5.02. Found: C, 40.63; H, 4.19; N, 5.05. Single crystals of **3** were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **3**.

Synthesis of *fac*-[Pt{$CH_2C(O)Me$}$_3$Cl(phen)] (7). To a suspension of **1·K** (32 mg, 0.04 mmol) in acetone (4 mL) was added phen·H_2O (29 mg, 0.14 mmol), and the mixture was stirred for 6 h and then filtered through Celite. The filtrate was concentrated (1 mL), Et_2O (10 mL) was added, and the resulting suspension was stirred in a water/ice bath. The suspension was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give **7** as a yellow solid. Yield: 32 mg, 75%. Mp: 167 °C. IR (Nujol, cm^{-1}): ν(CO) 1669, ν(PtCl) 265. ^1H NMR (400 MHz, $CDCl_3$): δ 9.89 (dd, 2 H, CH, phen, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.3 Hz), 8.55 (dd, 2 H, CH, phen, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.3 Hz), 8.03 (dd, 2 H, CH, phen, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 5.2 Hz), 8.01 (s, 2 H, CH, phen), 3.75 (H_A, AB system, 2 H, CH_2 trans to phen, $^2J_{H_AH_B}$ = 8.5 Hz, $^2J_{H_APt}$ = 92.7 Hz), 3.69 (H_A, AB system, 2 H, CH_2, $^2J_{H_AH_B}$ = 8.5 Hz, $^2J_{H_BPt}$ = 98.2 Hz), 2.66 (s, 2 H, CH_2 trans to Cl, $^2J_{HPt}$ = 92.1 Hz), 2.33 (s, 6 H, Me trans to phen), 1.08 (s, 3 H, Me trans to Cl). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 214 (CO trans to phen, $^2J_{CPt}$ = 33 Hz), 210.0 (CO trans to Cl, $^2J_{CPt}$ = 31 Hz), 150.1 (CH, phen, J_{CPt} = 15 Hz), 146.2 (C, phen), 138.8 (CH, phen), 131.1 (C, phen, J_{CPt} = 10 Hz), 127.7 (CH, phen), 125.9 (CH, phen, J_{CPt} = 17 Hz), 33.8 (Me trans to phen), 31.2 (Me trans to Cl), 24.4 (CH_2 trans to Cl, $^1J_{CPt}$ = 584 Hz), 19.9 (CH_2 trans to phen, $^1J_{CPt}$ = 586 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −2017. Anal. Calcd for $C_{21}H_{23}ClN_2O_3Pt$: C, 43.34; H, 3.98; N, 4.81. Found: C, 42.85; H, 3.94; N, 4.78.

Synthesis of *fac*-[Pt{$CH_2C(O)Me$}$_3$(CN^tBu)(bpy)]OTf (8). To a suspension of complex **6** (61.6 mg, 0.11 mmol) in acetone (5 mL) were added TlOTf (40 mg, 0.11 mmol) and ^{t}BuNC (12.5 μL, 0.11 mmol). The reaction mixture was concentrated to dryness, and the residue was extracted with CH_2Cl_2 (10 mL) and filtered through Celite. The filtrate was concentrated (3 mL), and Et_2O (10 mL) was added. The resulting oil was stirred for 1 h at 0 °C, and the resulting solid was filtered, washed with Et_2O (5 mL), and air-dried to give **8** as a yellow solid. Yield: 54 mg, 65%. Mp: 122 °C. Λ_M (acetone, 4.9×10^{-4} mol L^{-1}): 124 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(CN) 2232, ν(CO) 1661. ^1H NMR (400 MHz, $CDCl_3$): δ 8.95 (m, 4 H, CH, bpy), 8.39 (m, 2 H, CH, bpy), 7.87 (m, 2 H, CH, bpy), 3.34 (H_A, AB system, 2 H, CH_2 trans to bpy, $^1J_{HH}$ = 12 Hz, $^2J_{HPt}$ = 101 Hz), 3.19 (H_B, AB system, 2 H, CH_2 trans to bpy, $^1J_{HH}$ = 12 Hz, $^2J_{HPt}$ = 59 Hz), 2.36 (s, 6 H, *Me*C(O) trans to bpy), 2.23 (s, 2 H, CH_2 *trans* to ^{t}BuNC, $^2J_{HPt}$ = 77.4 Hz), 1.26 (s, 9 H, ^{t}Bu), 1.24 (s, 3 H, *Me*C(O) trans to ^{t}BuNC). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 211.1 (CO trans to bpy, $^2J_{CPt}$ = 35.3 Hz), 210.4 (CO trans to ^{t}BuNC, $^2J_{CPt}$ = 34.7 Hz), 154.8 (C, bpy), 148.8 (CH, bpy, J_{CPt} = 14.3 Hz), 142.1 (CH, bpy), 128.5 (CH, bpy, J_{CPt} = 15.9 Hz), 126.5 (CH, bpy, J_{CPt} = 10.0 Hz), 59.6 (*C*Me_3), 32.1 (*Me*C(O) trans to ^{t}BuNC), 31.3 (*Me*C(O) trans to bpy, $^3J_{CPt}$ = 9.5 Hz), 29.3 (CH_2 trans to ^{t}BuNC, $^1J_{CPt}$ = 482 Hz), 24.5 (CH_2 trans to bpy, $^1J_{CPt}$ = 595 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −2670. Anal. Calcd for $C_{25}H_{32}F_3N_3O_6PtS$: C, 39.79; H, 4.27; N, 5.57; S, 4.25. Found: C, 39.66; H, 4.49; N, 5.62; S, 4.28. Single crystals of **8** were obtained by slow diffusion of Et_2O into an acetone solution of **8**.

Synthesis of *mer*-[Pt{$CH_2C(O)Me$}Cl$_3$(bpy)] (9). To a suspension of [Pt{$CH_2C(O)Me$}Cl(bpy)] (57 mg, 0.13 mmol) in CH_2Cl_2 (3 mL) was added $PhICl_2$ (40 mg, 0.15 mmol), and the resulting yellow suspension was filtered through Celite. The filtrate was concentrated (2 mL), Et_2O (10 mL) was added, and the suspension was filtered off. The solid was washed with Et_2O (5 mL) and air-dried to give **9** as a yellow solid. Yield: 46 mg, 70%. Mp: 131−134 °C. IR (Nujol, cm^{-1}): ν(CO) 1673, ν(PtCl) 347. ^1H NMR (400 MHz, $CDCl_3$): δ 9.81 (m, 1 H, CH, bpy, $^3J_{HPt}$ = 30 Hz), 9.63 (m, 1 H, CH, bpy), 8.20−8.25 (m, 2 H, CH, bpy), 7.84−7.88 (m, 2 H, CH, bpy), 4.39 (s, 2 H, CH_2, $^2J_{HPt}$ = 85 Hz), 2.34 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 214.2 (CO), 155.4 (C, bpy), 153.0 (C, bpy), 151.6 (CH, bpy), 147.9 (CH, bpy), 141.2 (CH, bpy), 140.7 (CH, bpy), 129.0 (CH, bpy, J_{CPt} = 31 Hz), 128.2

(CH, bpy, J_{CPt} = 13 Hz), 124.1 (CH, bpy, J_{CPt} = 21 Hz), 123.6 (CH, bpy), 32.6 (Me), 26.0 (*C*H_2, $^1J_{CPt}$ = 458.7 Hz). ^{195}Pt{^{1}H} NMR (86.18 MHz, $CDCl_3$): δ −937 (br). Anal. Calcd for $C_{13}H_{13}Cl_3N_2OPt$: C, 30.34; H, 2.55; N, 5.44. Found: C, 30.23; H, 2.46; N, 5.43. Single crystals of **9** were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **9**.

Synthesis of [*OC*-6-43]-[Pt{$CH_2C(O)Me$}$_2$(Me)I(bpy)] (11). To a solution of [Pt{$CH_2C(O)Me$}$_2$(bpy)] (80 mg, 0.17 mmol) in CH_2Cl_2 (2 mL) was added MeI (21.5 μL, 0.35 mmol). After 14 h the solution was concentrated (0.5 mL) and cooled for 1 h in a water/ice bath. The suspension was filtered and the solid washed with Et_2O (2 mL) and air-dried to give **11** as a pale yellow solid. Yield: 30 mg, 30%. A second crop of **11** was obtained by addition of Et_2O (10 mL) to the filtrate, but it contained traces of **12** as an impurity. Mp: 153 °C. IR (cm^{-1}): ν(CO) 1667. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (m, 2 H, CH(6), bpy), 8.21 (m, 2 H, CH(3), bpy), 8.08 (m, 2 H, CH(4), bpy), 7.71 (m, 2 H, CH(5), bpy), 3.71 (H_A, AB system, 2 H, CH_2, $^1J_{H_AH_B}$ = 8.6 Hz, $^1J_{H_APt}$ = 101 Hz), 3.42 (H_B, AB system, 2 H, CH_2, $^1J_{H_AH_B}$ = 8.6 Hz, $^1J_{H_BPt}$ = 98 Hz), 2.32 (s, 6 H, *Me*C(O)), 0.87 (s, 3 H, Me, $^1J_{HPt}$ = 66 Hz). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 215.2 (CO), 154.5 (C, bpy), 150.4 (CH(6), bpy, $^2J_{CPt}$ = 17 Hz), 139.2 (CH(4), bpy), 127.5 (CH(5), bpy, $^3J_{CPt}$ = 17 Hz), 123.4 (CH(3), bpy, $^3J_{CPt}$ = 11 Hz), 33.3 (*Me*C(O)), 17.9 (CH_2, $^1J_{CPt}$ = 593 Hz), 8.7 (Me, $^1J_{CPt}$ = 588 Hz). ^{195}Pt{^{1}H} NMR (86.18 MHz, $CDCl_3$): δ −2491. Anal. Calcd for $C_{17}H_{21}IN_2O_2Pt$: C, 33.62; H, 3.49; N, 4.61. Found: C, 33.40; H, 3.40; N, 4.69.

Synthesis of [*OC*-6-34]-[Pt{$CH_2C(O)Me$}$_2$(Me)I(bpy)] (12). A solution of **11** (105 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) was heated at 70 °C for 24 h and then filtered through Celite. The filtrate was concentrated (ca. 1 mL), Et_2O (15 mL) was slowly added, and the resulting suspension was filtered off. The solid was air-dried to give **12** as a yellow solid. Yield: 70 mg, 70%. Mp: 144−147 °C. IR (Nujol, cm^{-1}): ν(CO) 1665. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (m, 1 H, H6, py trans to Me, $^3J_{HPt}$ = 6.8 Hz), 8.87 (m, 1 H, H6, py trans to acetonyl, $^3J_{HPt}$ = 18.1 Hz), 8.24 (m, 2 H, H3 py trans to acetonyl and H3 py trans to Me), 8.11−8.05 (m, 2 H, H4 py *trans* to acetonyl and H4 py trans to Me), 7.71−7.64 (m, 2 H, H5 py trans to acetonyl and H5 py trans to Me), 3.62 (H_A, AB system, 2 H, CH_2 trans to bpy, $^1J_{HH}$ = 7.6 Hz, $^2J_{HPt}$ = 104 Hz), 3.30 (H_B, AB system, 2 H, CH_2 trans to bpy, $^1J_{HH}$ = 7.6 Hz, $^2J_{HPt}$ = 96 Hz), 2.67 (H_A, AB system, 2 H, CH_2 trans to I, $^1J_{HH}$ = 6.8 Hz, $^2J_{HPt}$ = 93 Hz), 2.60 (H_B, AB system, 2 H, CH_2 trans to I, $^1J_{HH}$ = 6.8 Hz, $^2J_{HPt}$ = 93 Hz), 2.31 (s, 3 H, *Me*C(O) trans to bpy), 1.88 (s, 3 H, Me, $^2J_{HPt}$ = 67.8 Hz), 1.39 (s, 3 H, *Me*C(O) trans to I). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 215.3 (CO, $^2J_{CPt}$ = 33 Hz), 209.3 (CO, $^2J_{CPt}$ = 48 Hz), 155.1 (C, bpy), 154.7 (C, bpy), 149.2 (C6, py trans to Me, $^2J_{CPt}$ = 12 Hz), 147.0 (C6, py trans to acetonyl, $^2J_{CPt}$ = 14 Hz), 139.5 (C4 py trans to Me or acetonyl), 139.2 (C4 py trans to Me or acetonyl), 127.1 (C5 py trans to Me or acetonyl, $^3J_{CPt}$ = 14 Hz), 126.6 (C5 py trans to Me or acetonyl, $^3J_{CPt}$ = 18 Hz), 124.0 (C3 py trans to Me or acetonyl, $^3J_{CPt}$ = 11.5 Hz), 123.6 (C3 py trans to Me or acetonyl, $^3J_{CPt}$ = 9.2 Hz), 33.7 (CH_2 trans to I, $^1J_{CPt}$ = 550.1 Hz), 32.6 (*Me*C(O) trans to N), 31.4 (*Me*C(O) trans to I), 19.1 (CH_2 trans to N, $^1J_{CPt}$ = 540.7 Hz), −4.05 (Me, $^1J_{CPt}$ = 597 Hz). ^{195}Pt{^{1}H} NMR (86.18 MHz, $CDCl_3$): δ −2692. Anal. Calc for $C_{17}H_{21}IN_2O_2Pt$: C, 33.62; H, 3.49; N, 4.61. Found: C, 33.92; H, 3.50; N, 4.58.

Synthesis of [*OC*-6-33]-[Pt{$CH_2C(O)Me$}$_2${$CH_2C(O)Ph$}Br(bpy)] (13). To a solution of [Pt{$CH_2C(O)Me$}$_2$(bpy)] (123 mg, 0.26 mmol) in CH_2Cl_2 (4 mL) was added $BrCH_2C(O)Ph$ (105 mg, 0.53 mmol). The reaction mixture was stirred for 32 h and then filtered through Celite. The filtrate was concentrated (ca. 1 mL), and Et_2O (10 mL) was slowly added to give a suspension, which was filtered off. The yellow solid was air-dried and recrystallized in CH_2Cl_2/Et_2O. Yield: 131 mg, 75%. Mp: 173−175 °C. IR (Nujol, cm^{-1}): ν(CO) 1667, 1645. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.49−9.43 (m, 2 H, CH, bpy), 7.91−7.86 (m, 2 H, CH, bpy), 7.71−7.68 (m, 2 H, CH, bpy), 7.65−7.61 (m, 2 H, CH, bpy), 7.22−7.17 (m, 1 H, Ph), 6.84−6.82 (m, 4 H, Ph), 3.72 (H_A, AB system, 2 H, MeC(O)*C*H_2, $^1J_{HH}$ = 8.2 Hz, $^2J_{HPt}$ = 94.1 Hz), 3.69 (H_B, AB system, 2 H, MeC(O)*C*H_2, $^1J_{HH}$ = 8.2 Hz, $^2J_{HPt}$ = 98.6 Hz), 3.20 (s, 2 H, PhC(O)*C*H_2, $^2J_{HPt}$ = 91.2 Hz), 2.33 (s, 6 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 214.6 (Me*C(O)*CH_2, $^2J_{CPt}$ = 31 Hz), 200.9 (Ph*C(O)*CH_2, $^2J_{CPt}$ = 48 Hz), 154.8 (C, bpy, J_{CPt} = 5 Hz), 149.5 (CH, bpy, J_{CPt} = 14 Hz), 139.2 (CH, bpy), 137.8 (Ph), 131.9 (Ph), 127.7 (Ph), 127.2 (CH, bpy, J_{CPt} = 17 Hz), 126.6 (Ph), 123.0 (CH, bpy, J_{CPt} = 11 Hz), 33.8 (Me), 21.3 (PhC(O)*C*H_2, $^1J_{CPt}$ = 568 Hz), 19.6 (MeC(O)*C*H_2, $^1J_{CPt}$ = 574 Hz). ^{195}Pt{^{1}H} NMR (86.18 MHz, $CDCl_3$): δ −2187. Anal. Calcd for $C_{24}H_{25}BrN_2O_3Pt$: C, 43.38; H, 3.79; N, 4.22. Found: C, 43.21; H, 3.80; N, 4.20.

X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker Smart Apex CCD for **1·C**, **6**, and **8** and Siemens P4 for **9**). Data were collected using monochromated Mo Kα radiation in the ω mode. Absortion corrections were based on multi scans (program SADABS) for compounds **1·C**, **6**, and **8** and on ψ scans for compound **9**. The structures were refined anisotropically using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Göttingen, Germany). Hydrogen atoms were included using rigid methyl groups or a riding model. Special features of refinement are as follows. **1·C**: half of the crown ether is disordered over two sites, ca. 0.57:0.43. The closeness of some atoms in the two disordered components caused convergence to be slow.

Crystallographic data for complexes **1·C**, **6**, **8**, and **9** are given in Table 1.

Results and Discussion

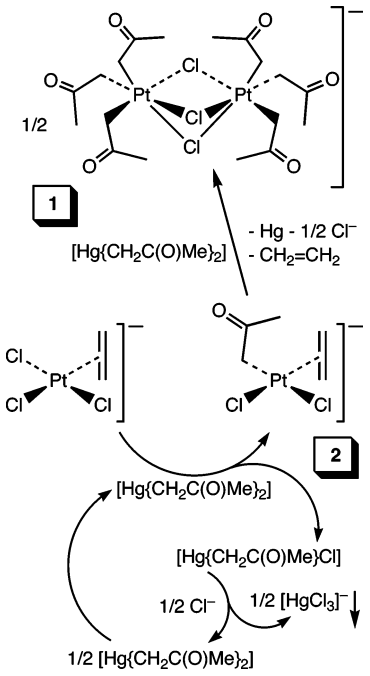
Reactivity of [Hg{$CH_2C(O)Me$}$_2$] toward K[$PtCl_3(C_2H_4)$]. Synthesis of Q[Pt$_2${$CH_2C(O)Me$}$_6(\mu$-Cl)$_3$] (Q = K (1·K), K(18-C-6) (1·C)) and *cis*-(Me_4N)[Pt{$CH_2C(O)Me$}$Cl_2(\eta^2$-CH_2=CH_2)] (2·NMe_4). The attempts to transmetalate an acetonyl group from [Hg{$CH_2C(O)Me$}$_2$] to Pt(II) by reacting it with $(NMe_4)_2[PtCl_4]$, [K(18-C-6)]$_2[PtCl_4]$, $[PtCl_2(PhCN)_2]$, or $(NMe_4)_2[Pt_2Cl_6]$ under different reaction conditions failed, since only complex mixtures formed or no reaction took place. However, [Hg{$CH_2C(O)Me$}$_2$] and K[$PtCl_3(C_2H_4)$] react at room temperature in a 2:1 molar ratio to give a gray precipitate, from which K[Pt$_2${$CH_2C(O)Me$}$_6(\mu$-Cl)$_3$] (**1·K**) was isolated as a colorless and poorly soluble compound after washing with CH_2Cl_2, to separate the other reaction product [Hg{$CH_2C(O)Me$}Cl], and extracting with hot MeCN, to remove elemental mercury. Using different solvents and conditions, **1·K** always crystallized as small crystals not suitable for a single-crystal X-ray diffraction study. In similar cases, it proved very convenient to try to solve the structure using X-ray powder diffraction (XRPD).[17] With the aid of ab initio XRPD methods, the structure of complex **1·K** was eventually solved (Scheme 1).[10] Incidentally, we originally thought of a cubane [Pt$_4${$CH_2C(O)Me$}$_{12}(\mu_3$-Cl)$_4$] species, in agreement with its reactivity toward bpy (it gives [Pt{$CH_2C(O)Me$}$_3$Cl(bpy)] the single-crystal structure of which was determined; see below), elemental

(17) Masciocchi, N.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 4643. Masciocchi, N.; Ragaini, F.; Sironi, A. *Organometallics* **2002**, *21*, 3489. Vicente, J.; Gil-Rubio, J.; Bautista, D. *Inorg. Chem.* **2001**, *40*, 2636. Vicente, J.; Gil-Rubio, J.; Bautista, D.; Sironi, A.; Masciocchi, N. *Inorg. Chem.* **2004**, *43*, 5665.

Table 1. Crystallographic Data for Complexes 1·C, 6, 8, and 9

	1·C	**6**	**8**	**9**
formula	$C_{30}H_{54}Cl_3KO_{12}Pt_2$	$C_{19}H_{23}ClN_2O_3Pt$	$C_{25}H_{32}F_3N_3O_6PtS$	$C_{13}H_{13}Cl_3N_2OPt$
M_r	1142.36	557.93	754.69	514.69
cryst habit	Block	needle	lath	needle
cryst size (mm)	0.45 × 0.28 × 0.17	0.37 × 0.15 × 0.08	0.32 × 0.28 × 0.08	0.22 × 0.16 × 0.06
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
cell constants				
a, Å	16.3432(8)	7.7305(5)	10.7533(6)	6.7239(8)
b, Å	13.3360(7)	27.1799(19)	11.5279(6)	10.6002(7)
c, Å	19.0526(9)	9.7153(7)	12.4871(7)	11.6152(11)
α, deg			89.267(2)	92.998(6)
β, deg	103.262(2)	111.032(1)	72.360(2)	105.748(9)
γ, deg			78.155(2)	106.808(6)
V (Å^3)	4041.8(3)	19.05.3(2)	1441.71(14)	755.03(13)
Z	4	4	2	2
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ(calcd) (Mg m^{-3})	1.877	1.945	1.738	2.264
μ (mm^{-1})	7.269	7.526	5.001	9.818
F(000)	2224	1080	744	484
T (K)	100	100	100	173
$2\theta_{max}$ (deg)	26.37	27.10	26.37	24.99
no. of rflns measd	43 594	20 958	16 047	5282
no. of indep rflns	8270	4167	5786	2641
transmissions	0.3713−0.1384	0.5843−0.1672	0.6904−0.2975	0.9578−0.3865
R_{int}	0.0271	0.0283	0.0350	0.0193
no. of restraints/params	0/434	6/238	263/358	0/182
$R_w(F^2$, all rflns)	0.0537	0.0509	0.0713	0.0585
$R(F, > 4\sigma(F))$	0.0217	0.0224	0.0303	0.0237
S	1.055	1.187	1.134	0.996
max $\Delta\rho$ (e Å^{-3})	1.341	1.391	2.478	1.433

Scheme 1



analyses, NMR, IR and ESI MS data, and in analogy with most known Pt^{IV}(alkyl) complexes $[Pt_4R_{12}X_4]$ (R = Me, Et, X = halogen).[18]

The reaction between **1·K** and 18-crown-6 (18-C-6) (1:1.5 molar ratio) gives $[K(18\text{-C-}6)][Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$ (**1·C**), which, unlike **1·K**, is soluble in most common organic solvents. A single-crystal X-ray diffraction study of **1·C** shows the anion to be the same as that in **1·K** and thus proves the suitability of the previous X-ray powder diffraction study.[10]

The formation of **1·K** involves both the transmetalation of the acetonyl group and the oxidation of Pt(II) to Pt(IV). A study using different molar ratios and reaction times was carried out in order to elucidate the mechanism of this process. The 1:1 reaction was followed by ^{1}H NMR in d_6-acetone. After 15 min, the spectrum of the reaction mixture showed the presence of $[PtCl_3(C_2H_4)]^-$, $[Hg\{CH_2C(O)Me\}Cl]$, traces of **1·K**, and the platinum complex **2·K**, containing the acetonyl group and ethylene. The presence of $[Hg\{CH_2C(O)Me\}_2]$ could not be detected, since the resonances of the methylene and methyl protons overlap with those of $[PtCl_3(C_2H_4)]^-$ and d_6-acetone, respectively. After 30 min, the spectrum showed the presence of **2·K** and $[Hg\{CH_2C(O)Me\}Cl]$ and only traces of $[PtCl_3(C_2H_4)]^-$ and **1·K**. The complex **2·K** could not be separated from the other reaction product $[Hg\{CH_2C(O)Me\}Cl]$ when the reaction was repeated on a preparative scale. In similar circunstances, we have solved this problem by adding an excess of $(Me_4N)Cl$ to the reaction mixture.[19] The use of this reagent has a double purpose: (i) to symmetrize[12,20] $[Hg\{CH_2C(O)Me\}Cl]$, allowing us to recover half of $[Hg\{CH_2C(O)Me\}_2]$ (Scheme 1) and work with a [Pt]:[Hg] = 1:0.5 molar ratio, and (ii) to produce $[HgCl_3]^-$ salts that can be separated, along with the excess of $(Me_4N)Cl$, from the reaction mixture, because both are insoluble in CH_2Cl_2. This transmetalation/symmetrization

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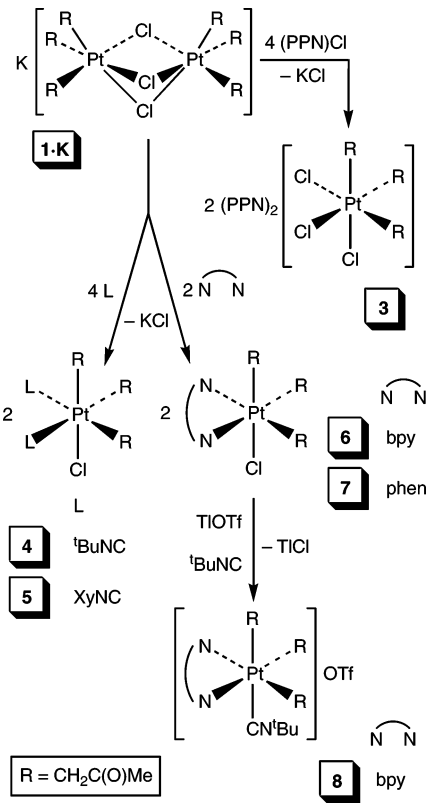
Scheme 2



method gives the first anionic ketonyl Pt(II) complex, *cis*-(Me_4N)[Pt{$CH_2C(O)Me$}$Cl_2(\eta^2$-$CH_2{=}CH_2)$] (**2·NMe$_4$**), the spectroscopic data of which agree with those of **2·K**. Therefore, we propose that the first step in the synthesis of **1·K** is a transmetalation reaction giving K[Pt{$CH_2C(O)Me$}$Cl_2(\eta^2$-$CH_2{=}CH_2)$] (**2·K**; Scheme 1).

The 1:2 reaction between K[$PtCl_3(\eta^2$-$CH_2{=}CH_2)$] and [Hg{$CH_2C(O)Me$}$_2$] in d_6-acetone was also followed by ^{1}H NMR spectroscopy. The initial formation of **2·K** was observed, but its concentration decreased while the amount of **1·K** and free $CH_2{=}CH_2$ increased. No other species were detected at room temperature or below (−10 °C). We propose that, because [Hg{$CH_2C(O)Me$}Cl] and **2·K** were in contact in the 1:1 reaction and only traces of **1·K** were observed, this complex results from the reaction of **2·K** with [Hg{$CH_2C(O)Me$}$_2$] through a redox transmetalation reaction (Scheme 1). Alternatively, a normal transmetalation reaction could lead to a unobserved Pt(II) intermediate, K[Pt{$CH_2C(O)Me$}$_2$Cl(η^2-$CH_2{=}CH_2$)] or K_2[Pt{$CH_2C(O)Me$}$_2$(μ-Cl)]$_2$, which would rapidly react with the other reaction product, [Hg{$CH_2C(O)Me$}Cl], to give **1·K** and Hg through a redox transmetalation reaction. The Hg formed is responsible for the gray color of the initial precipitate obtained in the reaction. We have confirmed that the complex **2·NMe$_4$** reacts with [Hg{$CH_2C(O)Me$}$_2$] to give Hg and **1·NMe$_4$**.

Reactivity of 1·K. The complex **1·K** is a suitable precursor for the synthesis of tris(acetonyl) Pt(IV) complexes. With neutral or anionic ligands in organic solvents, the reactions take place with bridge splitting and precipitation of KCl. Thus, **1·K** reacts with (PPN)Cl to give *fac*-$(PPN)_2$[Pt{$CH_2C(O)Me$}$_3Cl_3$] (**3**; Scheme 2). A slight excess of **1·K** over the stoichiometric amount is recommended, because such an excess can be removed, due to the insolubility of **1·K** in the reaction solvent (CH_2Cl_2), while unreacted (PPN)Cl would contaminate **3** after addition of the precipitating solvent (Et_2O). The reaction of a suspension of **1·K** in acetone with an excess of RNC or N∧N, followed by removal of KCl, gives the neutral complex *fac*-[Pt{$CH_2C(O)Me$}$_3$Cl(CNR)$_2$] (R = ^{t}Bu (**4**), Xy (**5**)) or *fac*-[Pt{$CH_2C(O)Me$}$_3$Cl(N∧N)] (N∧N = bpy (**6**), phen (**7**)), respectively. Complexes **4** and **5** are very soluble in organic solvents, even in *n*-pentane. To isolate them, it was necessary to evaporate the solvent, to wash the residue with the minimum volume of *n*-pentane to remove the excess isocyanide, and to maintain the residue under vacuum for 24 h. In this way, **4** or **5** was obtained as a pale yellow solid or oil, respectively. The reaction of **6** with TlOTf and ^{t}BuNC in a 1:1:1 molar ratio gives *fac*-[Pt{$CH_2C(O)Me$}$_3$(CN^{t}Bu)(bpy)]OTf (**8**; Scheme 2). The analogous reaction of **7** and XyNC led to the formation of [Pt{$CH_2C(O)Me$}$_3$(CNXy)(phen)]OTf, which could not be isolated analytically pure; however, its ^{1}H NMR spectrum is in agreement with a structure similar to that proposed for **8**.

Oxidative Addition Reactions. One of the most widely used methods for the synthesis of Pt(IV) complexes is the oxidative addition of halogens or alkyl/acyl halides to Pt(II) derivatives.[21] Despite the fact that the reactivity of alkyl platinum(II) complexes with alkyl halides has been widely studied, only two examples of oxidative addition of an haloketone to a platinum(II) complex to give a ketonyl Pt(IV) complex have been reported.[5,7] Both are monoacetonyl derivatives, and only one is an acetonyl complex.[7] This moved us to apply the oxidative addition reaction as a method to synthesize mono-, bis-, and tris(ketonyl) Pt(IV) complexes by reacting our complexes[2] [Pt{$CH_2C(O)Me$}$_2$(bpy)] and [Pt{$CH_2C(O)Me$}Cl(bpy)] with different substrates ($PhICl_2$,[16] as a solid surrogate of chlorine, MeI, or haloketones). Thus, the reaction between [Pt{$CH_2C(O)Me$}Cl(bpy)] and $PhICl_2$ gives the Pt(IV) complex *mer*-[Pt{$CH_2C(O)Me$}Cl_3(bpy)] (**9**; Scheme 3). $PhICl_2$ must be added in small excess (1:1.1) to ensure the total conversion of the Pt(II) complex. The reaction of [Pt{$CH_2C(O)Me$}$_2$(bpy)] with $PhICl_2$ in a 1:1.2 molar ratio gives the product of the trans addition of two chloro ligands: [*OC*-6-13]-[Pt{$CH_2C(O)Me$}$_2Cl_2$(bpy)] (**10**). However, the product could not be obtained in analytically pure form, even after several recrystallizations. Although several isomers are possible, the IR and NMR spectra agree with the proposed structure (see Scheme 3 and the Supporting Information). We have recently reported the use of $PhICl_2$ to oxidize Pt(II) to Pt(IV) complexes.[22]

The reaction of [Pt{$CH_2C(O)Me$}$_2$(bpy)] with MeI at room temperature yields the complex resulting from trans addition, [*OC*-6-43]-[Pt{$CH_2C(O)Me$}$_2$(Me)I(bpy)] (**11**). This complex slowly isomerizes in solution at room temperature to [*OC*-6-34]-[Pt{$CH_2C(O)Me$}$_2$(Me)I(bpy)] (**12**). On a preparative scale, complex **12** was obtained by warming a solution of **11** in CH_2Cl_2 at 70 °C in a Carius tube for 12 h. Similarly, [Pt{$CH_2C(O)Me$}$_2$(bpy)] reacts with $PhC(O)CH_2Br$ at room temperature in $CDCl_3$ to give the first mixed ketonylmetal complex, [*OC*-6-33]-[Pt{$CH_2C(O)Me$}$_2${$CH_2C(O)Ph$}Br(bpy)] (**13**). In solution, complex **13** evolves to a mixture of complexes that could not be separated. The complex **6** described above can also be obtained by reacting [Pt{$CH_2C(O)Me$}$_2$(bpy)] with $MeC(O)CH_2Cl$ (90 °C in CH_2Cl_2) or [Pt{$CH_2C(O)Me$}$_2$(bpy)] with [Hg{$CH_2C(O)Me$}Cl] in refluxing acetone. The latter takes place with formation of Hg(0), and the product is obtained with traces of the starting material that can be separated by recrystallization.

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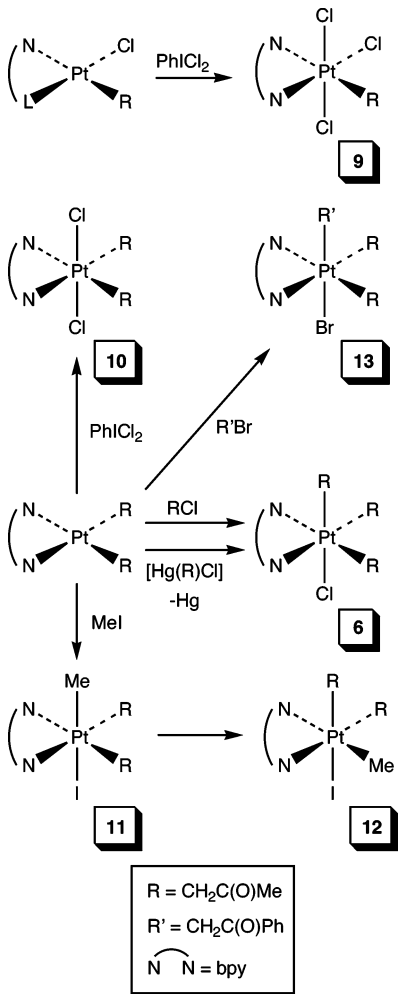
Scheme 3



Crystal Structures. The crystal structure of **1·K** was solved using ab initio X-ray powder diffraction (XRPD) methods,[10] and those of **1·C** (Figure 1), **6** (Figure 2), **8** (Figure 3), and **9** (Figure 4) were solved by single-crystal X-ray diffraction studies. For complex **13**, the atom connectivity shown in Scheme 3 was established using crystals apparently suitable for an X-ray crystallographic study. However, repeated attempts and data collection at low temperature did not give satisfactory refinement of the structure. All of the structures show the platinum atom in a distorted-octahedral environment. The structures of the anion in complexes **1·C** and **1·K**[10] are analogous: two octahedra with a common face containing the three bridging chloro ligands (Figure 1) similar to what is observed in the Pt(II) complex $[Pt_2\{\eta^4\text{-}C_4{}^nPr_4\}_2(\mu\text{-}Cl)_3]^+$ [23] and in the well-known isoelectronic $[Re_2(\mu\text{-}Cl)_3(CO)_6]^-$.[24] The six Pt−C bond distances in **1·C** are not significantly different (range 2.075(3)−2.062(4) Å), while the Pt(1)−Cl bond lengths are in a wider range (2.4762(8)−2.5099(8) Å). Due to the intrinsic low precision of power diffraction, the corresponding values found in **1·K** (Pt−C = 2.20(2) Å and PtCl = 2.533(7) Å) are barely comparable.[10] In **1·C**, a hexagonal-bipyramidal environment for K is reached with the oxygen atoms of 18-C-6 in equatorial positions and two oxygen atoms of two acetonyl ligands of different anions in axial positions; this results in the formation of a chain (Figure 5). The K cations adopt two different dispositions: K(1), with axial K(1)−O(6) distances of 2.711(3) Å, and K(2), with shorter K(2)−O(1) distances of 2.625(3) Å. Both are shorter than the equatorial distance (2.755(6)−2.841(3) Å). The coordination of the acetonyl ligand to K^+ does not cause the lengthening of the C−O bond distances (1.223(5) and 1.211(5) Å) with respect to those in the terminal acetonyl ligands (1.232(5)−1.211(4) Å), and all are within the range observed for complexes **6**, **8**, and **9** (1.228(7)−1.212(5) Å) and for the ketonyl platinum(II) complexes reported in the literature (1.25(3)−1.226(12) Å).[2,25,26]

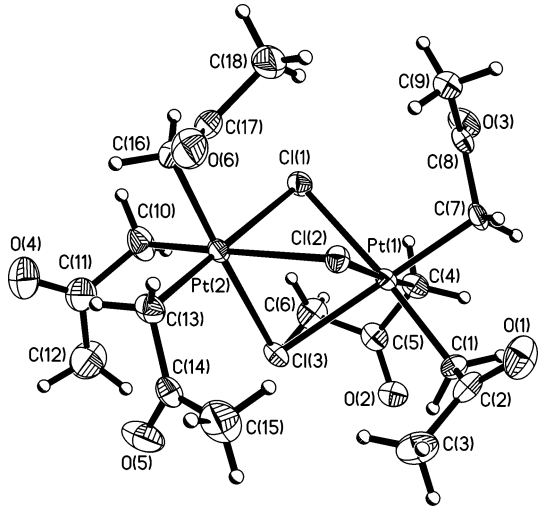


Figure 1. Ellipsoid representation of the anion of **1·C** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(1) = 2.062(3), Pt(1)−C(4) = 2.064(3), Pt(1)−C(7) = 2.072(3), Pt(1)−Cl(1) = 2.4838(8), Pt(1)−Cl(3) = 2.4961(8), Pt(1)−Cl(2) = 2.5099(8), Pt(2)−C(10) = 2.073(4), Pt(2)−C(13) = 2.075(3), Pt(2)−C(16) = 2.062(4), Pt(2)−Cl(1) = 2.4762(8), Pt(2)−Cl(3) = 2.4851(8), Pt(2)−Cl(2) = 2.5010(8), O(1)−C(2) = 1.211(5), O(2)−C(5) = 1.217(4), O(3)−C(8) = 1.211(4), O(4)−C(11) = 1.232(5), O(5)−C(14) = 1.219(5), O(6)−C(17) = 1.223(5), C(1)−C(2) = 1.488(5), C(2)−C(3) = 1.499(6), C(4)−C(5) = 1.498(5), C(5)−C(6) = 1.511(5), C(7)−C(8) = 1.498(5), C(8)−C(9) = 1.501(5), C(10)−C(11) = 1.488(6), C(11)−C(12) = 1.461(6), C(13)−C(14) = 1.480(5), C(14)−C(15) = 1.481(6), C(16)−C(17) = 1.486(6), C(17)−C(18) = 1.497(6); C(1)−Pt(1)−C(4) = 85.79-(14), C(1)−Pt(1)−C(7) = 85.59(14), C(4)−Pt(1)−C(7) = 86.25-(14), C(4)−Pt(1)−Cl(1) = 92.89(11), C(7)−Pt(1)−Cl(1) = 98.80-(10), C(1)−Pt(1)−Cl(3) = 93.59(10), C(4)−Pt(1)−Cl(3) = 99.14(10), Cl(1)−Pt(1)−Cl(3) = 82.19(3), C(1)−Pt(1)−Cl(2) = 100.15(10), C(7)−Pt(1)−Cl(2) = 94.17(10), Cl(1)−Pt(1)−Cl(2) = 81.19(3), Cl(3)−Pt(1)−Cl(2) = 80.59(3), C(16)−Pt(2)−C(10) = 85.95(17), C(16)−Pt(2)−C(13) = 84.92(15), C(10)−Pt(2)-C(13) 95.36(15), C(16)−Pt(2)-Cl(1) 93.52(11), C(10)−Pt(2)−Cl(1) = 89.20(11), C(10)−Pt(2)−Cl(3) = 92.58(13), C(13)−Pt(2)−Cl(3) = 99.10(10), Cl(1)−Pt(2)−Cl(3) = 82.56(3), C(16)−Pt(2)−Cl(2) = 99.89(11), C(13)−Pt(2)−Cl(2) = 94.11(11), Cl(1)−Pt(2)−Cl(2) = 81.52(3), Cl(3)−Pt(2)−Cl(2) = 80.97(3).

The oxidation state of the metal has little effect on the Pt−C distances, since the range in **1·C**, **6**, **8**, and **9** (2.100(4)−2.063-(4) Å) is similar to that found in acetonyl platinum(II) compounds (2.116(8)−2.03(4) Å).[2,25,26] The same effect was observed for methyl platinum(II) and platinum(IV) complexes.[27] In **9**, the Pt−Cl bond distance trans to N (2.3073(13) Å) is shorter than the two mutually trans Pt−Cl bond distances (2.3178(14), 2.3124(13) Å). These three distances are shorter

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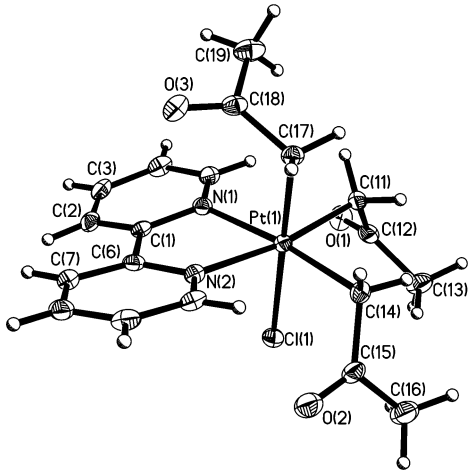

Figure 2. Ellipsoid representation of **6** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(11) = 2.078(3), Pt(1)−C(14) = 2.090(3), Pt(1)−C(17) = 2.095(3), Pt(1)−N(2) = 2.122(3), Pt(1)−N(1) = 2.135(3), Pt(1)−Cl(1) = 2.4338(8), O(1)−C(12) = 1.218(4), O(2)−C(15) = 1.214(5), O(3)−C(18) = 1.219(4), C(11)−C(12) = 1.498(5), C(12)−C(13) = 1.503(5), C(14)−C(15) = 1.516(5), C(15)−C(16) = 1.512(5), C(17)−C(18) = 1.494(5), C(18)−C(19) = 1.510(5); C(11)−Pt(1)−C(14) = 88.87(13), C(11)−Pt(1)−C(17) = 86.43(13), C(14)−Pt(1)−C(17) = 87.11(13), C(14)−Pt(1)−N(2) = 97.02(12), C(17)−Pt(1)−N(2) = 87.20(12), C(11)−Pt(1)−N(1) = 96.77(12), C(17)−Pt(1)−N(1) = 96.49(11), N(2)−Pt(1)−N(1) = 77.79(10), C(11)−Pt(1)−Cl(1) = 93.89(9), C(14)−Pt(1)−Cl(1) = 92.31(9), N(2)−Pt(1)−Cl(1) = 92.55(8), N(1)−Pt(1)−Cl(1) = 84.06(7).

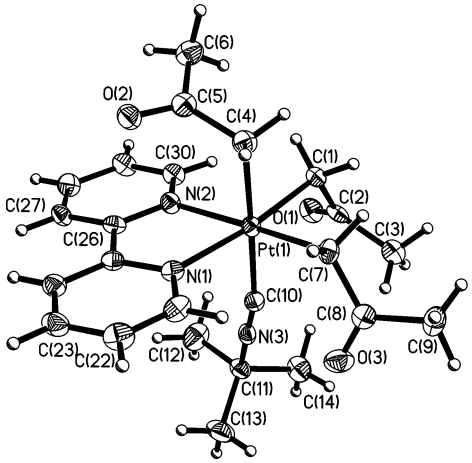

Figure 3. Ellipsoid representation of **8** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(10) = 2.023(4), Pt(1)−C(7) = 2.069(4), Pt(1)−C(1) = 2.091(4), Pt(1)−C(4) = 2.100(4), Pt(1)−N(1) = 2.127(3), Pt(1)−N(2) = 2.147(3), N(3)−C(10) = 1.145(5), O(1)−C(2) = 1.227(5), O(2)−C(5) = 1.224(5), O(3)−C(8) = 1.212(5), C(1)−C(2) = 1.501(6), C(2)−C(3) = 1.499(6), C(4)−C(5) = 1.478(6), C(5)−C(6) = 1.512(6), C(7)−C(8) = 1.509(6), C(8)−C(9) = 1.499(6); C(10)−Pt(1)−C(7) = 98.63(17), C(10)−Pt(1)−C(1) = 93.10(16), C(7)−Pt(1)−C(1) = 87.50(17), C(7)−Pt(1)−C(4) = 83.03(17), C(1)−Pt(1)−C(4) = 87.33(17), C(10)−Pt(1)−N(1) = 90.10(14), C(7)−Pt(1)−N(1) = 97.99(15), C(4)−Pt(1)−N(1) = 89.29(15), C(10)−Pt(1)−N(2) = 83.80(15), C(1)−Pt(1)−N(2) = 97.15(15), C(4)−Pt(1)−N(2) = 94.51(15), N(1)−Pt(1)−N(2) = 77.18(13).

than those trans to the acetonyl ligand in **6** (2.4338(8) Å), showing that the trans influence decreases in the series acetonyl > Cl > N-donor ligand. For the same reason, the Pt−N bond trans to Cl (2.042(4) Å) in complex **9** is shorter than that trans to the acetonyl group in **6**, **8**, or **9** (2.122(3)−2.147(3) Å). In

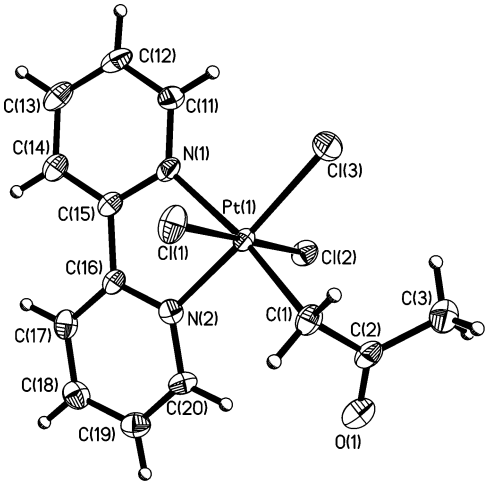

Figure 4. Ellipsoid representation of **9** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−N(2) = 2.042(4), Pt(1)−C(1) = 2.089(6), Pt(1)−N(1) = 2.136(5), Pt(1)−Cl(3) = 2.3073(13), Pt(1)−Cl(2) = 2.3124(13), Pt(1)−Cl(1) = 2.3178(14), O(1)−C(2) = 1.228(7), C(1)−C(2) = 1.479(8), C(2)−C(3) = 1.505(8); N(2)−Pt(1)−C(1) = 96.4(2), N(2)−Pt(1)−N(1) = 78.76(17), C(1)−Pt(1)−Cl(3) = 89.15(16), N(1)−Pt(1)−Cl(3) = 95.97(12), N(2)−Pt(1)−Cl(2) = 87.03(13), C(1)−Pt(1)−Cl(2) = 95.44(16), N(1)−Pt(1)−Cl(2) = 91.82(12), Cl(3)−Pt(1)−Cl(2) = 90.27(5), N(2)−Pt(1)−Cl(1) = 92.42(13), C(1)−Pt(1)−Cl(1) = 85.19(16), N(1)−Pt(1)−Cl(1) = 87.50(12), Cl(3)−Pt(1)−Cl(1) = 90.23(5).

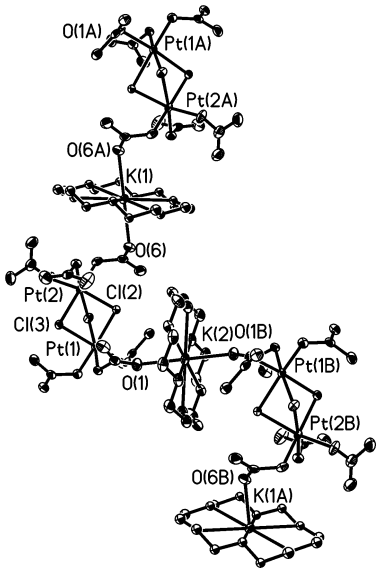

Figure 5. Ellipsoid representation of anions and cations in **1·C** (50% probability). Selected K−O bond lengths (Å): K(1)−O(6) = 2.711(3), K(1)−O_{18-C-6} (range) = 2.755(6)−2.825(9), K(2)−O(1) = 2.625(3), K(2)−O_{18-C-6} (range) = 2.806(2)−2.841(3).

1·C, the PtCl bond distances (2.4762(8)−2.5099(8) Å) are much longer than those in **6** and **9**, mainly because they are bridging. In complexes **6**, **8**, and **9**, the Pt−N bond distance trans to the acetonyl group (2.122(3)−2.147(3) Å) is longer than that reported for acetonyl platinum(II) complexes (2.082(3), 2.091(4) Å),[2,25] probably because of the greater π-acceptor character of bpy in acetonyl Pt(II) complexes.

Spectroscopic Properties. The ^{1}H and ^{13}C{^{1}H} NMR spectra of all complexes are in agreement with the structures shown in Schemes 1−3. For complex **10**, these spectra would also agree with a trans arrangement of the acetonyl ligands, but we discard this geometry on the basis of the great transphobia[28] between

two C-donor ligands.[28,29] In fact, all Pt(IV) complexes $[PtR_2X_2(L)(L')]$ (R = C-donor ligand, X = any halogen, L, L′ = any ligand, except C-donor) contain the R ligands mutually cis.[4,30,31] The ^{1}H NMR spectrum of **12** shows the nonequivalence of the halves of the bpy ligand, and the methylene protons as two AB systems, with ^{195}Pt satellites. This is only compatible with two geometries having the Me group trans to bpy or to one acetonyl group. The latter can be discarded, because the Me ligand has an NOE effect only with the H6 proton of bpy. This is a new example of the preference of two C-donor ligands to be cis because of their mutual transphobia.[28,29]

The ^{1}H NMR spectra of complexes **6**−**8** and **12** show the Me protons of one acetonyl (1.39−1.08 ppm) shielded by ca. 1 ppm with respect to the others (2.25−2.34 ppm) or to those in complexes **4** and **5** (2.34−2.25 ppm), due to the induced paramagnetic anisotropy of the bpy and phen ligands.

The values of $\delta(^1H)$ and $\delta(^{13}C)$ for the CH_2 nuclei trans to bpy and the corresponding $\delta(^{195}Pt)$ values follow the order (in ppm): **6** (3.62, 3.56; 19.9; −2012) < **10** (3.90; 21.4; −1500) < **9** (4.39; 26.0; −937), due to the successive replacement of an acetonyl group by a Cl ligand. The $^1J_{CPt}$ value is greater in complexes with the acetonyl ligand trans to Cl (585−568 Hz) or N-donor ligands (593−541 Hz) than to ligands with greater trans influence such as isocyanides (468−459 Hz).

As expected, the shielding of the platinum nuclei in the Pt(IV) complexes increases as chloro ligands are replaced by acetonyl ligands, **9** (−937 ppm) > **10** (−1500 ppm) > **6** (−2012 ppm), or when, in complexes with three C-donor ligands and one bpy, a chloro ligand is replaced by a bromo ligand, **6** (−2012 ppm) > **13** (−2187 ppm), or an iodo ligand, **11** (−2491 ppm), **12** (−2692 ppm). The significantly greater shielding of **12** with respect to its isomer **11** (Δ = 200 ppm) must be attributed to the paramagnetic component of the shielding constant, because the greater thermodynamic stability of **12** must be associated with a larger excitation energy. The platinum nucleus in the Pt(II) complex $[Pt\{CH_2C(O)Me\}_2(bpy)]$ (−3351 ppm) is, as expected, more shielded than that in its Pt(IV) derivatives **6** and **10**−**13** (range −1500 to −2692 ppm). The $^{195}Pt\{^1H\}$ spectrum of complex **4** shows a quintuplet at −3343 ppm due to the coupling with the ^{14}N nuclei of the equivalent ^{t}BuNC ligands. Replacement of bpy in **6** (−2012 ppm) or **7** (−2017 ppm) by isocyanide (**4**, −3343 ppm; **5**, −3307 ppm) increases the shielding of the ^{195}Pt nuclei. This effect has been reported previously.[32]

The chloro complexes show band(s) assignable to ν(PtCl) modes at different wavenumbers depending on the nature of the ligands in trans positions, the coordination mode of the chloro ligand, and the charge of the complex. Thus, in complexes **1**, one (**1·K**, 245 cm^{-1}) or two (**1·C**, 250, 232 cm^{-1}) bands appear in the lower energy region of the spectrum, as expected for bridging chloro ligands trans to C-donor ligands in an anionic complex. In complex **3** an increase in the energy of the ν(PtCl) absorptions (265, 241(br) cm^{-1}) is observed, due to the terminal nature of the chloro ligands, but the shift is only small because the complex is dianionic. In neutral complexes containing terminal chloro ligands trans to acetonyl (**4**, **6**, and **7**), one band appears in the range 273−265 cm^{-1}, while similar complexes with chloro trans to ligands with low trans influence such as chloro and bpy (**9** and **10**) show ν(PtCl) absorptions in the range 347−341 cm^{-1}. In *trans*-dichloroplatinum(IV) complexes, characterized by X-ray diffraction studies, one band in the region 344−360 cm^{-1} has been assigned.[30,33] The cis geometry of **2·NMe$_4$** is proposed on the basis of the IR spectrum, which shows two bands at 311 and 264 cm^{-1}, assignable to ν(PtCl) trans to ethylene and the acetonyl group, respectively, in agreement with the assignment made for **3** and the stronger trans influence of the acetonyl ligand with respect to the ethylene ligand.

The number of ν(CO) bands in the IR spectra of complexes is usually lower than expected. Thus, while the two expected ν(CO) bands in complexes **1** are observed in **1·C** (1686, 1682 cm^{-1}), both are coincident in **1·K** (1689 cm^{-1}). The other complexes show one or two (only **6**, **13**) bands in the range 1689−1645 cm^{-1}.

Conclusions

We have found that acetonyl Pt(IV) complexes can be prepared (i) by a transmetalation/oxidation reaction using $[Hg\{CH_2C(O)Me\}_2]$ and $K[PtCl_3(C_2H_4)]$ and (ii) by oxidative addition reactions of $PhICl_2$, MeI, RX (R = ketonyl, X = Cl, Br), or $[Hg\{CH_2C(O)Me\}Cl]$ to $[Pt\{CH_2C(O)Me\}Cl(bpy)]$ or $[Pt\{CH_2C(O)Me\}_2(bpy)]$. The mechanism of the transmetalation/oxidation reaction has been proved to occur in at least two steps: formation of the anionic acetonyl Pt(II) complex $K[Pt\{CH_2C(O)Me\}Cl_2(\eta^2\text{-}CH_2{=}CH_2)]$ and a redox transmetalation reaction leading to metallic Hg and $K[Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$. The oxidative addition reactions give mono(acetonyl), the first bis(acetonyl), and new tris(acetonyl) Pt(IV) complexes. The last group, along with $K[Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]$ and its neutral, anionic, and cationic substitution products, are the first tris(ketonyl) complexes of any metal. One of them, [*OC*-

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6-33]-[Pt{$CH_2C(O)Me$}$_2${$CH_2C(O)Ph$}Br(bpy)], is the first mixed ketonylmetal complex.

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Supporting Information Available: Text giving details of the synthesis and spectroscopic properties of [*OC*-6-13]-[Pt{$CH_2C(O)Me$}$_2$-Cl_2(bpy)] (**10**) and CIF files giving crystallographic data for **1·C**, **6**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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