Acetonyl Platinum(II) Complexes†

José Vicente,* Aurelia Arcas,* and Jesús M. Fernández-Hernández

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Aptdo. 4021, E-30071 Murcia, Spain

Gabriel Aullón*

Departament de Química Inorgànica and Centre de Recerca en Química Teórica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Delia Bautista*

SAI, Universidad de Murcia, Aptdo. 4021, E-30071 Murcia, Spain

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$Me_4N[Pt\{CH_2C(O)Me\}Cl_2(\eta^2\text{-}C_2H_4)]$ (**1**), reacts either (1) with neutral ligands to afford *cis*-Me_4N-$[Pt\{CH_2C(O)Me\}Cl_2(L)]$ (L = CO (**2**), η^2-PhCH=CH_2 (**3**), η^2-PhC≡CPh (**4**), η^2-H_2C=C=CMe_2 (**5**), PPh_3 (**6**), $AsPh_3$ (**7**)), *trans*- or/and *cis*-$[Pt\{CH_2C(O)Me\}ClL_2]$ (L = PPh_3 (**8**), $AsPh_3$ (**9**), tht (**10**), XyNC (**11**), ^{t}BuNC (**12**), py (**17**)), $[Pt\{CH_2C(O)Me\}Cl(\eta^2\text{-}C_2H_4)(L)]$ (L = py (**16**)), or *cis*-$[Pt\{CH_2C(O)Me\}ClL_2]$ (L_2 = norbornadiene (nbd, **18**), 1,5-cyclooctadiene (cod, **19**), bis(diphenylphosphino)methane (dppm, **20**), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dbbpy, **21**)) or (2) with [Tl(acac)] to give $[Pt\{CH_2C(O)Me\}(O,O\text{-acac})(\eta^2\text{-}C_2H_4)]$ (**22**) which reacts with neutral ligands to give $[Pt\{CH_2C(O)Me\}(O,O\text{-acac})(L)]$ (L = CO (**23**), PPh_3 (**24**), XyNC (**25**)). The different behavior of py and stronger π-acceptor ligands, as CO and PR_3 toward **1**, has been explained through a DFT study. Reaction of **11***trans* with 2 equiv of XyNC affords a mixture of *trans*-$[Pt\{C(O)NHXy\}Cl(CNXy)_2]$ (**13**) and *trans*-$[Pt\{C(NHXy)_2\}Cl(CNXy)_2]Cl$ (**14**). The first was isolated by recrystallization and the latter by reacting *cis*-$[PtCl_2(CNXy)_2]$ with 2 equiv of XyNC. However, *cis*-$[Pt\{CH_2C(O)Me\}_2(bpy)]$ reacts with 4 equiv of XyNC to give *cis*-$[Pt\{CH_2C(O)Me\}_2(CNXy)_2]$ (**15**).

Introduction

The chemistry of ketonylplatinum complexes has been studied to a lesser extent than that of the palladium analogues. During the late 1970s and early 1980s Bennett,[1,2] Pidcock,[3] and Otsuka[4] developed most of the chemistry of ketonyl complexes of Pt(II). They synthesized these compounds by reacting hydroxocomplexes with ketones. The reported acetonyl Pt(II) complexes contained other strongly coordinated ligands, such as phosphines or pyridine, which make them not appropriate to prepare derivatives. Acetonyl Pt(II) complexes containing the easily exchangeable ligand cod (cod = 1,5-cyclooctadiene) have been reported but in low yield.[5,6] Ketonyl complexes of Pt(IV) have been obtained by reacting $[PtMe_2L_2]$ with $XCH_2C(O)Ph$, by light irradiation of a $[PtCl_6]^{2-}$ solution in acetone, by reacting $K_2[PtCl_4]$ with iodoacetone in water, or by a redox transmetallation reaction using $[Hg\{CH_2C(O)Me\}_2]$.[7,8] Among ketonyl Pt(II) derivatives, only five have been characterized by X-ray diffraction studies and four of them are acetonyl complexes.[5,9−11]

We are studying the synthesis and properties of acetonyl metal complexes and finding some interesting results.[11−13] Thus, we

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* To whom correspondence should be addressed. E-mail: jvs1@um.es (J.V.); aurelia@um.es (A.A.). Web: http://www.scc.um.es/gqo/. Correspondence regarding the DFT studies should be addressed to G.A (gabriel.aullon@antares.qi.ub.es); correspondence regarding the X-ray diffraction studies should be addressed to D.B. (dbc@um.es).

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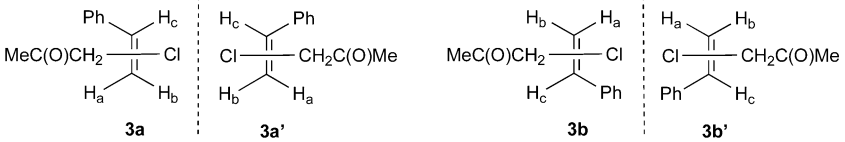
Chart 1. View of the Isomers of 3 through the Cl−Pt−Olefin Axis



have recently found that the reaction between [Hg{$CH_2C(O)Me$}$_2$] and the Pt(II) complex K[$PtCl_3(\eta^2$-$C_2H_4)$] (2:1) affords the Pt(IV) complex K[$Pt_2\{CH_2C(O)Me\}_6(\mu$-$Cl)_3$]. During the study carried out to elucidate the mechanism of formation of this Pt(IV) complex, the intermediate Pt(II) complex K[Pt{$CH_2C(O)Me$}$Cl_2(C_2H_4)$] was detected in solution and isolated as the Me_4N^+ salt (**1**).[8] Contrary to the previously reported Pt(II) acetonyl complexes, **1** offers the possibility of being used to prepare other monoacetonyl complexes by replacing any of the remaining three ligands.

From the studies of the reactivity of **1** toward XyNC we obtained fortuitously the carbamoyl and carbene complexes [Pt{C(O)NHXy}Cl(CNXy)$_2$] and [Pt{C(NHXy)$_2$}Cl(CNXy)$_2$]Cl, respectively, both resulting after hydrolysis of the acetonyl ligand and the nucleophilic attack of H_2O and $XyNH_2$, respectively, to a XyNC ligand. Although carbamoyl metal complexes are well-known,[14] no fully characterized [Pt(II){C(O)NRR′}(L)(L′)(L″)]$^{n-}$ complex with R or R′ = H is known and only a few with R = R′ = Et, n = 0, L = L′ = PPh_3, L″ = Cl,[15] C(O)Ph,[16] C(O)C(O)Ph, C(O)CO_2Me or[17] R = R′ = ^{i}Pr, n = 1, L = L′ = Cl, L″ = CO[18] have been reported. In addition, these complexes have been prepared using CO to form the carbamoyl ligand. As far as we are aware, the only examples of the synthesis of NH-carbamoyl Pt(II) complexes using isocyanides as the source of the carbamoyl ligand are the reaction of (1) nitrite or hydroxide ion with the cationic complex [$Pt(CNMe)_2(PPh_3)_2$]$^+$,[19,20] or (2) an isocyanide with [Pt(CF_3)(OH)(*cis*-$Ph_2PCH{=}CHPPh_2$)].[21] Conversely, a carbamoyl Pt(II) complex has been used to prepare the corresponding isocyanide complex.[22] The nucleophilic addition of amines to coordinated isocyanides to give amino carbene complexes is a very well-known process.[23]

Experimental Section

Unless otherwise stated, the reactions were carried out without precautions against 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 in Me_2CO (ca. 5×10^{-4} mol L^{-1}) 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. NMR spectra were recorded in a Brucker AC 200, Avance 300 or 400, or Brucker 600 spectrometer at room temperature unless otherwise stated. Chemical shifts were referred to TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P), or $Na_2[PtCl_6]$ (^{195}Pt). When needed, NMR assignments were performed with the help of APT, DEPT, COSY, one dimension NOE experiments, and HETCOR techniques. *cis*-[$PtCl_2$(CNXy)$_2$] has been prepared from *cis*-[$PtCl_2$(dmso)$_2$] and XyNC (1:2). [Hg{$CH_2C(O)Me$}$_2$],[24] K[$PtCl_3(C_2H_4)$],[25] *cis*-(Me_4N)[Pt{$CH_2C(O)Me$}$Cl_2(C_2H_4)$] (**1**),[8] [Pt{$CH_2C(O)Me$}$_2$(bpy)] (^{195}Pt{^{1}H} NMR, δ −3351), and [Pt{$CH_2C(O)Me$}Cl(bpy)][11] were prepared according to literature methods.

Synthesis of *cis*-Me_4N[Pt{$CH_2C(O)Me$}Cl_2(CO)] (2). A stream of CO was bubbled into a cooled (0 °C) solution of **1** (53.4 mg, 0.13 mmol) in Me_2CO (3 mL) for 10 min until a pale yellow solution was obtained. This solution was filtered through Celite, and the resulting solution was concentrated (to ca. 1 mL) in a water/ice bath. Addition of a saturated solution of CO in Et_2O (20 mL) gave a suspension that was filtered off. The filtrate was washed with Et_2O (5 mL) and air-dried to give **2** as a pale yellow solid that was stored at −34 °C. Yield: 43 mg, 81%; mp 94 °C. IR (cm^{-1}): ν(C≡O) 2086; ν(C═O) 1672; ν(Pt−Cl) 328, 284. ^{1}H NMR (300 MHz, acetone-d_6): δ 3.46 (t, {1:1:1}, 12 H, Me_4N) 2.94 (q, 2 H, CH_2, $^4J_{HH}$ = 0.8 Hz, $^2J_{HPt}$ = 148 Hz), 2.09 (t, MeC(O), $^4J_{HH}$ = 0.8 Hz, $^2J_{HPt}$ = 8.8 Hz). ^{13}C{^{1}H} NMR (75.45 MHz, acetone-d_6): δ 209.3 (Me*C*(O)), 159.3 (CO, $^1J_{CPt}$ = 1953 Hz), 55.2 (t, {1:1:1}, Me_4N, $^1J_{CN}$ = 4 Hz), 29.0 (MeC(O)), 21.1 ($PtCH_2$, $^1J_{CPt}$ = 532 Hz). ^{195}Pt{^{1}H} NMR (85.9 MHz, acetone-d_6): δ −3726.3. Anal. Calcd for $C_8H_{17}Cl_2NO_2Pt$: C, 22.60; H, 4.03; N, 3.29. Found: C, 22.61; H, 4.05; N, 3.32. ESI-MS(−): 350.7 [M]$^-$

Synthesis of *cis*-Me_4N[Pt{$CH_2C(O)Me$}$Cl_2(\eta^2$-$CH_2{=}CHPh)$] (3). To a solution of **1** (92 mg, 0.22 mmol) in Me_2CO (3 mL), $PhCH{=}CH_2$ (100 μL, 0.87 mmol) was added. The resulting solution was heated at 50 °C for 1 h and then was filtered through Celite. The filtrate was concentrated to dryness, and the solid residue was stirred with Et_2O (10 mL). The suspension was filtered off and the solid was washed with Et_2O (5 mL) and air-dried to give **3** as a colorless solid. Yield: 80 mg, 74%; mp 147−149 °C. Λ_M (Me_2CO, 2.49×10^{-4} mol L^{-1}): 121 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═O) 1671, ν(Pt−Cl) 305, 267. ^{1}H NMR (400 MHz, acetone-d_6, −20 °C): **3aa′** (Chart 1), δ 7.56−7.54 (m, 2 H, Ph), 7.32−7.28

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(m, 3 H, Ph), 6.15 (dd, 1 H, Hc, $^3J_{HbHc}$ = 8.4 Hz, $^3J_{HaHc}$ = 13.1 Hz, $^2J_{HcPt}$ = 81.1 Hz), 4.14 (d, 1 H, Ha, $^3J_{HaHc}$ = 13.1 Hz, $^2J_{HaPt}$ = 52.7 Hz), 3.71 (d, 1 H, Hb, $^3J_{HbHc}$ = 8.4 Hz, $^2J_{HbPt}$ = 76.7 Hz), 3.37 (s, Me_4N), 2.06 (s, 3 H, Me), 2.96 (d, 1 H, CH_2, $^2J_{HH}$ = 5.4 Hz, $^2J_{HPt}$ = 128 Hz), 1.06 (d, 1 H, CH_2, $^2J_{HH}$ = 5.4 Hz, $^2J_{HPt}$ = 89 Hz); **3bb′**, δ 7.50−7.22 (m, 2 H, Ph), 7.22−7.17 (m, 3 H, Ph), 5.66 (dd, 1 H, Hc, $^3J_{HbHc}$ = 8.1 Hz, $^3J_{HaHc}$ = 13.3 Hz, $^2J_{HcPt}$ = 73.8 Hz), 4.66 (d, 1 H, Ha, $^3J_{HaHc}$ = 13.3 Hz, $^2J_{HaPt}$ = 67.8 Hz), 3.43 (d, 1 H, Hb, $^3J_{HbHc}$ = 8.1 Hz, $^2J_{HcPt}$ = 69 Hz), 3.37 (s, Me_4N), 3.05 (d, 1 H, CH_2, $^2J_{HH}$ = 5.2 Hz, $^2J_{HPt}$ = 123 Hz), 2.18 (3 H, Me), 1.87 (d, 1 H, CH_2, $^2J_{HH}$ = 5.2 Hz, $^2J_{HPt}$ = 99 Hz). $^{13}C\{^1H\}$ NMR (100.8 MHz, acetone-d_6, −20 °C): **3aa′**, δ 211.1 (CO), 139.3 (C, Ph), 129.5 (CH, Ph), 129.1 (CH, Ph), 127.9 (CH, Ph), 79.6 (=*C*HPh, $^2J_{CPt}$ = 204 Hz), 55.3 (t, {1:1:1}, Me_4N, $^1J_{NC}$ = 4 Hz), 24.2 (CH_2, $^1J_{CPt}$ = 627 Hz); **3bb′**, δ 211.6 (CO), 139.0 (C, Ph), 129.4 (CH, Ph), 128.4 (CH, Ph), 127.7 (CH, Ph), 79.1 (=*C*HPh, $^2J_{CPt}$ = 210 Hz), 55.36 (t, {1:1:1}, Me_4N, $^1J_{CN}$ = 16 Hz), 55.1 (*C*H_2=), 23.9 (CH_2, $^1J_{CPt}$ = 591 Hz). $^{195}Pt\{^1H\}$ NMR (85.9 MHz, acetone-d_6, −20 °C): δ −3167.6, −3186.6. Anal. Calcd for $C_{15}H_{25}Cl_2NOPt$: C, 35.94; H, 5.03; N, 2.79. Found: C, 35.95; H, 5.16; N, 2.88. Single crystals of **3bb′** were obtained by slow diffusion of Et_2O into a solution of **3** in Me_2CO.

Synthesis of *cis*-Me_4N[Pt{$CH_2C(O)Me$}Cl_2(η^2-PhC≡CPh)] (4). To a solution of **1** (56 mg, 0.13 mmol) in Me_2CO (3 mL), PhC≡CPh was added (234 mg, 1.31 mmol). The resulting solution was stirred at 60 °C for 3.5 h and then concentrated to dryness. The resulting residue was stirred in Et_2O (10 mL) until an orange suspension was obtained and then was filtered off. The solid was air-dried for 24 h, to give **4** as a yellow solid. Yield: 58 mg, 77%. IR (cm^{-1}): ν(C=O) 1654; ν(Pt−Cl) 317, 254. ^1H NMR (400 MHz, acetone-d_6): δ 8.05−8.03 (m, 4 H, Ph), 7.42−7.36 (m, 6 H, Ph), 3.38 (s, 12 H, Me_4N) 2.64 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 107 Hz), 1.93 (s, MeC(O)). $^{13}C\{^1H\}$ NMR (50.30 MHz, acetone-d_6): δ 209.6 (CO), 131.5 (CH, Ph), 128.9 (CH, Ph), 128.7 (CH, Ph), 124.7 (C, Ph), 80.2 (C≡C), 55.9 (Me_4N), 29.7 (Me), 23.0 (CH_2). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −2606. Anal. Calcd for $C_{21}H_{27}Cl_2NOPt$: C, 43.83; H, 4.73; N, 2.43. Found: C, 43.10; H, 4.62; N, 2.48 (see Discussion).

Synthesis of *cis*-Me_4N[Pt{$CH_2C(O)Me$}Cl_2(η^2-CH_2=C=CMe_2)] (5). A solution of **1** (52 mg, 0.12 mmol) in CH_2Cl_2 (1.5 mL) was stirred for 2.5 h with CH_2=C=CMe_2 (25 μL, 0.25 mmol) under N_2 to give a suspension, which was filtered. The solid was washed with Et_2O (5 mL) and air-dried to give **5** as a colorless solid. The filtrate was concentrated. Et_2O was added, and the suspension was filtered; the solid was washed with Et_2O to give a second crop of **5**. Yield: 46 mg, 81%; mp 159−161 °C. Λ_M (Me_2CO, 5.69×10^{-4} mol L^{-1}): 114 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=O) 1659, ν(Pt−Cl) 315, 265. ^1H NMR (400 MHz, acetone-d_6): δ 3.45 (s, 12 H, Me_4N), 3.27 (m, 1 H, $^2J_{HPt}$ = 76.1 Hz), 3.02 (m, 1 H, $^2J_{HPt}$ = 64.7 Hz), 2.97 (d, 1 H, $PtCH_2$, $^1J_{HH}$ = 5.5 Hz, $^2J_{HPt}$ = 122.3 Hz), 2.10 (s, 3 H, MeC(O)), 2.06 (m, 3 H, CMe_2), 1.93 (m, 3 H, CMe_2), 1.72 (d, 1 H, $PtCH_2$, $^1J_{HH}$ = 5.5 Hz, $^2J_{HPt}$ = 93.5 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, acetone-d_6): δ 210.7 (CO, $^2J_{CPt}$ = 47 Hz), 153.9 (C, allene, $^1J_{CPt}$ = 391 Hz), 106.1 (C, allene, $^2J_{CPt}$ = 31 Hz), 56.1 (t, {1:1:1}, Me_4N, $^1J_{CN}$ = 4 Hz), 31.8 (CH_2, allene, $^1J_{CPt}$ = 155.3 Hz), 29.4 (*Me*C(O)), 23.5 ($PtCH_2$, $^1J_{CPt}$ = 586 Hz), 23.6 (Me, allene, $^3J_{CPt}$ = 58 Hz), 20.4 (Me, allene, $^3J_{CPt}$ = 57 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, acetone-d_6): δ −3013. Anal. Calcd for $C_{12}H_{25}Cl_2NOPt$: C, 30.97; H, 5.42; N, 3.01. Found: C, 30.85; H, 5.40; N, 3.08.

Synthesis of *cis*-Me_4N[Pt{$CH_2C(O)Me$}Cl_2(PPh_3)] (6). A suspension of **1** (56 mg, 0.13 mmol) in THF (1 mL) was stirred for 1.5 h with PPh_3 (34.5 mg, 0.13 mmol) under N_2. The suspension was filtered an the solid was recrystallized in CH_2Cl_2/Et_2O and air-dried to give **6** as a colorless solid. Yield: 68 mg, 78%; mp 225 °C. Λ_M (Me_2CO, 5×10^{-4} mol L^{-1}): 93 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=O) 1662, ν(Pt−Cl) 293, 270. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77−7.73 (m, 6 H, Ph), 7.37 (m, 9 H, Ph), 3.32 (s, 12 H, Me_4N), 2.37 (d, 2 H, CH_2, $^3J_{HP}$ = 4 Hz, $^2J_{HPt}$ = 111 Hz), 2.01 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 214.8 (d, CO, $^2J_{CP}$ = 4.5 Hz, $^2J_{CPt}$ = 52 Hz), 134.7 (d, CH_{orto}, $^2J_{CP}$ = 10.5 Hz), 130.8 (d, C_{ipso}, $^1J_{CP}$ = 43 Hz), 130.1 (d, CH_{para}, $^4J_{CP}$ = 2.3 Hz), 127.7 (d, CH_{meta}, $^3J_{CP}$ = 11 Hz), 56.0 (t, {1:1:1}, Me_4N, $^1J_{CN}$ = 3.2 Hz), 31.8 (Me), 20.5 (d, CH_2, $^2J_{CP}$ = 4 Hz, $^1J_{CPt}$ = 661 Hz). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 14.2 ($^1J_{PPt}$ = 4662 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −4091 (d, $^1J_{PPt}$ = 4662 Hz). Anal. Calcd for $C_{25}H_{32}Cl_2NOPPt$: C, 45.53; H, 4.89; N, 2.12. Found: C, 45.15; H, 4.96; N, 2.17.

Synthesis of *cis*-Me_4N[Pt{$CH_2C(O)Me$}Cl_2($AsPh_3$)] (7). To a suspension of **1** (44 mg, 0.10 mmol) in THF (2 mL), $AsPh_3$ (31.7 mg, 0.10 mmol) was added under N_2. The reaction mixture was stirred for 1 h, and the suspension was filtered. The solid was washed with Et_2O, recrystallized in CH_2Cl_2/Et_2O, and dried for 1 day under vacuum to give **7** as a pale yellow solid. Yield: 54 mg, 75%; mp 196 °C. Λ_M (Me_2CO, 5×10^{-4} mol L^{-1}): 127 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=O) 1649, ν(PdCl) 297, 273. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74−7.71 (m, 6 H, Ph), 7.41−7.34 (m, 9 H, Ph), 3.29 (s, 12 H, Me_4N), 2.58 (s, 2 H, CH_2, $^2J_{HPt}$ = 102 Hz), 2.03 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 214.3 (CO), 134.1 (CH), 131.7 (C), 129.9 (CH), 128.3 (CH), 55.9 (unresolved t, Me_4N), 31.6 (Me), 15.1 (CH_2). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −3950. Anal. Calcd for $C_{25}H_{32}AsCl_2NOPt$: C, 42.70; H, 4.58; N, 1.99. Found: C, 42.37; H, 4.69; N, 2.08.

Synthesis of *cis*- and *trans*-[Pt{$CH_2C(O)Me$}$Cl(PPh_3)_2$] (8). Method a. To a solution of **1** (55 mg, 0.13 mmol) in CH_2Cl_2 (3 mL), PPh_3 (68 mg, 0.26 mmol) was added under N_2. The resulting suspension was filtered to remove Me_4NCl, and the filtrate was concentrated to dryness. The residue was stirred with Et_2O (10 mL) and filtered off. The resulting colorless solid was air-dried to give **8***trans*. Yield: 85 mg, 81%.

Method b. A suspension of [$Pt(PPh_3)_4$] (146 mg, 0.12 mmol) in toluene (8 mL) was stirred for 24 h with [Hg{$CH_2C(O)Me$}Cl] (39 mg, 0.13 mmol) under N_2. The suspension was filtered. The solid was stirred in CH_2Cl_2 and filtered through Celite to remove Hg. The filtrate was concentrated (to ca. 1 mL) and addition of Et_2O (5 mL) gave a suspension, which was filtered, and the solid was air-dried to give **8***cis* contaminated with *cis*-[$PtCl_2(PPh_3)_2$]. The filtrate from the reaction mixture was concentrated (2 mL), Et_2O (5 mL) was added and the resulting suspension filtered off. The solid was washed with Et_2O (2 mL) and air-dried to give a mixture of **8***cis* and **8***trans* contaminated with *cis*-[$PtCl_2(PPh_3)_2$]. IR (cm^{-1}): ν(C=O) 1688 (**8***trans*), 1650 (**8***cis*), ν(Pt−Cl) 276 (**8***trans*), 298 (**8***cis*). ^1H NMR (400 MHz, $CDCl_3$): **8***trans*, δ 7.84−7.81 (m, 12 H, Ph), 7.41−7.38 (m, 18 H, Ph), 2.14 (t, 2 H, CH_2, $^3J_{HP}$ = 7.8 Hz, $^2J_{HPt}$ = 87.6 Hz), 1.51 (s, 3 H, Me, $^4J_{HPt}$ = 10.4 Hz); **8***cis*, δ 2.63 (dd, 2 H, CH_2, $^3J_{HP}$ = 11 Hz, $^3J_{HP}$ = 5.7 Hz, $^2J_{HPt}$ = 76 Hz), 2.25 (s, 3 H, Me, $^4J_{HPt}$ = 10.4 Hz). $^{31}P\{^1H\}$ NMR (162.29 MHz, $CDCl_3$): **8***trans*, δ 25.6 (s, PPh_3, $^1J_{PPt}$ = 3065 Hz); **8***cis*, δ 21.8 (d, PPh_3 trans to acetonyl, $^2J_{PP}$ = 16 Hz, $^1J_{PPt}$ = 1973 Hz), 18.5 (d, PPh_3 cis to Cl, $^2J_{PP}$ = 16 Hz, $^1J_{PPt}$ = 4319 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): **8***trans*, δ −4584.8 (t, $^1J_{PPt}$ = 3065 Hz). Single crystals of **8***trans*·$CHCl_3$ were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of **8***trans*.

Synthesis of [Pt{$CH_2C(O)Me$}$Cl(AsPh_3)_2$] (9). To a solution of **1** (68 mg, 0.16 mmol) in CH_2Cl_2 (4 mL), $AsPh_3$ (98 mg, 0.32 mmol) was added. The resulting suspension was filtered through Celite to remove Me_4NCl, the filtrate was concentrated (to ca. 1 mL), Et_2O (10 mL) was added and the suspension was stirred for 15 min. The resulting suspension was filtered off, washed with Et_2O (2 mL) and air-dried to give **9***trans* as a colorless solid. Yield: 102 mg, 71%; mp 194−198 °C. IR (cm^{-1}): ν(C=O) 1659. ν(Pt−Cl) 284. A $CDCl_3$ solution of **9***trans* led, after 16 h at room temperature, to a mixture of cis/trans isomers (1:1). ^1H NMR (400 MHz, $CDCl_3$): **9***trans*, δ 7.79−7.76 (m, 12 H, Ph), 7.43−7.38 (m, 18 H,

Ph), 2.35 (s, 2 H, CH_2, $^2J_{HPt}$ = 96 Hz), 1.34 (s, 3 H, Me); **9***cis*, δ 7.52−7.08 (m, 30 H, Ph), 2.93 (s, 2 H, CH_2, $^2J_{HPt}$ = 89.6 Hz), 2.30 (s, 3 H, Me). ^{195}Pt{^{1}H} NMR (85.88 MHz, $CDCl_3$): **9***trans*, δ −4467; **9***cis*, δ −4542. Anal. Calcd for $C_{39}H_{35}As_2ClOPt$: C, 52.04; H, 3.90. Found: C, 51.60; H, 3.70.

Synthesis of *trans*-[Pt{CH$_2$C(O)Me}Cl(tht)$_2$] (10). To a solution of **1** (61 mg, 0.14 mmol) in CH_2Cl_2 (3 mL), tht (tetrahydrothiophen, 32 μL, 0.36 mmol) was added. The resulting suspension was concentrated to dryness, the residue was extracted with Et_2O (2 × 5 mL), and the extract was concentrated to dryness. The resulting yellow oil was washed with *n*-pentane (2 × 3 mL), treated in vacuo for 10 h, and stirred with Et_2O (1 mL) at 0 °C followed by the addition of pentane (5 mL) to give **10** as a yellow solid. Yield: 48 mg, 73%; mp 137 °C. IR (cm^{-1}): ν(C═O) 1645, ν(Pt−Cl) 285. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.32 (br, 8 H, CH_2, tht), 2.68 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 110.1 Hz), 2.20−2.14 (m, 8 H, CH_2, tht), 2.17 (s, 3 H, *Me*C(O)). ^{13}C{^{1}H} NMR (50.30 MHz, $CDCl_3$): δ 210.5 (CO, $^2J_{CPt}$ = 49.2 Hz), 37.7 (CH_2, tht, $^2J_{CPt}$ = 15.8 Hz), 30.2 (*Me*C(O)), 30.1 (CH_2, tht, $^3J_{CPt}$ = 11.7 Hz), 20.3 ($PtCH_2$, $^1J_{CPt}$ = 599 Hz). ^{195}Pt{^{1}H} NMR (85.9 MHz, $CDCl_3$): δ −3931. Anal. Calcd for $C_{11}H_{21}ClOPtS_2$: C, 28.48; H, 4.56; S, 13.82. Found: C, 28.08; H, 4.54; S, 13.43.

Synthesis of *cis*- and *trans*-[Pt{CH$_2$C(O)Me}Cl(CNXy)$_2$] (11). To a solution of **1** (75 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) was added XyNC (47 mg, 0.36 mmol). The suspension was filtered through Celite to remove Me_4NCl, the filtrate was concentrated to dryness and *n*-pentane (10 mL) was added. The suspension was stirred at 0 °C for 30 min and filtered off. The pale yellow solid obtained was washed with *n*-pentane (5 mL) and air-dried to give **11** (mainly the cis isomer). Yield: 77 mg, 80%; mp 121−133 °C. IR (cm^{-1}): ν(C≡N) 2200, 2171, ν(C═O) 1660, ν(Pt−Cl) 326 (cis). ^{1}H NMR (300 MHz, $CDCl_3$, cis:trans isomers 1:0.7): **11***cis*, δ 7.31−7.12 (m, Ph), 3.09 (q, 2 H, $PtCH_2$, $^4J_{HH}$ = 0.6 Hz, $^2J_{HPt}$ = 90 Hz), 2.50 (s, 6 H, Me, Xy), 2.47 (s, 6 H, Me, Xy), 2.25 (t, 3 H, MeC(O)), $^4J_{HH}$ = 0.6 Hz); **11***trans*, δ 7.31−7.12 (m, Ph), 3.04 (q, 2 H, $PtCH_2$, $^4J_{HH}$ = 0.9 Hz, $^2J_{HPt}$ = 114 Hz), 2.53 (s, 12 H, Me, Xy), 2.25 (t, 3 H, MeC(O), $^4J_{HH}$ = 0.9 Hz). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 213.3 (CO, cis isomer), 210.8 (CO, trans isomer), 136.3 (C), 135.8 (C), 135.7 (C), 130.3 (CH), 130.2 (CH), 129.7 (CH), 128.2 (CH), 128.1 (CH), 31.4 (CH_2, cis isomer, $^1J_{CPt}$ = 422 Hz), 31.2 (*Me*C(O), cis isomer), 30.2 (*Me*C(O), trans isomer), 18.7 (Me, Xy) 11.8 (CH_2, trans isomer, $^1J_{CPt}$ = 522 Hz). ^{195}Pt{^{1}H} NMR (85.88 MHz, $CDCl_3$): **11***cis*, δ −3999 (m); **11***trans*, δ −4130 (m). Anal. Calcd for $C_{21}H_{23}ClN_2OPt$: C, 45.86; H, 4.22; N, 5.09. Found: C, 45.50; H, 4.31; N, 5.17.

Synthesis of *trans*-[Pt{CH$_2$C(O)Me}Cl(CNXy)$_2$] (11*trans*). To a cooled solution (0 °C) of **1** (52 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was slowly added XyNC (31 mg, 0.24 mmol). The suspension was filtered through Celite to remove Me_4NCl. The filtrate was concentrated to dryness, and Et_2O (15 mL) was added. The suspension was filtered off to give **11***trans* as a pale yellow solid. By concentration of the filtrate, a second crop of **11***trans* was obtained. Yield: 60 mg, 95%; mp 145 °C. IR (cm^{-1}): ν(C≡N) 2186, ν(C═O) 1670, ν(Pt−Cl) 304. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31−7.14 (m, Ph), 3.04 (q, 2 H, $PtCH_2$, $^4J_{HH}$ = 0.9 Hz, $^2J_{HPt}$ = 114 Hz), 2.53 (s, 12 H, Me, Xy), 2.26 (t, 3 H, MeC(O), $^4J_{HH}$ = 0.9 Hz). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 210.8 (CO), 136.3 (C), 130.3 (CH), 128.1 (CH), 30.2 (*Me*C(O)), 18.7 (Me, Xy), 11.7 (CH_2, $^1J_{CPt}$ = 521 Hz).

Synthesis of *cis*- and *trans*-[Pt{CH$_2$C(O)Me}Cl(CN^{t}Bu)$_2$] (12). To a solution of **1** (57 mg, 0.13 mmol) in CH_2Cl_2 (3 mL), ^{t}BuNC (32 μL, 0.28 mmol) was added. After 20 min, the suspension was filtered through anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The resulting oil was washed with *n*-pentane (3 mL), stirred with *n*-pentane (5 mL), and concentrated to dryness. This treatement was repeated three more times and the resulting yellow oil was stirred at 0 °C for 3 h. The suspension was filtered off and air-dried to give **12** (mainly the cis isomer) as a yellow solid. Yield: 35 mg, 60%. IR (cm^{-1}): ν(C≡N) 2223, 2193, ν(C═O) 1662, ν(Pt−Cl) 325 (cis). ^{1}H NMR (300 MHz, $CDCl_3$, cis/trans isomers 1:0.9): **12***cis*, δ 2.80 (q, 2 H, CH_2, $^4J_{HH}$ = 0.6 Hz, $^2J_{HPt}$ = 92 Hz), 2.14 (t, 3 H, MeCO, $^4J_{HH}$ = 0.6 Hz), 1.58 (s, 18 H, ^{t}Bu co-incident with that of the trans isomer), 1.55 (s, 9 H, ^{t}Bu); **12***trans*, δ 2.73 (q, 2 H, CH_2, $^2J_{HPt}$ = 115 Hz, $^4J_{HH}$ = 0.6 Hz), 2.14 (t, 3 H, *Me*CO, $^4J_{HH}$ = 0.6 Hz), 1.58 (s, 18 H, ^{t}Bu co-incident with that of the cis isomer). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): **12***cis*, δ 213.7 (CO, $^2J_{CPt}$ = 29 Hz), 31.5 (CH_2, $^1J_{CPt}$ = 420 Hz), 30.7 (*Me*C(O)), 29.98 (C*Me*$_3$), 29.95 (C*Me*$_3$); **12***trans*, 211.1 (CO, $^2J_{CPt}$ = 54 Hz), 29.95 (C*Me*$_3$), 29.8 (*Me*CO), 11.7 (CH_2, $^1J_{CPt}$ = 523 Hz). ^{195}Pt{^{1}H} NMR (128.47 MHz, $CDCl_3$): **12***cis*, δ −4098 (m, {1:1:3:1:3:1:1}, $^2J_{PtN}$ = 129 Hz, $^2J_{NPt}$ = 64.5 Hz); **12***trans*, δ −4197 (quintuplet, {1:2:3:2:1}, $^2J_{NPt}$ = 103 Hz). Anal. Calcd for $C_{13}H_{23}ClN_2OPt$: C, 34.40; H, 5.11; N, 6.17. Found: C, 34.03; H, 5.16; N, 6.30.

Synthesis of *trans*-[Pt{CH$_2$C(O)Me}Cl(CN^{t}Bu)$_2$] (12*trans*). To a cooled solution (0 °C) of **1** (45 mg, 0.11 mmol) in CH_2Cl_2 (3 mL), ^{t}BuNC (22.5 μL, 0.20 mmol) was slowly added. The suspension was filtered through Celite to remove Me_4NCl, and the filtrate was concentrated to dryness in a cold bath. Et_2O (10 mL) was added to the resulting residue, and the suspension was filtered off. The filtrate was concentrated to dryness and then was vacuum-dried to give **12***trans* as a pale yellow solid. Yield: 35 mg, 60%; mp 104 °C. IR (cm^{-1}): ν(C≡N) 2206, ν(C═O) 1666, ν(Pt−Cl) 292. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (q, 2 H, CH_2, $^2J_{HPt}$ = 115 Hz, $^4J_{HH}$ = 0.6 Hz), 2.14 (t, 3 H, MeC(O), $^4J_{HH}$ = 0.6 Hz), 1.57 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 211.07 (CO, $^2J_{CPt}$ = 53 Hz), 29.96 (C*Me*$_3$), 29.86 (*Me*CO), 11.74 (CH_2, $^2J_{CPt}$ = 525 Hz).

Synthesis of *trans*-[Pt{C(O)NHXy}Cl(CNXy)$_2$] (13). Method A. To a solution of complex **11***trans* (60 mg, 0.11 mmol) in acetone (5 mL), XyNC (15 mg, 0.114 mmol) was added and the mixture was heated at 60 °C for 24 h. The suspension was concentrated to dryness and acetone (3 mL) was added to the residue. The suspension was filtered off and the solid was air-dried to give **13** as a colorless solid (29 mg, 40%)

Method B. To a solution of **11***trans* (62 mg, 0.11 mmol) in $CHCl_3$ (5 mL), XyNC (31 mg, 0.24 mmol) was added. After 64 h, the solution was filtered through Celite and the filtrate was concentrated to dryness. The solid was stirred with Et_2O (5 mL), the suspension was filtered, and the solid recrystallized in $CHCl_3$/Et_2O and air-dried to give **13** as a colorless solid. Yield: 24 mg, 36%; mp 190 °C. IR (cm^{-1}): ν(N−H) 3296, ν(C−N) 2190, ν(C═O) 1626, ν(Pt−Cl) 278. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.26 (m, 2 H, Xy), 7.15−7.13 (m, 4 H, Xy), 7.06−7.04 (m, 3 H, Xy), 6.80 (s, 1 H, NH), 2.50 (s, 12 H, XyNC), 2.27 (s, 6 H, XyNHC(O)). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$): δ 154.4 (CO, $^1J_{CPt}$ = 1013 Hz), 136.3, 134.6, 130.4 (CH, XyNC), 128.2 (CH, XyNC), 128.1 (CH, XyNC), 126.8, 19.1 (Me, XyNH), 18.8 (Me, Xy). Anal. Calcd for $C_{27}H_{28}ClN_3OPt$: C, 50.59; H, 4.40; N, 6.55. Found: C, 50.15; H, 4.97; N, 6.62. Single crystals of **13**·1.5$CHCl_3$ were obtained by slow evaporation of a $CDCl_3$ solution of **13**.

Synthesis of *trans*-[Pt{C(NHXy)$_2$}Cl(CNXy)$_2$]Cl (14). To a suspension of *cis*-[$PtCl_2$(CNXy)$_2$] (74 mg, 0.14 mmol) in $CHCl_3$ (5 mL), XyNC (37 mg, 0.28 mmol) was added. After 72 h, the yellow solution was filtered, and the filtrate was concentrated to dryness. The solid was stirred with Et_2O (5 mL) and the suspension was filtered off and air-dried to give **14** as a colorless solid. Yield: 85 mg, 77%; mp 236 °C. IR (cm^{-1}): ν(N−H) 3296, ν(C≡N) 2204, ν(Pt−Cl) 310. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.04 (s, 2 H, NH, $^3J_{HPt}$ = 84 Hz), 7.36−7.31 (m, 2 H, Xy), 7.18−7.08 (m, 6 H, Xy), 6.94−6.92 (m, 4 H, Xy), 2.47 (s, 12 H, Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 171.0 (C carbene, $^1J_{CPt}$ = 1131 Hz), 137.6 (C), 136.05 (C), 136.02 (C), 132.1 (*C*NXy), 131.0 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 19.5 (Me), 18.5 (Me). Anal. Calcd for

$C_{35}H_{38}Cl_2N_4Pt$: C, 53.85; H, 4.91; N, 7.18. Found: C, 53.30; H, 4.96; N, 7.18. Single crystals of **15** were obtained by slow diffusion of Et_2O into a solution of **15** in $CDCl_3$.

Synthesis of *cis*-[Pt{$CH_2C(O)Me$}$_2$(CNXy)$_2$] (15). XyNC (225 mg, 1.71 mmol) was added to a solution of [Pt{$CH_2C(O)Me$}$_2$-(bpy)] (200 mg, 0.43 mmol) in CH_2Cl_2 (7 mL). After 15 min the suspension was filtered through Celite to remove Me_4NCl, and the filtrate was concentrated to dryness. The residue was extracted with Et_2O (10 mL). The extract was concentrated (4 mL), and *n*-pentane (15 mL) was added to precipitate a solid that was stirred for 1 h at 0 °C. The resulting suspension was filtered off, and the yellow solid obtained was washed with *n*-pentane (5 mL) and air-dried to give **15**. Yield: 160 mg, 65%; mp 104−109 °C. IR (cm^{-1}): ν(C≡N) 2182, 2148; ν(C═O) 1659. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27−7.22 (m, 2 H, Xy), 7.12−7.01 (m, 4 H, Xy), 2.88 (s, 4 H, CH_2, $^2J_{HPt}$ = 102 Hz), 2.47 (s, 12 H, Me, Xy), 2.14 (s, 6 H, MeC(O), $^4J_{HPt}$ = 16 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 213.9 (CO, $^2J_{CPt}$ = 39 Hz), 143.2 (br, CN), 135.3 (C, Xy), 129.4 (CH, Xy), 128.1 (CH, Xy), 126.6 (br, C, Xy), 32.0 ($PtCH_2$, $^1J_{CPt}$ = 471 Hz), 30.8 (*Me*C(O)), 18.7 (Me, Xy). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −4167 (m). Anal. Calcd for $C_{24}H_{28}N_2O_2Pt$: C, 50.43; H, 4.94; N, 4.90. Found: C, 50.32; H, 4.95; N, 5.12.

Synthesis of [Pt{$CH_2C(O)Me$}Cl(η^2-C_2H_4)(py)] (16). To a solution of **1** (62 mg, 0.15 mmol) in CH_2Cl_2 (3 mL), py (24 μL, 0.29 mmol) was added. The resulting suspension was stirred for 30 min and then was filtered through Celite to remove Me_4NCl. The filtrate was concentrated (to ca. 1 mL) and Et_2O (5 mL) was added. The solution was concentrated until a colorless solid precipitated. Addition of *n*-pentane (10 mL) gave more precipitate, which was filtered off, washed with *n*-pentane (5 mL), and air-dried to give **16** as a colorless solid. Yield: 47 mg, 82%; mp 64 °C. IR (cm^{-1}): ν(C═O) 1657; ν(Pt−Cl) 317. ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (m, 2 H, py), 7.85 (m, 1 H, py), 7.48 (m, 2 H, py), 3.89 (s, 4 H, C_2H_4, $^2J_{HPt}$ = 68.6 Hz), 2.65 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 100.4 Hz), 2.32 (s, 3 H, MeC(O)). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 215.5 (CO), 150.5 (CH, *o*-py), 139.0 (CH, *p*-py), 126.8 (CH, *m*-py, $^3J_{CPt}$ = 18 Hz), 66.0 (C_2H_4, $^1J_{CPt}$ = 221 Hz), 31.5 (*Me*C-(O)), 18.4 (s, $PtCH_2$, $^1J_{CPt}$ = 562 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −3366. Anal. Calcd for $C_{10}H_{15}ClNOPt$: C, 30.35; H, 3.82; N, 3.54. Found: C, 30.31; H, 3.61; N, 3.52.

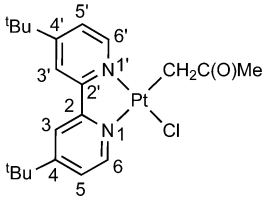
Synthesis of [Pt{$CH_2C(O)Me$}Cl(py)$_2$] (17). To a solution of **16** (51.7 mg, 0.13 mmol) in Me_2CO (3 mL) was added py (53 μL, 0.65 mmol). The resulting solution was refluxed for 4.5 h, the suspension was filtered through Celite, and the filtrate was concentrated to ca. 0.5 mL. Addition of *n*-pentane (5 mL) gave a suspension, which was stirred for 30 min at 0 °C and then filtered off. The solid was air-dried to give **17** as a colorless solid. Yield: 40 mg, 69%. IR (cm^{-1}): ν(C═O) 1650; ν(Pt−Cl) 332, 290. ^1H RMN: (400 MHz, $CDCl_3$, cis:trans isomers 3:1): **17***cis*, δ 8.79−8.77 (m, 2 H, py, $^3J_{HPt}$ = 46 Hz), 8.61−8.60 (m, 2 H, py), 7.81−7.75 (m, 2 H, py), 7.36−7.26 (m, 2 H, py), 3.16 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 110 Hz), 2.33 (s, 3 H, Me); **17***trans*, δ 8.77−8.92 (m, 2 H, py), 7.81−7.75 (m, 2 H, py), 7.36−7.26 (m, 2 H, py), 2.90 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 122 Hz), 1.73 (s, 3 H, Me). $^{13}C\{^1H\}$ (100.81 MHz, $CDCl_3$): **17***cis*, δ 215.7 (CO), 152.3 (CH, *o*-py), 150.4 (CH, *o*-py), 137.7 (CH, *p*-py), 126.3 (CH, *m*-py), 125.5 (CH, *m*-py), 30.3 (Me), 15.2 (CH_2, $^1J_{CPt}$ = 569 Hz); **17***trans*, δ 210.9 (CO), 153.5 (CH, *o*-py), 137.5 (CH, *p*-py), 125.6 (CH, *m*-py), 29.4 (Me), 25.0 (CH_2, $^1J_{CPt}$ = 679 Hz). Anal. Calcd for $C_{13}H_{15}ClN_2OPt$: C, 35.02; H, 3.39; N, 6.28. Found: C, 34.67; H, 3.38; N, 6.28.

Synthesis of [Pt{$CH_2C(O)Me$}Cl(nbd)] (18). To a solution of **1** (65 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added norbornadiene (30 μL, 0.29 mmol). After 2 h, the suspension was filtered through Celite to remove Me_4NCl, and the filtrate was concentrated to dryness. The residue was dissolved in Et_2O (10 mL) and filtered off. The filtrate was concentrated to dryness and dried under vacuum to give **18** as a colorless solid. Yield: 41 mg, 71%; mp 91−94 °C. IR (cm^{-1}): ν(C═O) 1656, ν(Pt−Cl) 317. ^1H NMR (400 MHz, $CDCl_3$): δ 5.55 (m, 2 H, C*H* trans to acetonyl, $^2J_{HPt}$ = 38.6 Hz), 4.82 (m, 2 H, C*H* trans to Cl, $^2J_{HPt}$ = 74.6 Hz), 4.15 (m, 2 H, CH), 2.91 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 121.5 Hz), 2.07 (s, 3 H, Me), 1.78 (m, 2 H, CH_2, $^4J_{HPt}$ = 12 Hz). $^{13}C\{^1H\}$ NMR (50.30 MHz, $CDCl_3$): δ 209.1 (CO, $^2J_{CPt}$ = 44 Hz), 99.1 (CH trans to acetonyl, $^1J_{CPt}$ = 29 Hz), 74.1 (CH trans to Cl, $^1J_{CPt}$ = 171.4 Hz), 70.3 (CH_2, $^3J_{CPt}$ = 109 Hz), 48.8 (CH, $^2J_{CPt}$ = 51 Hz), 37. 5 ($PtCH_2$, $^1J_{CPt}$ = 613 Hz), 30.9 (s, Me). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −3381. Anal. Calcd for $C_{10}H_{13}ClOPt$: C, 31.63; H, 3.45. Found: C, 31.96; H, 3.64.

Synthesis of [Pt{$CH_2C(O)Me$}Cl(cod)] (19). Method a. To a solution of **1** (76 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) was added cod (33 μL, 0.27 mmol). After stirring for 30 min, the resulting suspension was filtered to remove Me_4NCl, and the filtrate was concentrated to dryness. The residue was extracted with Et_2O (3 × 5 mL) and the resulting solution was concentrated to dryness and dried under vacuum for 6 h to give **19** as a colorless solid. Yield: 36 mg, 51%.

Method b. A suspension of [$PtCl_2$(cod)] (72 mg, 0.19 mmol) and [Hg{$CH_2C(O)Me$}$_2$] (61 mg, 0.19 mmol) in Me_2CO (10 mL) was refluxed for 28 h. The resulting solution was concentrated to dryness, and the residue was extracted with Et_2O (10 mL) and filtered through Celite. The filtrate was concentrated to dryness to give a colorless solid, which was washed with H_2O (3 × 5 mL), dissolved in Et_2O (10 mL), stirred with anhydrous $MgSO_4$, and then filtered off. The filtrate was concentrated to dryness, and the residue was stirred with *n*-pentane (5 mL). The suspension was filtered off, and the resulting colorless solid was air-dried to give **19**. Yield: 20 mg, 20%. IR (cm^{-1}): ν(C═O) 1656, ν(Pt−Cl) 316. ^1H NMR (300 MHz, $CDCl_3$): δ 5.61 (m, 2 H, CH trans to acetonyl, $^2J_{HPt}$ = 40 Hz), 4.93 (m, 2 H, CH trans to Cl, $^2J_{HPt}$ = 71 Hz), 2.91 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 103 Hz), 2.57−2.24 (m, 8 H, CH_2, cod), 2.24 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 211.4 (CO), 112.6 (CH trans to acetonyl, $^1J_{CPt}$ = 48.6 Hz), 90.0 (CH trans to Cl, $^1J_{CPt}$ = 194 Hz), 35.8 ($PtCH_2$, $^1J_{CPt}$ = 551.4 Hz), 31.9 (CH_2, $^2J_{CPt}$ = 18.8 Hz), 31.0 (Me), 28.2 (CH_2, $^2J_{CPt}$ = 17.7 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −3507. Anal. Calcd for $C_{11}H_{17}ClOPt$: C, 33.38; H, 4.33. Found: C, 33.73; H, 4.60.

Synthesis of [Pt{$CH_2C(O)Me$}Cl(dppm)] (20). A suspension of **1** (62 mg, 0.15 mmol) in THF (5 mL) was stirred for 30 min with dppm (bis(diphenylphosphino) methane, 56.6 mg, 0.15 mmol) under N_2. The resulting yellow suspension was filtered through Celite to remove Me_4NCl, the filtrate was concentrated, and Et_2O (20 mL) was added. The resulting suspension was filtered off, and the solid was recrystallized from toluene/Et_2O to give **20** as a yellow solid. Yield: 47 mg, 50%; mp 182−184 °C. IR (cm^{-1}): ν(C═O) 1646; ν(Pt−Cl) 293. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85−7.68 (m, Ph), 7.52−7.40 (m, Ph), 4.27 (t, 2 H, CH_2, dppm, $^2J_{HP}$ = 6.6 Hz), 2.93 (dd, 2 H, $PtCH_2$, $^2J_{HP}$ = 12.6 Hz, $^2J_{HP}$ = 1.8 Hz, $^2J_{HPt}$ = 90 Hz), 1.90 (s, 3 H, MeC(O)). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −43.7, −45.8 (AB system, P trans to Cl: $^2J_{PP}$ = 55 Hz, $^1J_{PPt}$ = 3645 Hz, P trans to acetonyl, $^2J_{PP}$ = 55 Hz, $^1J_{PPt}$ = 1656 Hz). Anal. Calcd for $C_{28}H_{27}ClOP_2Pt$: C, 50.05; H, 4.05. Found: C, 49.82; H, 4.08.



Synthesis of [Pt{$CH_2C(O)Me$}Cl(dbbpy)] (21). To a solution of **1** (100 mg, 0.24 mmol) in CH_2Cl_2 (3 mL), dbbpy (4,4′-ditertbutyl-2,2′-bipyridine, 65 mg, 0.24 mmol) was added. The resulting suspension was filtered through Celite to remove Me_4-

NCl, and the filtrate was concentrated (1 mL). Addition of Et_2O (10 mL) gave a suspension that was filtered off, washed with Et_2O (5 mL), and air-dried to give **21** as a yellow solid. Yield: 113 mg, 86%; mp 295−300 °C. IR (cm^{-1}): ν(C═O) 1650, ν(Pt−Cl) 326. ^1H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, 1 H, H6′, $^3J_{HH}$ = 6.3 Hz, $^2J_{HPt}$ = 44.9 Hz), 9.47 (d, 1 H, H6, $^3J_{HH}$ = 5.9 Hz), 7.88 (d, 1 H, H3, $^4J_{HH}$ = 1.4 Hz), 7.84 (d, 1 H, H3′, $^4J_{HH}$ = 1.4 Hz), 7.59 (dd, 1 H, H5, $^4J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 5.9 Hz), 7.56 (dd, 1 H, H5′, $^4J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 6.3 Hz), 3.34 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 108 Hz), 2.31 (s, MeC(O)), 1.43 (s, 9 H, ^{t}Bu), 1.41 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 216.3 (CO, $^2J_{CPt}$ = 42 Hz), 163.4 (C, dbbpy), 162.3 (C, dbbpy), 157.1 (C, dbbpy), 154.9 (C, dbbpy, $^2J_{CPt}$ = 40 Hz), 151.3 (C6′, $^2J_{CPt}$ = 34 Hz), 147.8 (C6), 124.9 (C5′, $^3J_{CPt}$ = 49 Hz), 123.9 (C5), 119.0 (C3′, $^3J_{CPt}$ = 25 Hz), 118.3 (C3), 35.6 (*C*Me_3), 30.0 (*Me*C(O)), 30.0 (C*Me*$_3$), 19.7 ($PtCH_2$, $^1J_{CPt}$ = 594 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −2953. Anal. Calcd for $C_{21}H_{29}ClN_2OPt$: C, 45.36; H, 5.26; N, 5.04. Found: C, 45.03; H, 5.36; N, 5.03.

Synthesis of [Pt{$CH_2C(O)Me$}(acac)(C_2H_4)] (22). To a solution of **1** (52 mg, 0.12 mmol) in CH_2Cl_2 (4 mL), [Tl(acac)] (39 mg, 0.13 mmol) was added. After stirring for 15 min, the suspension was concentrated to dryness, and the residue was extracted with Et_2O (2 × 5 mL). The resulting solution was concentrated to dryness, and the solid treated for 2 h under vacuum to give **22** as a pale yellow solid that was stored at −30 °C. Yield: 44 mg, 95%; mp 44 °C. IR (cm^{-1}): ν(C═O) 1674, 1581, 1518. ^1H NMR (400 MHz, $CDCl_3$): δ 5.49 (s, 1 H, CH), 3.86 (s, 4 H, C_2H_4, $^2J_{HPt}$ = 67 Hz), 2.53 (s, 2 H, $PtCH_2$, $^2J_{HPt}$ = 106.4 Hz), 2.15 (s, 3 H, *Me*C(O)CH_2), 2.10 (s, 3 H, Me, acac), 1.95 (s, 3 H, Me, acac). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 213.7 (CO, $^2J_{CPt}$ = 49 Hz), 188.5 (CO, acac), 183.4 (CO, acac), 101.3 (CH, $^3J_{CPt}$ = 61 Hz), 62.5 (C_2H_4, $^1J_{CPt}$ = 238 Hz), 30.4 (*Me*C(O)CH_2), 28.3 (s, Me, acac), 26.8 (s, Me, acac), 16.2 ($PtCH_2$, $^1J_{CPt}$ = 663 Hz). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −3204.7. Anal. Calcd for $C_{10}H_{16}O_3Pt$: C, 31.66; H, 4.25. Found: C, 31.52; H, 4.22.

Synthesis of [Pt{$CH_2C(O)Me$}(acac)(CO)] (23). A stream of CO was bubbled at atmospheric pressure into a solution of **22** (60 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) for 15 min. The mixture was filtered through Celite, and the filtrate was concentrated to dryness under vacuum to give **23** as a pale yellow solid that was stored at −30 °C. Yield: 50 mg, 84%; mp 81−84 °C. IR (cm^{-1}): ν(C≡O) 2093, ν(C═O) 1681, 1573, 1523. ^1H NMR: (400 MHz, $CDCl_3$): δ 5.60 (s, 1 H, CH), 3.14 (s, 2 H, CH_2, $^2J_{HPt}$ = 109 Hz), 2.21 (s, 3 H, MeC(O)CH_2), 2.08 (s, 3 H, Me, acac), 2.06 (s, 3 H, Me, acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 212.1 (Me*C*(O)CH_2, $^2J_{CPt}$ = 46 Hz), 188.6 (CO, acac, $^2J_{CPt}$ = 22 Hz), 183.7 (CO, acac, $^2J_{CPt}$ = 16 Hz), 157.4 (CO), 102.4 (CH, $^3J_{CPt}$ = 66 Hz), 30.5 (*Me*C(O)-CH_2), 27.8 (Me, acac, $^3J_{CPt}$ = 14 Hz), 26.7 (Me, acac, $^3J_{CPt}$ = 38 Hz), 16.9 (CH_2, $^1J_{CPt}$ = 595 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −3598. Anal. Calcd for $C_9H_{12}O_4Pt$: C, 28.50; H, 3.19. Found: C, 28.60; H, 3.35.

Synthesis of [Pt{$CH_2C(O)Me$}(acac)(PPh_3)] (24). To a solution of **22** (27.7 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), PPh_3 (19.5 mg, 0.07 mmol) was added. The reaction mixture was filtered through Celite, and the filtrate was concentrated to dryness. The residue was stirred with Et_2O (2 mL), and the solvent was removed under vacuum for 6 h to give **24** as a colorless solid. Yield: 44 mg, 97%; mp 112−119 °C. IR (cm^{-1}): ν(C═O) 1657, 1571, 1521. ^1H NMR (300 MHz, $CDCl_3$): δ 7.71−7.64 (m, 9 H, Ph), 7.44−7.39 (m, 6 H, Ph), 5.40 (s, 1 H, CH, acac), 2.58 (d, 2 H, CH_2, $^3J_{HP}$ = 3.3 Hz, $^2J_{HPt}$ = 100 Hz), 2.03 (s, 3 H, *Me*C(O)CH_2), 1.97 (s, 3 H, Me, acac), 1.57 (s, 3 H, Me, acac). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 215.6 (Me*C*(O)CH_2), 184.9 (CO, acac), 183.4 (CO, acac), 134.6 (d, C_{orto}, PPh_3, $^2J_{CP}$ = 11 Hz), 130.6 (d, CH_{para}, PPh_3, $^4J_{CP}$ = 2 Hz), 128.7 (d, C_{ipso}, PPh_3, $^1J_{CP}$ = 48 Hz), 101.1 (CH, $^3J_{CPt}$ = 61 Hz), 31.6 (Me, acac), 27.8 (d, *Me*C(O)CH_2, $^4J_{CP}$ = 6 Hz), 27.5 (Me, acac), 14.0 (d, $PtCH_2$, $^2J_{CP}$ = 6 Hz, $^1J_{CPt}$ = 672.7 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 8.86 ($^1J_{PPt}$ = 4601 Hz). $^{195}Pt\{^1H\}$ NMR: δ (85.88 MHz, $CDCl_3$): −3648 (d, $^1J_{PPt}$ = 4601 Hz). Anal. Calcd for $C_{26}H_{27}O_3PPt$: C, 50.90; H, 4.44. Found: C, 51.40; H, 4.63.

Synthesis of [Pt{$CH_2C(O)Me$}(acac)(CNXy)] (25). To a solution of **22** (32 mg, 0.08 mmol) in CH_2Cl_2 (1 mL) was added XyNC (11 mg, 0.08 mmol). The pale yellow solution was concentrated to dryness, and the residue was extracted with *n*-pentane (2 mL) and filtered. The filtrate was concentrated to dryness under vacuum for 5 h to give **25** as a colorless solid. Yield: 20 mg, 50%; mp 80−83 °C. IR (cm^{-1}): ν(C≡N) 2179; ν(C═O) 1675, 1582, 1521. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (m, 1 H, Xy), 7.10 (m, 2 H, Xy), 5.52 (s, 1 H, CH, acac), 3.14 (s, 2 H, CH_2, $^2J_{HPt}$ = 112 Hz), 2.47 (s, 6 H, Me, Xy), 2.21 (s, 3 H, *Me*C(O)CH_2), 2.02 (s, 3 H, Me, acac), 1.99 (s, 3 H, Me, acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 213.8 (CO, $^2J_{CPt}$ = 47 Hz), 186.8 (CO, acac, $^2J_{CPt}$ = 21 Hz), 183.7 (CO, acac, $^2J_{CPt}$ = 16 Hz), 135.5 (C, Xy), 128.8 (CH, Xy), 127.8 (CH, Xy), 101.9 (CH, acac, $^3J_{CPt}$ = 67 Hz), 30.3 (*Me*C(O)), 27.8 (Me, acac, $^3J_{CPt}$ = 12 Hz), 27.1 (Me, acac, $^3J_{CPt}$ = 34 Hz), 18.2 (Me, Xy), 14.1 ($PtCH_2$, $^1J_{CPt}$ = 612 Hz). $^{195}Pt\{^1H\}$ NMR (85.88 MHz, $CDCl_3$): δ −3355 (t {1:1:1}, $^2J_{PtN}$ = 146 Hz). Anal. Calcd for $C_{17}H_{21}NO_3Pt$: C, 42.32; H, 4.39; N, 2.90. Found: C, 42.70; H, 4.49; N, 3.07.

Crystallography. Crystals were measured on a Bruker Smart APEX machine. Data were collected using monochromated Mo Kα radiation in w scan. The structures of **3**, **13**, **14**, and [$PtCl_2(CNXy)_2$] were solved by direct methods, that of **1** and **8***trans* by the heavy atom method. All were refined anisotropically on F^2. Restraints to local aromatic-ring symmetry or light-atom displacement factor components were applied in some cases. The ordered methyl groups were refined using rigid groups, the NH (**13** and **14**) was refined as free, and the other hydrogens were refined using a riding mode. The methyl (C3) of the acetonyl ligand of compound **8***trans* is disordered over two positions, ca. 54:46.

Computational Details. Density functional calculations were carried out using the Gaussian 03 package.[26] The hybrid density functional B3LYP method was applied.[27] Effective core potentials (ECP) and their associated double-ζ basis set, LANL2DZ, were used for platinum atoms.[28] Similar description was used for heavy elements as Cl or P, supplemented with an extra *d*-polarization function.[29] The basis set for the light elements as C, N, O, and H was 6-31G*.[30] Geometry optimizations were carried out on the full potential-energy surface, without symmetry restrictions, and they were characterized by a vibrational analysis. Since decoordination of chloride from TPBC is always unfavored in gas phase for

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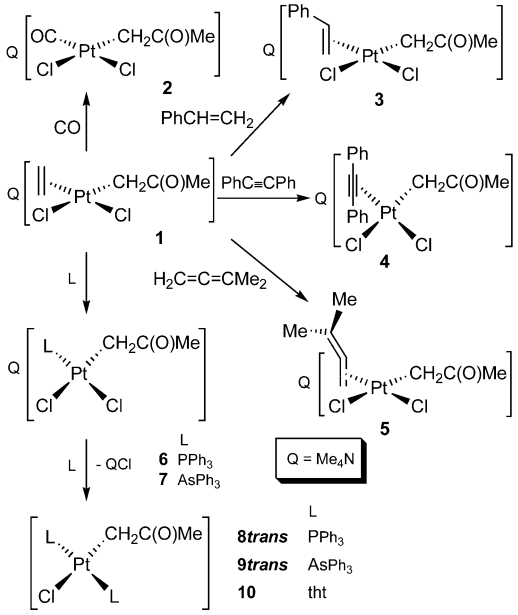
Scheme 1



carbonyl as entering ligand, their corresponding transition states SPY2C are not available. Solvent effects were taken into account through the PCM algorithm,[31] using standard options of PCM and cavity keywords,[26] by calculating the energies at the geometries optimized for gas phase.

Results and Discussion

Synthesis of Anionic Acetonyl Pt(II) Complexes from $Me_4N[Pt\{CH_2C(O)Me\}Cl_2(C_2H_4)]$ (1). Complex **1** has been used as starting material to prepare other anionic acetonyl complexes by replacing ethylene by CO, styrene, diphenylacetylene, 1,1-dimethylallene, PPh_3, or $AsPh_3$. Thus, after bubbling CO for a few minutes through a cooled (0 °C) Me_2CO solution of **1**, *cis*-$Me_4N[Pt\{CH_2C(O)Me\}Cl_2(CO)]$ (**2**) was obtained (Scheme 1). In the solid state, this carbonyl complex must be stored below −30 °C as it decomposes at room temperature. When the reaction was carried out in CH_2Cl_2, complex **2** was also formed but it decomposed faster than in Me_2CO. Similarly, the room-temperature reaction between **1** and an excess of $H_2C{=}C{=}CMe_2$ (1:2) in CH_2Cl_2 gave *cis*-$Me_4N[Pt\{CH_2C(O)Me\}Cl_2(\eta^2\text{-}H_2C{=}C{=}CMe_2)]$ (**5**), as the result of the η^2 coordination of the allene through the less substituted double bond, as shown in Scheme 1. A similar behavior has been reported for a Pt(II) complex.[32] Insertion of allenes into alkyl metal bonds to give η^3-allylic complexes have been described.[33−36] However, complex **5** was recovered unchanged when it was heated in Me_2CO for 24 h (80 °C, Carius tube). Substitution of ethylene in **1** by styrene (1:5, 50 °C, Me_2CO) or diphenylacetylene (1:10, 60 °C, Me_2CO or room temperature, $CHCl_3$) gave *cis*-$Me_4N[Pt\{CH_2C(O)Me\}Cl_2(\eta^2\text{-L})]$ (L = $PhCH{=}CH_2$ (**3**), $PhC{\equiv}CPh$ (**4**); Scheme 1). When the latter reaction was carried out using a smaller molar ratio, a mixture of **4** and **1** was obtained. However, even when a strong excess of alkyne was used, an analytically pure sample of **4** could not be isolated (see Experimental Section). Complexes **3**−**5** are stable at room temperature in the solid state and in organic solvents solutions.

The room-temperature reaction of a THF suspension of **1** with PPh_3 or $AsPh_3$, in 1:1 molar ratio, took place with precipitation of *cis*-$Me_4N[Pt\{CH_2C(O)Me\}Cl_2(L)]$ [L = PPh_3 (**6**), $AsPh_3$ (**7**)] (Scheme 1). When these reactions were carried out in CH_2Cl_2 or Me_2CO, Me_4NCl precipitated and a mixture of *trans*-$[Pt\{CH_2C(O)Me\}Cl(L)_2]$ [L = PPh_3 (**8***trans*), $AsPh_3$ (**9***trans*)], and **1** + **6** or **1** + **7**, respectively, was isolated. This suggests that the precipitation of **6** or **7** in THF is crucial to isolate them. In fact, when the mixture **1** + **6** + **8** or **1** + **7** + **9**, obtained in CH_2Cl_2, was stirred in THF and Me_4NCl was added, complex **6** or **7**, respectively, was obtained. The attempts to prepare *cis*-$Me_4N[Pt\{CH_2C(O)Me\}Cl_2(tht)]$ (tht = tetrahydrothiophene) by reacting **1** with 1 equiv of tht in THF led to a complex mixture, containing *trans*-$[Pt\{CH_2C(O)Me\}Cl(tht)_2]$ (**10**) and **1**.

Synthesis of Neutral Acetonyl Platinum(II) Complexes from 1. By reacting a CH_2Cl_2 solution of **1** with two or more equiv of PPh_3, $AsPh_3$, or tht, complex **8***trans*, **9***trans*, or **10**, respectively, was obtained (Scheme 1). The complex **8***trans* or **9***trans* was also obtained by reacting **6** or **7** with 1 equiv of the corresponding neutral ligand. A $CDCl_3$ solution of **9***trans* led to a mixture of cis/trans isomers (1:1) after 16 h at room temperature. In the same conditions, no isomerization was observed for **8***trans*. The room-temperature reaction of $[Hg\{CH_2C(O)Me\}Cl]$ with $[Pt(PPh_3)_4]$ in toluene gave Hg, an 1:3 mixture of **8***cis* and **8***trans*, and traces of *cis*-$[PtCl_2(PPh_3)_2]$. It has been reported that **8***cis* is obtained by oxidative addition of $ClCH_2C(O)Me$ to $[Pt(PPh_3)_4]$ at room temperature and that **8***trans*, impurified with *cis*-$[PtCl_2(PPh_3)_2]$, is isolated by refluxing **8***cis* in benzene, in the presence of PPh_3.[10,37]

We have reported the synthesis of complexes $[Pd\{CH_2C(O)Me\}Cl(CNR)_n]$ (n = 1, 2) and $[Pd\{CH_2C(O)Me\}(CNR)_3]^+$ (R = ^{t}Bu, Xy = 2,6-dimethylphenyl) and the easy transformation of these compounds into *C*-palladated β-ketoenamine complexes after insertion of one molecule of isocyanide into the C−Pd bond followed by a β-ketoimine to β-ketoenamine tautomerization process.[38] However, fast addition at room temperature of 2 equiv of RNC to **1** in CH_2Cl_2 gave almost inmediately a mixture of *cis*- and *trans*-$[Pt\{CH_2C(O)Me\}Cl(CNR)_2]$ (R = Xy (**11**; 1:0.4), ^{t}Bu (**12**; 1:0.3)) (Scheme 2) without insertion products. The cis isomer transformed gradually into the trans in $CDCl_3$ until the equilibrium was reached at 1:0.7 for **11** (after 5 h at room temperature or 80 °C in a Carius tube for 4 days in CH_2Cl_2) or 1:0.9 for **12** (after 48 h at room temperature). The slow addition of 1 equiv of isocyanide to a stirred and cooled (0 °C) solution of **1** gave **11***trans* (in THF) or **12***trans* (in CH_2Cl_2) and unreacted **1**. When 2 equiv were slowly added at 0 °C in CH_2Cl_2, only the trans isomer was obtained and no isomerization after 2 days in a $CDCl_3$ solution was observed. The addition of 0.3 equiv of isocyanide to a $CDCl_3$ solution of **11***trans* led to the 1:0.7 cis/trans equilibrium mixture. This means that the local excess of isocyanide produced in the fast addition reaction is responsible for the trans to cis isomerization. However, the addition of 0.3 equiv of ^{t}BuNC to a $CDCl_3$ solution of **12***trans* led to a mixture of unidentified products.

Another attempt to insert XyNC into the Pt−acetonyl bond was carried out by reacting **11***trans* with 1 equiv of XyNC at

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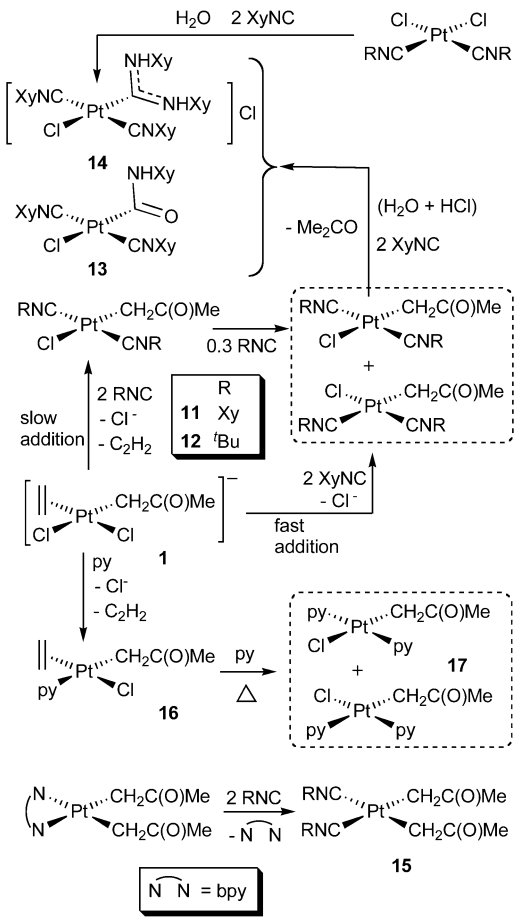
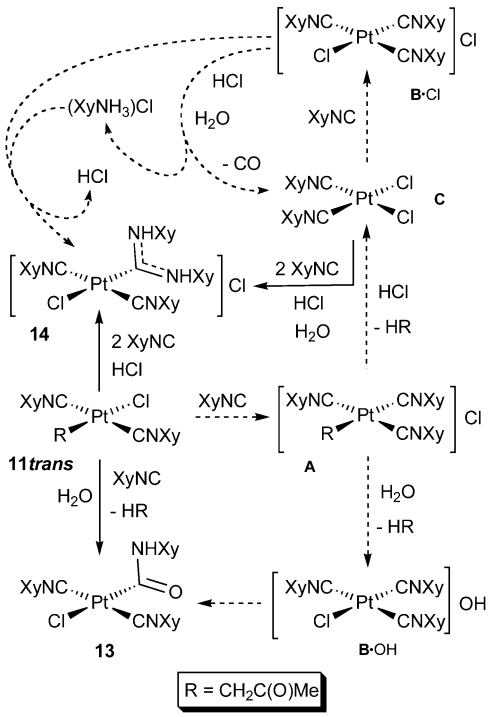
Scheme 2



60 °C for 24 h in acetone. However, we obtained the insoluble carbamoyl complex *trans*-[Pt{C(O)NHXy}Cl(CNXy)$_2$](**13**) and a solution containing a complex mixture of compounds. The reaction with 2 equiv of XyNC in $CHCl_3$ (room temperature, 64 h) gave a mixture insoluble in Et_2O that, after recrystallization, led to pure **13** and a mixture of **13** and [Pt{C(NHXy)$_2$}Cl(CNXy)$_2$]Cl(**14**). Complex **13** could be formed through the intermediate [Pt{$CH_2C(O)Me$}(CNXy)$_3$]Cl (**A**; Scheme 3) which, in the presence of H_2O might afford acetone (detected in the reaction mixture), $[PtCl(CNXy)_3]^+$, and OH^- (**B**·OH) that may well attack an isocyanide ligand to give **13**. The previously reported OH^- attack to $[Pt(CNMe)_2(PPh_3)_2]^{2+}$, to give [Pt{C(O)NHMe}(CNMe)(PPh$_3$)$_2$]$^+$,[20] is a precedent for this process. Formation of **14** requires the presence of an additional chloride and $XyNH_2$. We propose that HCl, formed from $CHCl_3$, could give acetone and **C** which might react with 1 equiv of XyNC to give the cationic complex $[PtCl(CNXy)_3]Cl$ (**B**·Cl). Its reaction with $(H_3O)Cl$ is expected to give CO + $(XyNH_3)Cl$[20] + **C**. This complex would react again with another equiv of XyNC and $XyNH_2$ giving **14**, recovering half of the HCl used in the process. To support our proposal we have succeeded in preparing **14** by reacting $[PtCl_2(CNXy)_2]$ with two equiv of XyNC in $CHCl_3$.

After these unexpected results, we consider of interest to explore the reaction of 4 equiv of XyNC with our previously reported diacetonyl isocyanide complex [Pt{$CH_2C(O)Me$}$_2$(bpy)].[11] However, the substitution product *cis*-[Pt{$CH_2C(O)Me$}$_2$(CNXy)$_2$] (**15**) was obtained (Scheme 2), probably because formation of a cationic complex, as that proposed above, more

Scheme 3. Proposed Reaction Pathway (Dashed Arrows) for the Synthesis of 13 and 14[a]



[a] The solid arrows indicate the reagents and isolated products.

suitable for a nuclephilic attack, could not be formed. Heating a $CDCl_3$ solution of **15** for 3 days at 40 °C did not produce insertion of the isocyanide into the Pt−C bond, isomerization, or hydrolysis. The greater stability of the cis isomer can be a consequence of a stronger *transphobia*[39,40] between the pair of acetonyl ligands than that between an acetonyl and an isocyanide ligand.

Complex **1** reacted with 2 equiv of py (1:2) in CH_2Cl_2 leading to the precipitation of Me_4NCl and formation of [Pt{$CH_2C(O)Me$}Cl(η^2-C_2H_4)(py)] (**16**; Scheme 2). This complex was also obtained using Me_2CO as solvent. When an Me_2CO solution of **16** and py (1:1) was refluxed for 4.5 h, ethylene was displaced and a 3:1 mixture of *cis*- and *trans*-[Pt{$CH_2C(O)Me$}Cl(py)$_2$] (**17**) was obtained. No reaction was observed between a $CDCl_3$ solution of **1** and $OPPh_3$ or pyridine *N*-oxide, after 2 days at room temperature.

Complexes **6**−**17** are stable in the solid state and dissolved in organic solvents (Me_2CO, CH_2Cl_2, $CHCl_3$, THF) at room temperature.

On the Mechanism of Substitution Reactions from Complex 1. Starting from complex **1**, ethylene is replaced by various ligands (CO, PhCH=CH_2, PhC≡CPh, H_2C=C=CMe_2, PPh_3, $AsPh_3$) to give complexes **2**−**7** (Scheme 1). However, a chloro ligand is displaced when the entering ligand is py (Scheme 2). DFT calculations on the reactions with CO, PMe_3 and py have been carried out to explain this difference. Because the results for CO and PMe_3 are similar, we will discuss here only those with PMe_3 and py. The data for the reaction with CO will also

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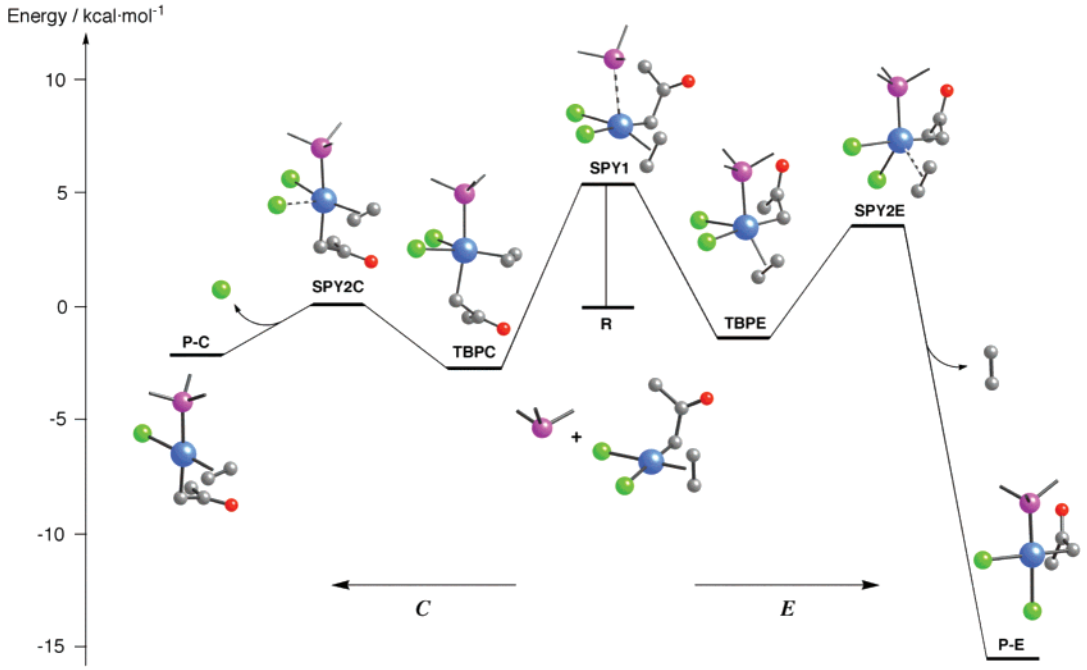


Figure 1. Energy profile for the reaction pathway of substitution of chloride (path C) or ethylene (path E) by PMe_3 in CH_2Cl_2 as solvent.

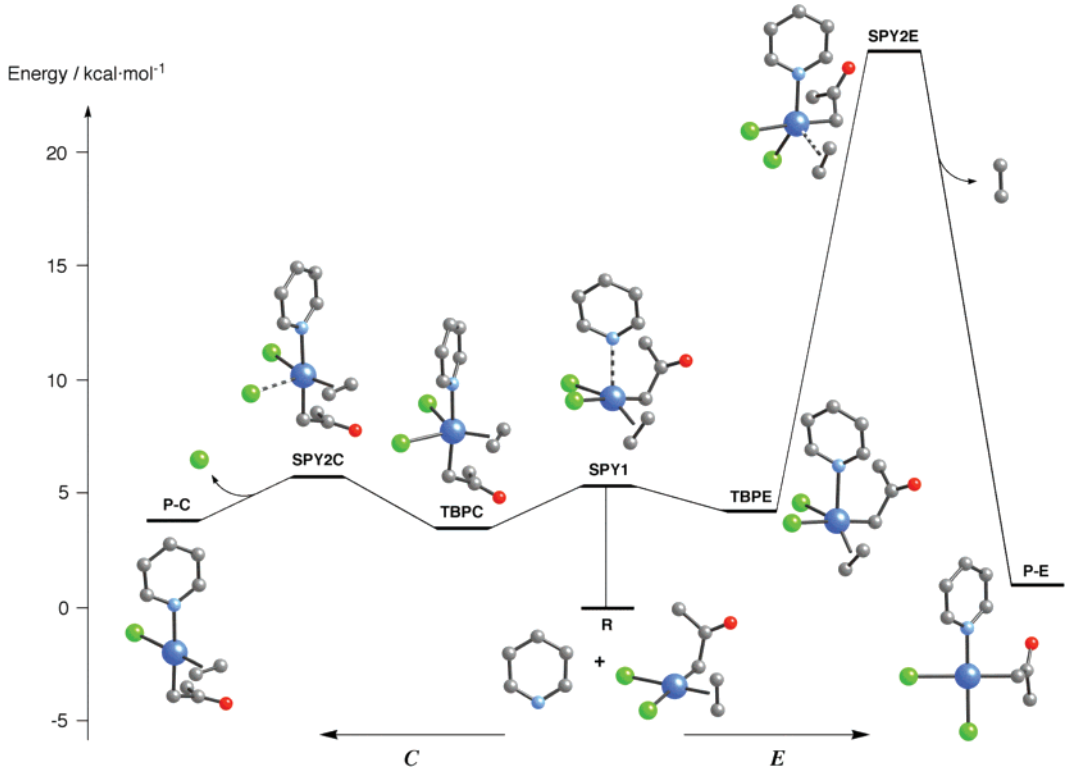
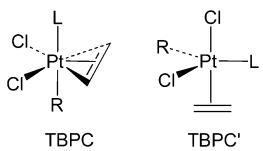


Figure 2. Energy profile for the reaction pathway of substitution of chloride (path C) or ethylene (path E) by pyridine in CH_2Cl_2 as solvent.

be used here to compare the three ligands and have been included in the Supporting Information.

Figures 1 and 2 show the energies of intermediates and final products (P) with respect to the reagents (R) when the entering ligand L is PMe_3 or py, respectively, and the leaving ligand is ethylene (path E) and Cl^- (path C). The optimized geometries for the intermediates agree with those usually proposed for square-planar substitution reactions (see Figures 1 and 2 and Supporting Information), except in the case of TBPC. The expected intermediate TBPC′ (Chart 2) proves to be unstable because the energy of the structure resulting after closing up to

Chart 2



135° the R−Pt−Cl from SPY1 is around 20−26 kcal/mol higher than that of TBPC, and if an additional closing is forced, removal of L occurs. The geometry of the TBPC intermediate can be better described as distorted octahedral because the Pt

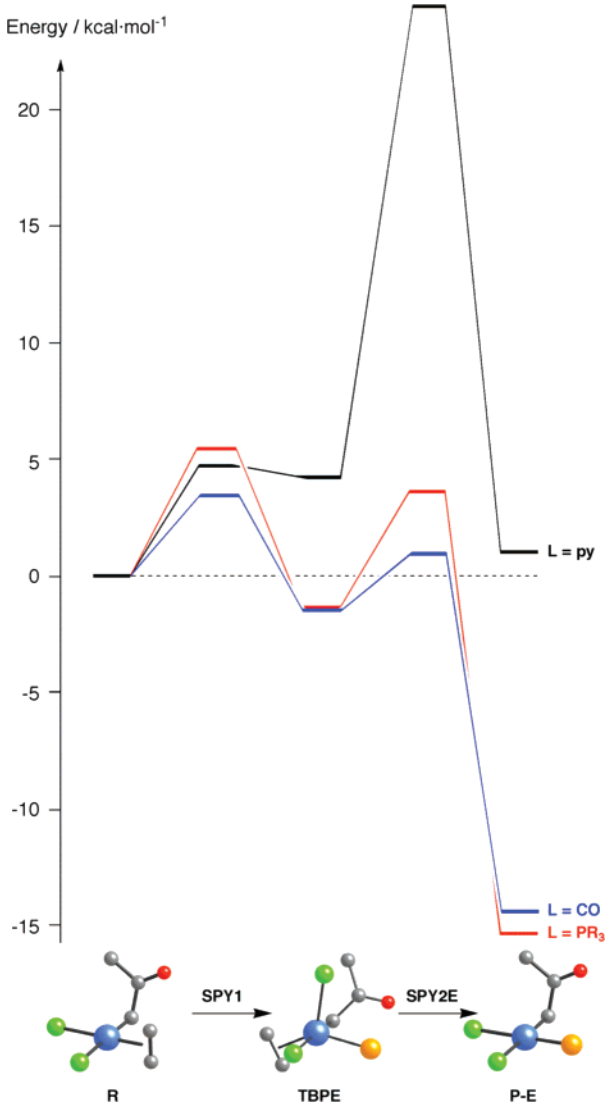


Figure 3. Comparative of energetic pathway for the substitution of ethylene by pyridine, CO and PMe_3. The donor atom of the entering ligand is represented by an orange ball.

atom and both carbon atoms of ethylene and chloro ligands are almost coplanar (see Chart 2): the angles between Cl−Pt−Cl and C−Pt−C planes are around 5° and the calculated Cl−Pt−Cl angles are around 97°; similar values are obtained for TBPE structures. This is not unexpected as this is the preferred mode of coordination for ethylene in trigonal bipyramidal complexes.[41,42]

Figures 3 and 4 compare the substitution of the ethylene and chloro ligands, respectively, by the three studied ligands L. From our calculations the substitution of ethylene by pyridine (Figures 2 and 3) is kinetically inhibited because of the high energy of the intermediate SPY2E (Figure 2), containing the ethylene ligand in the apical position. This contrasts with the moderate energy of SPY2C having the ethylene in the pyramidal base which, therefore, favors the substitution of the chloro ligand. This was, from a kinetic point of view, the expected process because the order of trans influence is C_2H_4 > R > Cl.[41]

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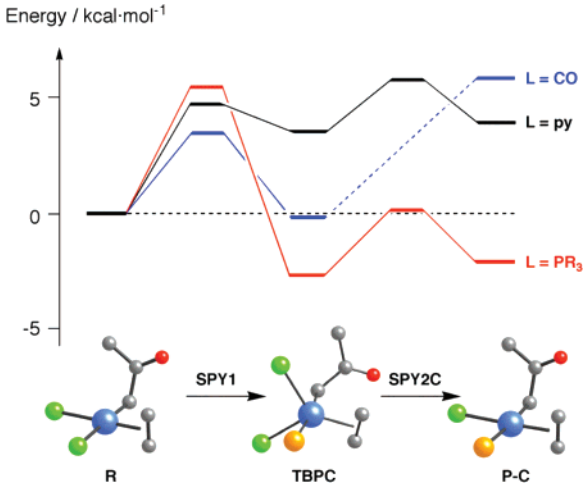
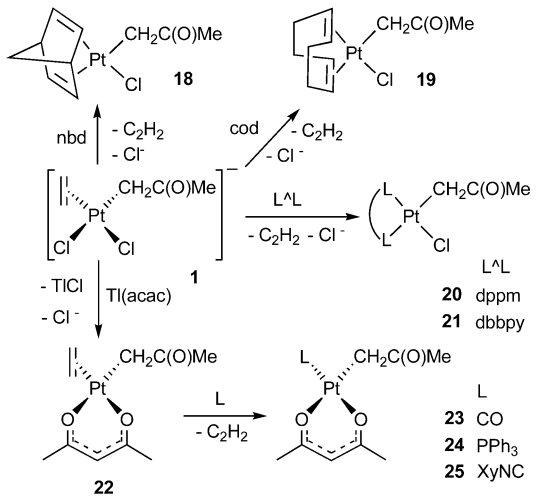


Figure 4. Comparative of energetic pathway for the substitution of chloro by pyridine, CO and PMe_3. The donor atom of the entering ligand is represented by an orange ball.

Scheme 4



Although this substitution is slightly endoergonic (Figures 2 and 3) the precipitation of Me_4NCl in CH_2Cl_2 forces the substitution. When L is the strong π-acceptor ligand PMe_3 or CO, there are not kinetic barriers for chloro or ethylene substitution (the energy of all intermediates is ≤5 kcal/mol; Figures 3 and 4) but the very low energy of the resulting products of the ethylene substitution favors this process.

The influence of solvents ($CHCl_3$, THF, CH_2Cl_2, Me_2CO, MeCN) and the direction of the attack of the ligand with respect to the acetonyl substituent are negligible (see Supporting Information).

Reactions of $Me_4N[Pt\{CH_2C(O)Me\}Cl_2(C_2H_4)]$ (1) with Bidentate Ligands. Reaction of **1** with excess of norbornadiene (nbd) or cyclooctadiene (cod) (Scheme 4) took place with precipitation of Me_4NCl and formation of complex $[Pt\{CH_2C(O)Me\}Cl(L_2)]$ (L_2 = nbd (**18**), cod (**19**)). The precipitate in the reaction of **1** with cod contained, along with Me_4NCl, a platinum complex, that could not be identified; this is the reason for the moderate yield of **19** (51%). Complex **19** was also obtained in low yield (20%) by refluxing an Me_2CO solution of $[PtCl_2(cod)]$ and $[Hg\{CH_2C(O)Me\}_2]$ in a molar ratio of 1:1. Reactions of **1** with bidentate ligands bis(diphenylphosphino)-methane (dppm) or 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dbbpy) in the molar ratio 1:1 gave complexes $[Pt\{CH_2C(O)Me\}Cl(L_2)]$ [L_2 = dppm (**20**), dbbpy (**21**)]. Complex **20** was contaminated

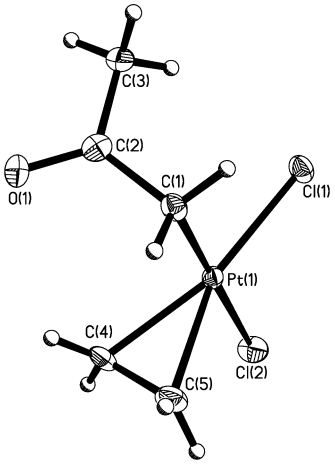


Figure 5. Ellipsoid representation of complex **1** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(1) = 2.075(4), Pt(1)−C(5) = 2.118(4), Pt(1)−C(4) = 2.125(4), Pt(1)−Cl(1) = 2.3267(9), Pt(1)−Cl(2) = 2.3845(10), O(1)−C(2) = 1.225(4), C(1)−C(2) = 1.490(5), C(2)−C(3) = 1.502(5), C(4)−C(5) = 1.396(5), C(1)−Pt(1)−C(5) = 90.52(15), C(1)−Pt(1)−C(4) = 90.06(15), C(5)−Pt(1)−C(4) = 38.41(14), C(1)−Pt(1)−Cl(1) = 90.55(10), C(5)−Pt(1)−Cl(2) = 88.52(12), C(4)−Pt(1)−Cl(2) = 89.98(11), Cl(1)−Pt(1)−Cl(2) = 89.88(3), C(2)−C(1)−Pt(1) = 109.6(2), O(1)−C(2)−C(1) = 121.8(3), O(1)−C(2)−C(3) = 120.8(3), C(1)−C(2)−C(3) = 117.4(3).

with traces of [$PtCl_2$(dppm)] (^{1}H and ^{31}P NMR spectra) in the reaction mixture, but it could be obtained with moderated yield (50%) by recrystallization in toluene/Et_2O. Complexes **18**−**21** are stable at room temperature, in the solid state, and in solution of common organic solvents.

The reaction of **1** with [Tl(acac)] gives [Pt{$CH_2C(O)Me$}(acac)(C_2H_4)] (**22**), which is a suitable precursor for the synthesis of other acetonyl complexes containing the acac ligand. Thus, the reactions with XyNC, CO, or PPh_3 gave the corresponding complex [Pt{$CH_2C(O)Me$}(acac)L] (L = CO (**23**), PPh_3 (**24**), XyNC (**25**); Scheme 4). However, **22** does not react with pyridine even when a molar ratio of 1:4 was used. This behavior can be explained, like in the case of the reaction of **1** with pyridine, as the consequence of the high activation energy required to form the square-pyramid complex necessary for ethylene substitution. Complexes **24** and **25** are stable solids at room temperature; however, **22** and **23** are not stable and must be stored below −30 °C.

Structure of Complexes. The X-ray crystal structures of complexes **1**, **3**, **8***trans*, **13**, **14** and *cis*-[$PtCl_2(CNXy)_2$] have been determined (Figures 5−10 and Table 1). The structure of **3** was refined as a racemate. In the anionic complexes **1** and **3**, the platinum atom shows slightly distorted square planar coordination with the chloro ligands in the mutually cis position. In both complexes, the two Pt−Cl distances are different, the Pt−Cl trans to the acetonyl ligand [**1**, 2.3845(10); **3**, 2.4106(11) Å] being longer than the Pt−Cl trans to olefin (**1**, 2.3267(9); **3**, 2.3364(11) Å), showing the stronger trans influence of the acetonyl group than the olefin ligand. In both complexes, the olefin is, as usual,[33] perpendicular to the platinum coordination plane (88.5° and 85.1°, respectively). The C−O distance in the acetonyl complexes (mean value 1.218(5) Å) is similar to that in complex **13** (1.224(3) Å); therefore, the C−O bond order in **13** is ca. two and the corresponding C−N (1.371(3) Å) bond order ca. 1, which is lower than those in the carbene ligand of complex **14** (mean value 1.330(4) Å) in accord with the electron delocalization present in this ligand.

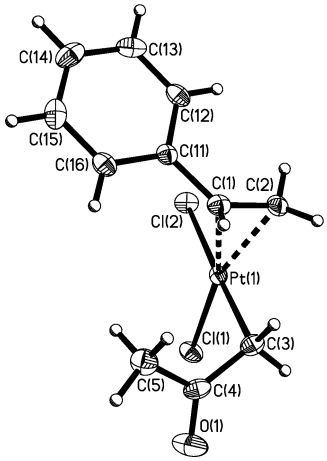


Figure 6. Ellipsoid representation of complex **3** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(3) = 2.069(4), Pt(1)−C(2) = 2.095(4), Pt(1)−C(1) = 2.164(4), Pt(1)−Cl(1) = 2.3364(11), Pt(1)−Cl(2) = 2.4106(11), O(1)−C(4) = 1.221(5), C(1)−C(2) = 1.412(6), C(1)−C(11) = 1.474(6), C(3)−C(4) = 1.482(6), C(4)−C(5) = 1.522(6), C(3)−Pt(1)−C(2) = 89.93(18), C(3)−Pt(1)−C(1) = 87.62(17), C(2)−Pt(1)−C(1) = 38.68(16), C(3)−Pt(1)−Cl(1) = 89.37(13), C(2)−Pt(1)−Cl(2) = 89.86(13), C(1)−Pt(1)−Cl(2) = 93.95(12), Cl(1)−Pt(1)−Cl(2) = 89.78(4), C(2)−C(1)−C(11) = 126.2(4).

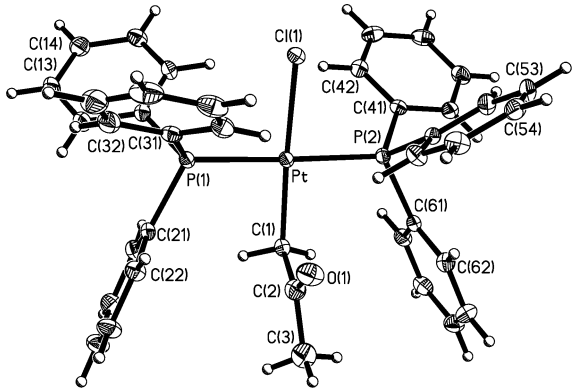


Figure 7. Ellipsoid representation of complex **8***trans* (50% probability). Selected bond lengths (Å) and angles (deg): Pt−C(1) = 2.061(2), Pt−P(2) = 2.2943(5), Pt−P(1) = 2.3028(5), Pt−Cl(1) = 2.4070(5), O(1)−C(2) = 1.209(3), C(1)−C(2) = 1.495(3), C(1)−Pt−P(2) = 91.29(6), C(1)−Pt−P(1) = 90.85(6), P(2)−Pt−Cl(1) = 87.307(17), P(1)−Pt−Cl(1) = 90.469(17), C(2)−C(1)−Pt = 113.42(14).

In **3**, the phenyl group of the styrene ligand is oriented away from the bulkier acetonyl ligand (**3bb′**, Chart 1). A similar arrangement has been found in analogous *cis*-[$PtCl_2$L(RCH=CH_2)].[33,43,44] In solution at −20 °C, the other pair of enantioners **3aa′** (Chart 1) is slightly more abundant than **3bb′** (1:0.8; see Spectroscopic Properties). The olefinic C−C distances in **1** (1.396(5) Å) and **3** (1.412(6) Å) are longer than those found for free ethylene [1.337(2) Å][45] or styrene [1.317 Å],[46] respectively, and shorter than a C_{sp3}−C_{sp3} single bond [1.514 Å].[47] The two Pt−C olefin distances in **1** are similar [2.125(4) and 2.118(4) Å], as is the case for other ethylene complexes

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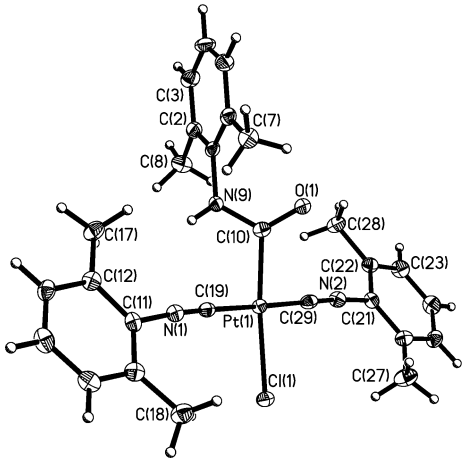

Figure 8. Ellipsoid representation of complex **13** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(19) = 1.955(3), Pt(1)−C(29) = 1.959(3), Pt(1)−C(10) = 2.004(3), Pt(1)−Cl(1) = 2.4117(6), C(19)−N(1) = 1.147(3), C(29)−N(2) = 1.150(3), O(1)−C(10) = 1.224(3), N(9)−C(10) = 1.371(3), C(19)−Pt(1)−C(10) = 91.45(10), C(29)−Pt(1)−C(10) = 87.47(11), C(19)−Pt(1)−Cl(1) = 90.07(7), C(29)−Pt(1)−Cl(1) = 90.98(8), N(1)−C(19)−Pt(1) = 177.9(2), N(2)−C(29)−Pt(1) = 178.1(2), C(10)−N(9)−C(1) = 123.2(2), O(1)−C(10)−N(9) = 121.2(2), O(1)−C(10)−Pt(1) = 121.22(19), N(9)−C(10)−Pt(1) = 117.56(19), C(19)−N(1)−C(11) = 175.4(3), C(29)−N(2)−C(21) = 175.6(3).

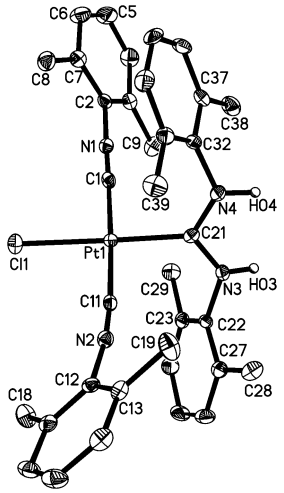

Figure 9. Ellipsoid representation of complex **14** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(1) = 1.953(3), Pt(1)−C(11) = 1.957(3), Pt(1)−C(21) = 1.996(3), Pt(1)−Cl(1) = 2.3595(8), N(1)−C(1) = 1.151(4), N(2)−C(11) = 1.147(4), N(3)−C(21) = 1.323(4), N(4)−C(21) = 1.336(4), C(1)−Pt(1)−C(21) = 90.29(12), C(11)−Pt(1)−C(21) = 91.66(12), C(1)−Pt(1)−Cl(1) = 89.94(9), C(11)−Pt(1)−Cl(1) = 88.03(9), C(1)−N(1)−C(2) = 172.2(3), C(11)−N(2)−C(12) = 172.0(3), C(21)−N(3)−C(22) = 127.1(3), C(21)−N(4)−C(32) = 126.5(3), N(1)−C(1)−Pt(1) = 178.3(3), N(2)−C(11)−Pt(1) = 173.7(3), N(3)−C(21)−N(4) = 115.1(3), N(3)−C(21)−Pt(1) = 123.4(2), N(4)−C(21)−Pt(1) = 121.5(2).

reported.[33] In **3** both Pt−C olefin distances are significantly different [2.164(4) and 2.095(4) Å], being longer the corresponding to Pt−CPh. This could be due to the different electronic effects of the substituents bound to either C atom of the styrene. A similar distortion has been reported in complexes with CH_2═CHR ligands (R = CH_2OH, Ph, $OCHMeCMe_3$).[33]

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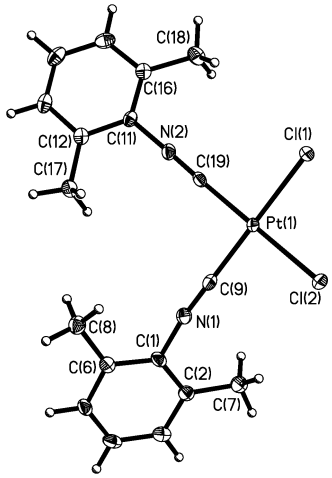

Figure 10. Ellipsoid representation of complex *cis*-[$PtCl_2(CNXy)_2$] (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)−C(9) = 1.908(3), Pt(1)−C(19) = 1.912(3), Pt(1)−Cl(1) = 2.3182(7), Pt(1)−Cl(2) = 2.3209(7), N(1)−C(9) = 1.149(4), N(2)−C(19) = 1.144(4), C(9)−Pt(1)−C(19) = 91.78(12), C(19)−Pt(1)−Cl(1) = 88.12(8), C(9)−Pt(1)−Cl(2) = 88.63(8), Cl(1)−Pt(1)−Cl(2) = 91.48(3), C(9)−N(1)−C(1) = 172.2(3), C(19)−N(2)−C(11) = 177.2(3), N(1)−C(9)−Pt(1) = 179.3(3), N(2)−C(19)−Pt(1) = 177.2(3).

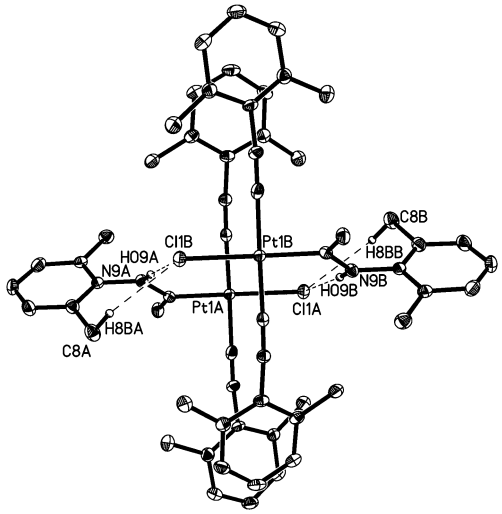

Figure 11. Association of two molecules of **13** via N−H···Cl and C−H···Cl hydrogen bonds.

Complex **8***trans* shows a square-planar coordination around the platinum atom. As expected, the Pt−P bond distances are similar (2.3028(5) and 2.2943(5) Å) and the Pt−C bond length (2.061(2) Å) is like those observed in complexes **1** and **3** (2.075(4) and 2.069(4) Å), because all are trans to Cl ligand. However, the Pt−Cl trans to acetonyl distances are sligthly different in the three complexes [**1**, 2.3845(10); **3**, 2.4106(11); **8***trans*, 2.4070(5) Å].

Several C−H···X (X = Cl, Pt, O) hydrogen bonds are observed in the three complexes (see Supporting Information). The H atoms involved are those of the cation (**1**, **3**), the acetonyl ligand (**1**), or the phenyl group (**3**, **8***trans*).

Complexes **13**, **14**, and *cis*-[$PtCl_2(CNXy)_2$] (Figures 8−10) show a square-planar coordination around the platinum atom. In **14**, the carbene moiety is in a *Z*,*Z* configuration. As expected, the Pt−CNXy distances are similar in complexes **13** (1.955(3) and 1.959(3) Å) and **14** (1.957(3) and 1.953(3) Å) and longer than those found in *cis*-[$PtCl_2(CNXy)_2$] (1.912(3) and 1.908(3)] Å), which shows the stronger trans influence of the

Table 1. Crystallographic Data for Complexes 1, 3, 8*trans*·$CHCl_3$, 13·1.5$CHCl_3$, 14 and *cis*-[$PtCl_2(CNXy)_2$]

	1	**3**	**8***trans*·$CHCl_3$	**13**·1.5$CHCl_3$	**14**	*cis*-[$PtCl_2(CNXy)_2$]
formula	$C_9H_{21}Cl_2NOPt$	$C_{15}H_{25}Cl_2NOPt$	$C_{40}H_{36}Cl_4OP_2Pt$	$C_{28.5}H_{29.5}Cl_{5.5}N_3OPt$	$C_{35}H_{38}Cl_2N_4Pt$	$C_{18}H_{18}Cl_2N_2Pt$
M_r	425.26	501.35	931.52	820.12	780.68	528.33
cryst habit	lath	block	prism	prism	prism	prism
cryst size (mm^3)	0.26 × 0.17 × 0.09	0.32 × 0.12 × 0.11	0.27 × 0.15 × 0.11	0.28 × 0.21 × 0.11	0.17 × 0.06 × 0.03	0.17 × 0.10 × 0.08
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*c*	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
			cell constants			
a, Å	12.4295(6)	15.6536(9)	12.2711(5)	33.0213(19)	10.0835(6)	8.0409(4)
b, Å	7.6154(4)	6.8386(4)	11.3098(4)	15.9116(9)	12.9030(8)	10.4023(5)
c, Å	15.0557(8)	16.5090(9)	27.4801(11)	11.9507(7)	13.2332(8)	10.8166(5)
α, deg	90	90	90	90	100.728(2)	85.016(2)
β, deg	105.857(2)	102.075(2)	99.633(2)	92.638(2)	99.835(2)	80.162(2)
γ, deg	90	90	90	90	100.983(2)	87.287(2)
V ($Å^3$)	1370.88(12)	1728.17(17)	3760.0(3)	6272.5(6)	1622.24(17)	887.58(7)
Z	4	4	4	8	2	2
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (Mg m^{-3})	2.060	1.927	1.646	1.737	1.598	1.977
μ mm^{-1}	10.599	8.424	4.133	4.970	4.520	8.205
F(000)	808	968	1840	3208	776	504
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$2\theta_{max}$ (deg)	53.46	52.74	54.2	54.2	56.32	56.16
no. of reflns measd	8018	18229	42123	34349	18876	10074
no. of independent reflns	2896	3542	8266	6881	7258	3933
transmissions	0.4488, 0.1692	0.4576, 0.1735	0.6592, 0.4016	0.6109, 0.3367	0.8763, 0.5138	0.5598, 0.3360
R_{int}	0.0207	0.0271	0.0203	0.0587	0.0279	0.0188
no. rest/params	0/132	131/186	48/433	4/380	0/395	0/212
$R_w(F^2$, all reflns)	0.0457	0.0562	0.0433	0.0613	0.0566	0.0475
$R(F, > 4\sigma(F))$	0.0212	0.0256	0.0179	0.0235	0.0259	0.0189
S	1.185	1.252	1.059	1.058	1.080	1.084
max $\Delta\rho$ (e $Å^{-3}$)	0.855, −1.180	1.585, −0.922	0.736, −0.390	2.000, −1.147	1.160, −0.918	1.789, −0.771

isocyanide than the chloro ligand. The Pt−C(O)NHXy distance in **13** (2.004(3) Å), is similar to the Pt−$C(NHXy)_2$ distance in **14** (1.996(3) Å). In the three complexes, the Pt−Cl distances are decreasing in the series **13** (2.4117(6) Å), **14** (2.3595(8) Å), and *cis*-[$PtCl_2(CNXy)_2$] (2.3209(7) and 2.3182(7) Å), following the scale of *trans* influence: $C(O)NHXy > C(NHXy)_2 > CNXy$.

In **13**, dimers due to N(9)−H(9)···Cl and C(8)−H(8)···Cl hydrogen bonds (Figure 11) are connected via O(1)···H(25) hydrogen bonds (see Supporting Information) to afford a zigzag catena structure. The angle between the mean planes of the two phenyl groups is 6.5°, and the distance between centroids is 4.13 Å, which is above the range found in other complexes with $\pi-\pi$ stacking (3.3−3.8 Å).[48] In complex **14**, an anion−cation pair is formed by means of N−H···Cl···H−N hydrogen bonds (see Supporting Information).

Spectroscopic Properties. Methyl protons of the acetonyl ligand appear in the ^{1}H NMR spectra in the range δ 1.90−2.33, except for **8***trans* (1.34) and **9***trans* (1.51), in which they are more shielded owing to the PPh_3 and $AsPh_3$ neighboring aromatic rings. They form a triplet, by coupling with the methylene protons in **2**, **11**, and **12** (Schemes 1 and 2) or a singlet in the others, The methylene protons are observed in the range δ 2.14−3.34 with ^{195}Pt satellites with $^1J_{HPt}$ in the range 76−148 Hz. The NH proton in complex **13** (6.80 ppm) is much more shielded than those in **14** (12.04 ppm) because in the latter the N−H···Cl hydrogen bonds observed in the solid state must persist in solution. The ^{1}H NMR spectrum of **14** shows that the *Z,Z* configuration is retained in $CDCl_3$ solution because the $^3J_{HPt}$ value (84 Hz) is similar to those reported for N−H trans to Pt (80−90 Hz) and different to those reported for N−H cis to Pt (ca. 30 Hz).[49]

The $^{13}C\{^1H\}$ NMR spectra of acetonyl complexes show the expected singlet for the methylene carbon atom, with the corresponding ^{195}Pt satellites. The $^1J_{CPt}$ values increase as the trans influence of the ligand in trans decreases:[2,50] ^{t}BuNC (**12***cis*: 420 Hz) < XyNC (**11***cis*, **15**: 422, 471 Hz) < $AsPh_3$ (**9***cis*: 474 Hz) < N− (**16**, **21**: 562, 594 Hz) ≈ olefin (**19**, **18**: 551, 613 Hz) ≈ Cl (**2**, **3**, **5**, **6**, **9***trans*, **10**, **11***trans*, **12***trans*, **17***trans*: 522−679 Hz) ≈ O− (**22**−**25**: 595−673 Hz). The same is observed for $^2J_{PtC(O)}$: ^{t}BuNC (**12***cis*: 29 Hz) < XyNC (**15***cis*: 39 Hz) < N−donor (**21**: 42 Hz) ≈ olefin (**18**: 44 Hz) ≈ Cl (**5**, **6**, **10**, and **12***trans*: 47−54 Hz) ≈ O−donor (**22**, **23**, and **25**: 46−49 Hz).

The ^{1}H NMR spectrum of **3** at 25 °C shows broad resonances which coalesce at 45 °C. At −20 °C the resonances resolve into two sets of signals because of the two possible pairs of enantiomers (see Chart 1) in 1:0.8 molar ratio, resulting from the rotation around the Pt−olefin axis. A phase-sensitive ^{1}H,^{1}H-NOESY spectrum measured at −20 °C shows that the two sets of resonances are in slow exchange. The NOE cross-peaks in the same spectrum allow the assignment of the major set of signals to the pair of enantiomers **3aa′** (see Chart 1), where the phenyl group is oriented toward the acetonyl ligand (there are NOE contacts between a methylene proton of the acetonyl and both H_a and the ortho phenyl protons of the olefin). For the other pair of enantiomers, **3bb′**, the NOE cross-peaks are found between the methylene proton and $H_{b,c}$ of the olefin. In complexes [$PtCl_2(L)(RCH{=}CH_2)$] it is more usual that the R group is closer to the ligand L[33,43,44] than the contrary.[51]

The $^{13}C\{^1H\}$ NMR spectrum of complex **4** shows the alkyne carbons shielded with respect to those in the free ligand, although $^1J_{CPt}$ coupling was not observed due to its low solubility.

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The proposed structure for **5** (Scheme 1), with the allene coordinated through the less-substituted double bond, is based on (1) the high values of $^2J_{HPt}$ (76.1 and 64.7 Hz) of the CH_2 protons of the allene, similar to that in complex **1** (68 Hz),[8] and $^1J_{CPt}$ of CH_2 (155.3 Hz) with respect to that of CMe_2 ($^2J_{CPt}$ = 31 Hz), as observed in similar complexes,[32−34,36] and (2) the CH_2 carbon nucleous is more shielded (31.8 ppm) than that in the free allene (72.55 ppm). The ^{1}H NMR spectra of some reported allene Pt(II) complexes reveal free rotation around the Pt−allene bond at room temperature.[34] In the case of **5**, the presence of two distinct resonances for the methylene protons (3.27 ($^2J_{HPt}$ = 76.1 Hz) and 3.02 ppm ($^2J_{HPt}$ = 64.7 Hz)) and other two for the methylene protons of the acetonyl ligand (2.97 ($^1J_{HH}$ = 5.5 Hz, $^2J_{HPt}$ = 122.3 Hz) and 1.72 ppm ($^1J_{HH}$ = 5.5 Hz, $^2J_{HPt}$ = 93.5 Hz) indicates restricted rotation around the Pt-allene bond in the range of studied temperatures (0 to 50 °C). A similar behavior has been described for complexes *cis*-[$PtCl_2(\eta^2$-CH_2═C═CMe_2)(L)] (L = $AsPh_3$, PPh_3).[32]

The $^{13}C\{^1H\}$ NMR spectra of complex **10** (Scheme 1) shows only two resonances for the tht ligands, which supports the proposed trans geometry. For complexes **9**, **11**, and **12** (Scheme 1 and 2) the ^{1}H and ^{13}C resonances corresponding to the methylene group in the cis and trans isomers were assigned on the basis of $^2J_{HPt}$ and $^1J_{CPt}$ coupling constants, since they should be higher for the trans than for the cis isomers, because $AsPh_3$ and RNC ligands have stronger trans influence than chloro ligand.[50] The geometry of complex **16** was elucidated by NOESY 2D experiments. The ethylene protons show NOE with the CH_2 protons of the acetonyl and the *o*-pyridine protons. No effect between acetonyl protons and the pyridine protons was observed. The olefinic ^{1}H and $^{13}C\{^1H\}$ nuclei are more shielded in complexes **18**, **19**, and **22** than in the free ligands.[33,44,52] NOE experiments for complexes **18** and **19**, carried out to assign the CH cis or trans to the acetonyl ligand, revealed NOE between the acetonyl CH_2 protons and the adjacent CH protons of the diolefin moiety. The ^{1}H NMR spectrum of **22** at room temperature shows the resonances of the ethylene protons as a singlet with ^{195}Pt satellites because of the fast rotation about the Pt−ethylene bond.

The $^{195}Pt\{^1H\}$ chemical shifts of the anionic complexes **1**−**7** seem to be inversely related with the trans influence of the L ligand (Scheme 1): PPh_3 (−4091 ppm) > $AsPh_3$ (−3950 ppm) > CO (−3726 ppm) > H_2C═CH_2 (−3379 ppm) > PhCH═CH_2 (−3167 and 3186 ppm) > H_2C═C═CMe_2 (−3013 ppm) > PhC≡CPh (−2606 ppm). Something similar occurs with complexes **22**−**25**: PPh_3 (−3647 ppm) > CO (−3598 ppm) > XyNC (−3355) > H_2C═CH_2 (−3204 ppm). This effect could be related to the paramagnetic component of the shielding constant.

The platinum nucleus of Pt(II) complexes is more shielded than the related Pt(IV) complexes previously reported for us. Thus, in [Pt{$CH_2C(O)Me$}$_2$(bpy)] $\delta(^{195}Pt\{^1H\})$ = −3351 ppm while in the family of Pt(IV) complexes [Pt{$CH_2C(O)Me$}$_n$-Cl_{4-n}(bpy)], $\delta(^{195}Pt\{^1H\})$ = −937 to −2692.[8] In **15**, $\delta(^{195}Pt\{^1H\})$ = −4167 while in [Pt{$CH_2C(O)Me$}$_3$Cl(CNXy)$_2$] $\delta(^{195}Pt\{^1H\})$ = −3307.

The IR spectra show one band, assignable to ν(C═O), in the region 1681−1645 cm^{-1}, which is similar to that reported for terminal acetonyl palladium(II) complexes.[13] The band due to ν(C≡O) in the carbonyl complexes **2** and **23** appears at 2086 and 2093 cm^{-1}, respectively, lower than that in CO (2143 cm^{-1}). The cis geometry of **1** was proposed on the basis of the IR spectrum, since it shows two bands at 276 and 311 cm^{-1} that we assign to ν(Pt−Cl) trans to acetonyl [$\nu(Pt-Cl)_{acetonyl}$] and trans to ethylene [$\nu(Pt-Cl)_{=}$] ligands, respectively.[8] The X-ray diffraction study of **1** we report here confirms both the geometry and the IR assignment (see above). Similarly, in accordance with the crystal structure of **3**, the bands at 267 and 305 cm^{-1} must be assigned to $\nu(Pt-Cl)_{acetonyl}$ and $\nu(Pt-Cl)_{=}$, respectively. Therefore, a cis geometry is proposed for **2**, **4**−**7**, since they show two bands at 254−284 and 293−328 cm^{-1} that can be assigned to $\nu(Pt-Cl)_{acetonyl}$ and $\nu(Pt-Cl)_{L}$, respectively. In complex **2**, the $\nu(Pt-Cl)_{CO}$ (328 cm^{-1}) appears in the same region as our palladium complexes *cis*-Me_4N[$PdRCl_2$(CO)] [R = C_6H_3Me-2-NO_2-6 (315 cm^{-1}), $C_6H_2(NO_2)_3$-2,4,6 (335 cm^{-1})].[53]

The following trans influence scale can be deduced from the position of the bands due to $\nu(Pt-Cl)_{L}$ in *cis*-[Pt{$CH_2C(O)Me$}Cl_2L]$^-$ complexes (**1**−**7**): PPh_3 (293 cm^{-1}) ≥ $AsPh_3$ (297 cm^{-1}) > PhCH═CH_2 (305 cm^{-1}) ≥ H_2C═CH_2 (311 cm^{-1}) ≥ H_2C═C═CMe_2 (315 cm^{-1}) ≥ PhC≡CPh (317 cm^{-1}) > CO (328 cm^{-1}), which is similar to that deduced on the basis of the $^{195}Pt\{^1H\}$ NMR spectra, except for the CO ligand. In our opinion, this IR-base scale is more appropriate because it gives account of the strenghening of the Pt−Cl bond due to the π-acceptor character of CO while the $\sigma_{paramagnetic}$ value is also influenced by the changes in C−O and C−Pt bond energies. From the data of neutral complexes [Pt{$CH_2C(O)Me$}ClL_2] (**8**−**12**, **16**−**21**) the order of trans influence would be: MeC(O)-CH_2 (**6**, **7**, **8***trans*, **9***trans*, **10**, **11***trans*, **12***trans*, 276−304 cm^{-1}) > dppm (**20**, 293 cm^{-1}) ≥ PPh_3 (**8***cis*, 298 cm^{-1}) > cod (**19**, 316 cm^{-1}) ≈ norbordiene (**18**, 317 cm^{-1}) = H_2C═CH_2 (**16**, 317 cm^{-1}) > dbbpy (**21**, 326 cm^{-1}) ≈ ^{t}BuNC (**12***cis*, 325 cm^{-1}) ≈ XyNC (**11***cis*, 326 cm^{-1}). Similarly, from the data of **13** (278 cm^{-1}) and **14** (310 cm^{-1}), C(O)NHXy > $C(NHXy)_2$, which is in accord with the X-ray crystal data.

The ν(Pt−Cl) band in complex **16** at 317 cm^{-1} supports the mutual trans position of Cl and ethylene in the solid state, because it appears at the same frequency than in **18** and **19** (316−317 cm^{-1}) and not in the region 276−304 cm^{-1} ($\nu(Pt-Cl)_{acetonyl}$) or around 326 cm^{-1} ($\nu(Pt-Cl)_{Cl}$). The $\nu(Pt-Cl)_{acetonyl}$, $\nu(Pt-Cl)_{P}$, and $\nu(Pt-Cl)_{=}$ bands in the neutral complexes [Pt{$CH_2C(O)Me$}$Cl(L)_2$] are shifted to higher wavenumbers (276−304, 298, and 305−311 cm^{-1}, respectively) with respect to the corresponding ones in the anionic complexes (254−276, 293, and 316−317 cm^{-1}, respectively), because the strength of the pπ(Cl)→dπ(Pt) bond is smaller in the anionic complexes. We have observed a similar relationship in palladium(II)[54] and gold-(III)[55] complexes.

The expected two absorptions assignable to ν(C≡N) in the IR spectra of cis complexes are observed in **11***cis* (2200, 2171 cm^{-1}), **12***cis* (2223, 2193 cm^{-1}), and **15** (2182, 2148 cm^{-1}). Complexes *cis*- and *trans*-[$PtR_2(CNXy)_2$] [R = κ^1-*C*-$C_6(NO_2)_2$-2,6-$(OMe)_3$] show two (2199, 2179 cm^{-1}) and one (2196 cm^{-1}) bands, respectively.[40]

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Conclusions

We have isolated and characterized the first families of neutral (containing isocyanides, PPh_3, $AsPh_3$, dppm, dbbpy, py, tht, nbd, cod, $CH_2{=}CH_2$, CO, acac) and anionic acetonyl Pt(II) complexes. They could be prepared due to the versatility of Me_4N-[Pt{$CH_2C(O)Me$}$Cl_2(\eta^2\text{-}CH_2{=}CH_2)$] (**1**). Monosubstitution reactions occur differently depending on the π-acceptor ability of the ligands. Thus, when L = CO, $PhCH{=}CH_2$, $PhC{\equiv}CPh$, $H_2C{=}C{=}CMe_2$, PPh_3, $AsPh_3$ the anionic complexes Me_4N[Pt{$CH_2C(O)Me$}Cl_2(L)] result after ethylene substitution, while when L = pyridine, the product of chloro substitution [Pt{$CH_2C(O)Me$}Cl(py)(η^2-$CH_2{=}CH_2$)] is obtained. A DFT study concludes that the first ligands give the thermodynamic products while pyridine affords the kinetic product, due to the high activation energy required to form the square-pyramid complex necessary for ethylene substitution. Reactions of an acetonyl isocyanide complex with excess of XyNC in the presence of solvents moisture or HCl afford acetone and, respectively, platinum carbamoyl or amino carbene complexes.

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Supporting Information Available: Data obtained in the DFT study, hydrogen bond parameters, and CIF files for **1**, **3**, **8***trans*, **13**, **14**, and *cis*-[$PtCl_2(CNXy)_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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