Unusually Labile Organoplatinum Complexes: A Mechanistic Study of Insertion–Deinsertion into Platinum–Alkyl Complexes of Pyridine-2-carboxylic Acid

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Platinum–alkyl complexes of the general formula [PtR(pyca)L] [R = Me, Hpyca = pyridine-2-carboxylic acid, L = PPh_3, $P(CH_2Ph)_3$, $P(C_6H_{11})_3$, pyridine or 4-methylpyridine; R = Et, L = PPh_3 or $P(CH_2Ph)_3$] and the complex [PtMe(hoqu)(PPh_3)] (Hhoqu = 8-hydroxyquinoline) have been prepared and their carbonylation activity studied. The complexes show a large variation in carbonylation behaviour, which is markedly dependent on the ligands attached to the platinum centre. The donor capacity of L and the rigidity of the chelating ligand are major factors. For complexes containing pyca as the chelating ligand; where R = Me or Et and L = PPh_3, acyl complexes are readily prepared; where R = Et and L = $P(CH_2Ph)_3$, a mixture of two products is formed, the expected acyl complex [Pt(COEt)(pyca){$P(CH_2Ph)_2$}] and a compound with a terminal CO ligand in which the pyca ligand is monodentate [Pt(CO)(COEt)(pyca)-{$P(CH_2Ph)_3$}]; where L = $P(C_6H_{11})$, pyridine or 4-methylpyridine, no carbonylation occurs. With the complex containing the rigid hoqu ligand no carbonylation occurs. The complexes [Pt(COMe)(pyca)-(PPh_3)] and [PtEt(pyca)(PPh_3)] are unusually labile, eliminating CO or ethylene when warmed, giving [PtMe(pyca)(PPh_3)] or platinum–hydride complexes respectively. The behaviour of these complexes and the carbonylation behaviour of the platinum–alkyl complexes has been studied in detail and a mechanism for the insertion–deinsertion reactions is proposed.

Insertion of small molecules such as CO and ethylene into metal–carbon bonds is a key process with widespread applications in homogeneous catalysis.[1–7] An understanding of the mechanistic details of the insertion step including the influences of the associated ligands would assist in the effective design of catalysts for the desired process.

The insertion of CO in d^8 transition-metal compounds containing monodentate phosphine ligands is generally considered to follow either a dissociative or an associative route depending on the base strength of the ligand. Strongly basic ligands favour insertion *via* an associative route while less basic ligands favour a dissociative route.[8] For complexes with chelating ligands the mechanism is less clear. It has been noted that a weakly co-ordinating chelate or a ligand with a flexible backbone enhances carbonylation,[9,10] although, very recently van Asselt *et al.*[11] have shown that complexes containing a rigid, chelating diimine ligand can be effective in carbonylation. However, relatively few studies have been carried out on complexes containing chelating ligands.

Recently there has been considerable interest in the carbonylation of organo-palladium and -platinum complexes containing multidentate ligands. Complexes containing P–P,[10] P–N,[9,12] P–S,[9] N–N,[13–16] O–O[17] and O–S[17] ligands have been studied. Minghetti and co-workers[18] have studied an unusual palladium–tridentate ligand system in which the ligand itself is carbonylated. Our studies were the first reported that have employed bidentate, non-symmetrically co-ordinated anionic ligands.[17] The aim of our work has been to prepare metal–hydrocarbyl complexes containing hemilabile chelating ligands which may be employed to modify and hence study the insertion step. Concurrently with our studies a similar approach involving hemilabile P–N based chelates has recently been reported by Vrieze and co-workers.[12] This comprehensive study provided good evidence for partial chelate dissociation in Pt–Me complexes containing neutral, bidentate P–N ligands during insertion of CO into the Pt–Me bond.

Complexes which readily undergo reversible insertion–deinsertion of carbon monoxide and which undergo β-elimination under mild conditions also provide an opportunity to study the nature of the insertion process. Decarbonylation from palladium–acyl complexes occurs so readily that crystal-structure studies of such complexes are rare. However, reversible carbonylation was recently observed for a cationic palladium(II) complex containing a tridentate nitrogen-donor ligand. Both complexes in the equilibrium could be isolated and a crystal structure obtained for the acyl complex.[19] In contrast, decarbonylation from neutral platinum(II)–acyl complexes often requires forcing conditions, involving elevated temperatures and decarbonylation generally results in decomposition.[20a] There are very few examples of an observable equilibrium between platinum(II) alkyl and acyl compounds in which both complexes can be isolated and reacted repeatedly without significant decomposition.[20a,b]

We previously reported the preparation of palladium(II) and platinum(II) alkyl and phenyl complexes bearing β-diketonate type ligands and their reactions with CO to afford acyl complexes.[17,21] A kinetic study of the carbonylation reactions of these complexes demonstrated that the nature of the chelate ligand and the moieties present on the ligand markedly influence the reaction rate. In agreement with a subsequent proposal by Vrieze and co-workers[12] a CO insertion mechanism was suggested in which one arm of the chelating β-diketonate ligand initially dissociates to allow carbonylation to occur. An extensive crystal structure study on several of the metal alkyl complexes has provided information on metal–ligand bonding.[22] To continue our investigations of possible hemilabile chelate ligands and their influence on the insertion reaction, our research has been extended to include a study of new complexes containing anionic chelate ligands, which form a five-membered ring with the metal.

Accordingly we report here on the preparation, characterization and chemistry of a group of alkyl–platinum(II) complexes of pyridine-2-carboxylic acid (Hpyca); [PtMe(pyca)L] [L = PPh_3 **1**, $P(CH_2Ph)_3$ **2**, $P(C_6H_{11})_3$ **3**, pyridine (py) **4** or 4-methylpyridine (4Me-py) **5**] and [PtEt(pyca)L] [L = PPh_3 **6** or $P(CH_2Ph)_3$ **7**]. Of particular interest are the pairs of complexes

in which the alkyl groups and the phosphines differ only by a $-CH_2-$ unit (**1** and **6**, **2** and **7**, **1** and **2**, **6** and **7**). These apparently simple structural differences can lead to significant changes in chemistry, allowing valuable comparisons to be made between the complexes and their reactivity. The complex [PtMe(hoqu)-(PPh_3)] **8** (Hhoqu = 8-hydroxyquinoline) which contains a rigid chelating ligand was also prepared in this study. The reaction of complexes **1**–**8** with CO has been investigated and several acyl complexes were isolated and fully characterized. The unusual lability of complex **6** and of the acyl complex produced by the carbonylation of **1** was studied in detail. Unstable products from the decomposition of **6** were tentatively identified. From these studies a mechanism for the insertion–deinsertion of CO is discussed and the proposed carbonylation mechanism is considered in the context of the elimination reaction occurring in **6**.

Experimental

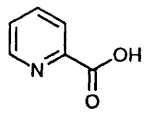
All reactions and manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques. All solvents were dried and purified by standard methods and freshly distilled before use. Chemical reagents were used as received and *trans*-[Pt(Me)I$(PPh_3)_2$], *trans*-[Pt(COMe)Cl-$(PPh_3)_2$] and *trans*-[Pt(H)Cl$(PPh_3)_2$] were prepared by literature methods.[23–25] The salt Tl(pyca) was prepared from the reaction of Tl_2CO_3 with pyridine-2-carboxylic acid in methanol.

Nuclear magnetic resonance (NMR) spectra were recorded at 22 °C on a Bruker AM-300 NMR spectrometer at 300.13 MHz (^{1}H), 75.48 MHz (^{13}C) and 121.50 MHz (^{31}P). Chemical shifts (δ) are reported in ppm relative to internal $SiMe_4$ (^{1}H, ^{13}C), or to external 85% H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz and NMR peaks are given as singlet (s), doublet (d), triplet (t) and multiplet (m). Infrared (IR) spectra were recorded in absorbance units on a Digilab FTS 20E FT-IR spectrophotometer using KBr disks in the mid-IR range (4000–500 cm^{-1}). Absorption bands (cm^{-1}) are described as very strong (vs), strong (s), medium (m) or weak (w) in intensity.

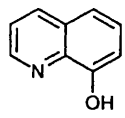
Microanalyses were performed by the Central Science Laboratory, University of Tasmania.

Synthesis of Complexes.—[PtMe(pyca)(PPh_3)] **1**. A solution of *trans*-[Pt(Me)I$(PPh_3)_2$] (0.18 g, 0.21 mmol) in tetrahydrofuran (thf) (*ca.* 30 cm^3) was treated with $TlPF_6$ (0.07 g, 0.21 mmol) at room temperature. After the cloudy solution had been stirred at room temperature for *ca.* 1 h, Na(pyca) (0.03 g, 0.21 mmol) in MeOH (*ca.* 2 cm^3) was added. A yellow solid precipitated immediately. The mixture was stirred overnight and then refluxed in a water-bath for 2 h. After the solution had been allowed to cool to room temperature it was evaporated to dryness and extracted with CH_2Cl_2. The resulting solution was filtered through a Celite column to remove yellow solid and the filtrate was evaporated to dryness. The oily residue was crystallized from CH_2Cl_2–MeOH–diethyl ether to give a white crystalline solid (yield: 0.077 g, 62%) (Found: C, 49.35; H, 4.10; N, 2.65. Calc. for $C_{25}H_{22}NO_2PPt{\cdot}0.5H_2O$: C, 49.75; H, 3.80; N, 2.30%). High resolution mass spectrum: Found m/z 593.112. $C_{25}H_{22}NO_2P^{195}Pt$ requires 593.109. NMR ($CDCl_3$): ^{31}P-{^{1}H}, two isomers (ratio 3:1), **1a** δ 14.3 (s, $^1J_{PtP}$ = 4438), **1b** δ 14.2 (s, $^1J_{PtP}$ = 4709); ^{1}H, two isomers, **1a** δ 0.65 (d, $^3J_{PH}$ = 2.6, $^2J_{PtH}$ = 78, $PtCH_3$), **1b** 0.73 (d, $^3J_{PH}$ = 3.1, $^2J_{PtH}$ = 71 Hz, $PtCH_3$), 7.2–7.7 (m, PPh_3) and 7.9–8.4 (m, H of pyridyl). IR (KBr): 1660vs (br) [ν(C=O)].

[PtMe(pyca){P$(CH_2Ph)_3$}] **2**. A solution of [Pt(Me)Cl(cod)] (cod = cycloocta-1,5-diene) (0.044 g, 0.125 mmol) in MeCN (15 cm^3) was treated with Tl(pyca) (0.041 g, 0.125 mmol) and stirred at room temperature for 4 h. Then $P(CH_2Ph)_3$ (0.039 g, 0.125 mmol) was added to the solution and the mixture was stirred overnight. After the solvent was evaporated the residue was extracted with CH_2Cl_2 and filtered. The solvent was removed under reduced pressure. A white crystalline solid was obtained by recrystallization from CH_2Cl_2–diethyl ether (yield: 0.06 g, 55%) (Found: C, 53.00; H, 4.45; N, 2.25. Calc. for $C_{28}H_{28}NO_2PPt$: C, 52.80; H, 4.40; N, 2.20%). NMR ($CDCl_3$): ^{1}H, δ 0.45 (d, 3 H, $^3J_{PH}$ = 3, $^2J_{PtH}$ = 81, $PtCH_3$), 3.3 (d, 6 H, $^2J_{PH}$ = 12, $^3J_{PtH}$ = 36, PCH_2) and 7.1–7.6 (m, 15 H, Ph), 8.05 (t), 8.3 (d), 8.6 (t) (4 H, $^3J_{PtH}$ = 33 Hz, H of pyridyl); ^{13}C-{^{1}H}, δ − 19.8 (d, $^2J_{PC}$ = 8.5, $^1J_{PtC}$ = 742, $PtCH_3$), 30.0 (d, $^1J_{PC}$ = 34.0, $^2J_{PtC}$ = 35 Hz, $PtPCH_2$); ^{31}P-{^{1}H}, δ − 0.72 (s, $^1J_{PtP}$ = 4312 Hz).



pyca



hoqu

[PtMe(pyca){P$(C_6H_{11})_3$}] **3**. This complex was prepared according to the method described for **2** and was obtained as a white crystalline solid. Mass spectrum: m/z 612 $[M]^+$ and 597 $[M - CH_3]^+$. High resolution mass spectrum: Found m/z 612.246; $C_{24}H_{40}NO_2P^{195}Pt$ requires 612.244. NMR ($CDCl_3$): ^{1}H, δ 0.68 (d, $^3J_{PH}$ = 1.2, $^2J_{PtH}$ = 89 Hz, $PtCH_3$); ^{13}C-{^{1}H}, δ − 23.1 (d, $^2J_{PC}$ = 7.6, $^1J_{PtC}$ = 744 Hz, $PtCH_3$); ^{31}P-{^{1}H}, δ 19.9 (s, $^1J_{PtP}$ = 4137 Hz).

[PtMe(pyca)(py)] **4**. This complex was prepared by the method described for **1**, except that the residue obtained on evaporation of the reaction mixture to dryness was extracted for 2 h with refluxing benzene (30 cm^3) containing a 2–3 molar excess of pyridine. The complex was obtained as a yellow solid (yield: 78%) (Found: C, 35.05; H, 3.05; N, 6.80. $C_{27}H_{24}NO_2Pt$ requires C, 35.05; H, 2.95; N, 6.80%). NMR ($CDCl_3$): ^{1}H, δ 1.02 (s, 3 H, $^2J_{PtH}$ = 84, $PtCH_3$), 7.3 (s), 7.5 (s), 7.8 (m), 8.0 (m), 8.6 (d, J_{PH} = 5.4, J_{PtH} = 40) and 8.8 (d, J_{PH} = 4.8, J_{PtH} = 48 Hz) (9 H, H of pyridyl and py). IR (KBr): 1640vs, 1600s and 1360s [ν(O=C–O) and ν(C=C)].

[PtMe(pyca)(4Me-py)] **5**. This complex was prepared by a similar method to that described for **4**. The complex was recrystallized from CH_2Cl_2–diethyl ether to give **5** as a yellow solid (yield: 73%) (Found: C, 36.80; H, 3.35; N, 6.50. $C_{13}H_{14}N_2O_2Pt$ requires C, 36.70; H, 3.30; N, 6.60%). NMR ($CDCl_3$): ^{1}H, δ 1.02 (s, 3 H, $^2J_{PtH}$ = 87, $PtCH_3$), 2.38 (s, 3 H, C_5H_4NMe), 7.1 (d), 7.2 (s), 7.4 (t), 8.0(t), 8.1 (d) and 8.6 (s, J_{PtH} = 51 Hz) (8 H, H of pyridyl and 4Me-py); ^{13}C-{^{1}H}, δ − 17.4 (s, $^1J_{PtC}$ = 850, $PtCH_3$), 21.8 (s, $NC_5H_4CH_3$), 127.2 (s, J_{PtC} = 45), 128.7 (s, J_{PtC} = 32), 138 (s), 146.6 (s, J_{PtC} = 46), 152.5 (s) and 172.6 (s) (C of pyridyl and 4Me-py). IR (KBr): 1650vs, 1350s [ν(O=C–O)] and 1600s [ν(C=C)].

[PtEt(pyca)(PPh_3)] **6**. A solution of *trans*-[Pt(H)Cl$(PPh_3)_2$] (0.15 g, 0.20 mmol) in acetone (*ca.* 35 cm^3) was treated with $AgBF_4$ (0.038 g, 0.20 mmol) in thf (2 cm^3) to precipitate white solid. After stirring for 0.5 h ethylene was bubbled through the solution for 1 h. A solution of Na(pyca) (0.029 g, 0.20 mmol) in methanol was then added and the mixture stirred overnight. The solvent was evaporated to dryness, the residue extracted with CH_2Cl_2 and filtered through Celite to remove black solid. The pale yellow filtrate was evaporated to dryness, the oily residue was redissolved in CH_2Cl_2 (*ca.* 1 cm^3) and heptane was added to form a precipitate and a yellow solution. The solution was filtered to remove mainly PPh_3 and then concentrated. The resulting yellow oil was crystallized from methanol–diethyl ether–heptane to give a white crystalline solid (yield: 0.51 g, 42%) (Found: C, 51.75; H, 4.10; N, 2.30. $C_{26}H_{24}NO_2PPt$ requires C, 51.30; H, 3.95; N, 2.30%). NMR ($CDCl_3$): ^{31}P-{^{1}H}, two isomers (ratio 1:1), **6a** δ 14.7 ($^1J_{PtP}$ = 4678), **6b** δ 16.2 ($^1J_{PtP}$ = 5014); ^{1}H, two isomers (ratio 1:1), **6a** δ 0.59 (t, $^3J_{HH}$ = 9, $^3J_{PtH}$ = 54, $PtCH_2CH_3$) and 1.2 (q*, J = 3, $^2J_{PtH}$ = 78, $PtCH_2CH_3$), **6b** δ 0.71 ($^3J_{HH}$ = 9, $^3J_{PtH}$ = 36, $PtCH_2CH_3$) and 1.5 (q*, J = 3, $^2J_{PtH}$ = 69 Hz, $PtCH_2CH_3$). IR (KBr): 1640vs, 1600s and 1360s [ν(O=C–O) and ν(C=C)].

[PtEt(pyca){$P(CH_2Ph)_3$}] **7**. To a solution of [Pt(Et)I(cod)] (0.08 g, 0.17 mmol) in thf (*ca.* 15 cm^3) at 0 °C was added Tl(pyca) (0.057 g, 0.17 mmol). The mixture was stirred for *ca.* 1 h, then $P(CH_2Ph)_3$ (0.053 g, 0.17 mmol) was added. The mixture was allowed slowly to reach room temperature and then stirred for 3 h. The solvent was evaporated to dryness and the residue extracted with CH_2Cl_2 (2 × 10 cm^3). The yellow solid was removed by filtration and the pale yellow filtrate was evaporated under reduced pressure leaving an oily residue. The residue was dissolved in benzene (2 cm^3) and light petroleum (b.p. 40–60 °C) was added to precipitate a white solid. The solvent was decanted and the solid dried *in vacuo* at 50 °C to give a white solid (yield: 0.05 g, 45%) (Found: C, 52.70; H, 4.60; N, 2.00. $C_{29}H_{30}NO_2PPt$ requires C, 53.5; H, 4.65; N, 2.15%). NMR ($CDCl_3$): ^1H, δ 0.8 (t, $^3J_{HH}$ = 6, $^3J_{PtH}$ = 57, $PtCH_2CH_3$) and 1.2 (q*, J = 3, $^2J_{PtH}$ = 75 Hz, $PtCH_2CH_3$): ^{31}P-{^1H}, δ − 0.49 (s, $^1J_{PtP}$ = 4502 Hz); ^{13}C-{^1H}, δ − 6.2 (d, $^2J_{PC}$ = 6, $^1J_{PtC}$ = 731, $PtCH_2CH_3$), 17.2 (s, $^2J_{PtC}$ = 40, $PtCH_2CH_3$), 29.6 (d, $^1J_{PC}$ = 19, $^2J_{PtC}$ = 29 Hz, PCH_2Ph) and 173 [s, OC(O)]. IR (KBr): 1660s, 1640vs, 1340s [ν(O–C=O)] and 1600s [ν(C=C) in pyridyl].

[PtMe(hoqu)(PPh_3)] **8**. This complex was prepared by the method described for **1**, using $AgBF_4$ to abstract the halide and employing the potassium salt of 8-hydroxyquinoline as the source of chelate ligand. Red-orange needle crystals were obtained by crystallization from CH_2Cl_2–light petroleum (b.p. 40–60 °C) (yield: 51%) (Found: C, 53.65; H, 3.90; N, 2.10. $C_{28}H_{24}NOPPt$ requires C, 54.05; H, 3.75; N, 2.15%). Mass spectrum: *m/z* 616 [M^+] and 600 [$M - CH_3$]$^+$; high resolution mass spectrum: Found 615.126; $C_{28}H_{24}NOP^{194}Pt$ requires 615.124. ^1H NMR ($CDCl_3$): δ 0.77 (d, $^3J_{PH}$ = 3, $^2J_{PtH}$ = 75 Hz, $PtCH_3$).

[Pt(COMe)(pyca)(PPh_3)] **9**. *Method* 1. A solution of [PtMe(pyca)(PPh_3)] **1** (0.08 g, 0.13 mmol) in $CHCl_3$ (*ca.* 10 cm^3) was added to a CO filled Schlenk flask (100 cm^3 capacity) and stirred under CO (1 atm) overnight. The solvent was evaporated to dryness and the residue was crystallized from CH_2Cl_2–diethyl ether to give a white solid (yield: 0.066 g, 82%) (Found: C, 49.45; H, 3.50; N, 2.30. $C_{26}H_{22}NO_3PPt$ requires C, 50.15; H, 3.55; N, 2.25%). NMR ($CDCl_3$): ^1H, 1.87 (s, 3 H, $PtCOCH_3$); ^{31}P-{^1H}, δ 8.9 ($^1J_{PtP}$ = 4685 Hz). IR (KBr): 1680vs, 1620s [ν(C=O) of pyca] and 1640vs [ν(C=O) of $PtCOCH_3$].

Method 2. A solution of *trans*-[PtCl(COMe)(PPh_3)$_2$] (0.10 g, 0.13 mmol) in freshly distilled MeCN (*ca.* 30 cm^3) was treated with $AgBF_4$ (0.024 g, 0.13 mmol) in thf (*ca.* 2 cm^3) to precipitate white solid. After the cloudy solution was stirred at room temperature for 3 h, a solution of Na(pyca) (0.018 g, 0.13 mmol) in MeOH (2 cm^3) was added. The mixture was stirred overnight and evaporated to dryness. The residue was extracted with CH_2Cl_2 and then filtered to remove black solid. The colourless filtrate was evaporated under reduced pressure to leave an oily residue. This was crystallized from CH_2Cl_2–diethyl ether to give a white crystalline solid (yield: 0.45 g, 55%). The complex was characterized spectroscopically by comparing data with those obtained by method 1.

[Pt(COEt)(pyca)(PPh_3)] **10**. Complex **10** was prepared by a similar method to that described for **9**, method 1. NMR ($CDCl_3$): ^1H, δ 0.50 (t, 3 H, $^3J_{HH}$ = 7.2, $PtCOCH_2CH_3$) and 2.1 (q, 2 H, $^3J_{HH}$ = 7.2 Hz, $PtCOCH_2CH_3$); ^{13}C-{^1H}, δ 9.5 (s, $PtCOCH_2CH_3$) and 50.7 ($^3J_{PC}$ = 5.3, $^2J_{PtC}$ = 158 Hz, $PtCOCH_2CH_3$). IR (KBr window): 1670s [ν(C=O), PtCOEt], 1640vs, 1600s and 1360s [ν(O=C–O) and ν(C=C)].

Reaction of [PtEt(pyca){$P(CH_2Ph)_3$}] **7** *with* CO.—Carbon monoxide was bubbled through a solution of [PtEt(pyca)-{$P(CH_2Ph)_3$}] **7** (0.04 g, 0.06 mmol) in $CDCl_3$ for 5 min. The NMR tube was fitted with a septum cap and secured with Teflon tape. The solution was then kept at room temperature overnight and NMR and IR spectra recorded *in situ*. Two new complexes (in the approximate ratio of 1:2) were observed and were assigned as **11** and **12**. Complex **11**: NMR ($CDCl_3$) ^1H, δ 1.3 (t, $^3J_{HH}$ = 7.5, $PtCOCH_2CH_3$) and 2.3 (q, $^3J_{HH}$ = 7.5 Hz, $PtCOCH_2CH_3$); ^{31}P-{^1H}, δ 2.94 (s, $^1J_{PtP}$ = 4590 Hz); IR (KBr) 1670vs [ν(C=O), PtCOEt] and 1630vs [ν(O=C–O), pyca]. Complex **12**: NMR ($CDCl_3$) ^1H, δ 0.82 (t, $^3J_{HH}$ = 7.3, $PtCOCH_2CH_3$) and 2.3 (q, $^3J_{HH}$ = 7.3 Hz, $PtCOCH_2CH_3$); ^{31}P-{^1H}, δ 10.1 ($^1J_{PtP}$ = 3283 Hz); IR (KBr) 2052vs [ν(PtC=O)], 1700s (br) [ν(O=C–O), pyca] and 1672s [ν(C=O), COEt].

Reaction of [PtMe(pyca)(py)] **4** *with* CO.—The reaction was carried out in the same manner as described above. After reaction two $PtCH_3$ resonances were observed in a ratio of approximately 3:1. Spectroscopic data indicate that the species are unreacted starting complex (major product) and a complex with a terminal Pt–CO (either a complex where CO has displaced the pyridine or a five-co-ordinate complex). ^1H NMR ($CDCl_3$): δ 1.0 (s, $^2J_{PtH}$ = 84) and 1.3 (s, $^2J_{PtH}$ = 72 Hz), ($PtCH_3$). IR (KBr window): 2050s [ν(Pt–C=O)], 1660vs, 1600s and 1360s [ν(O=C–O) and ν(C=C) pyca].

Decarbonylation of Acyl Complex **9**.—A solution of [Pt(COMe)(pyca)(PPh_3)] **9** (0.03 g, 0.05 mmol) in $CDCl_3$ (0.4 cm^3) was transferred into a N_2 filled 5 mm NMR tube which was fitted with a septum cap and secured with Teflon tape. The NMR tube was immersed in a pre-heated water-bath (60–65 °C) for 4–5 h. Only [PtMe(pyca)(PPh_3)] **1** was detected by ^1H NMR spectroscopy *in situ*. The regeneration of the acyl complex **9** was achieved by gently bubbling CO through the above solution for *ca.* 2–3 min. The NMR tube was then left at room temperature overnight. Formation of **9** was confirmed by ^1H NMR spectra recorded *in situ*. The decarbonylation of **9** in other deuteriated solvents, *e.g.* CD_3OD, C_5D_5N and $(CD_3)_2SO$ was carried out in a similar manner at the same temperature.

Ethylene Elimination Reaction of [PtEt(pyca)(PPh_3)] **6**.—A solution of [PtEt(pyca)(PPh_3)] **6** (0.03 g, 0.05 mmol) in $CDCl_3$ (0.4 cm^3) was prepared in an NMR tube and warmed in a water-bath (60 °C). The ^1H NMR spectrum was recorded *in situ*. The spectrum at high field consists of a doublet at δ − 26 ($^2J_{PH}$ = 20, $^1J_{PtH}$ = 1320 Hz), and a triplet at δ − 16 ($^2J_{PH}$ = 9, $^1J_{PtH}$ = 1230 Hz), in a 1:1 ratio. These high-field peaks are indicative of platinum hydrides. Peaks due to unreacted [PtEt(pyca)(PPh_3)] are also present. Prolonged heating (24 h) led to disappearance of peaks due to the original complex and also the peak at δ − 26; the triplet at δ − 16 remained unaffected.

Results and Discussion

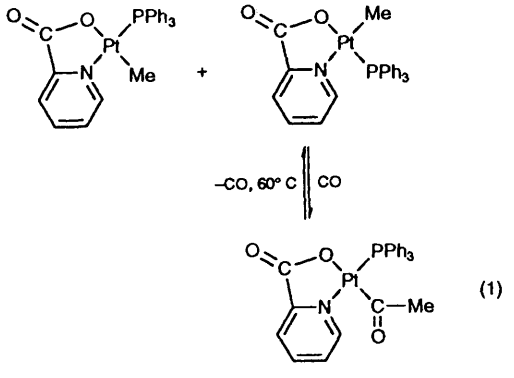
Synthesis and Characterization of the Complexes.—Platinum–alkyl complexes containing the anionic pyca ligand have been synthesised as shown in Scheme 1. Complexes **1**–**5** and **8** are readily prepared in moderate yield by simple ligand displacement reactions involving the interaction of salts of Hpyca with *trans*-[Pt(Me)I(PPh_3)$_2$] or [Pt(Me)Cl(cod)]. Complex **7** was prepared from [Pt(Et)I(cod)] by a similar ligand displacement reaction. The complex [PtEt(pyca)(PPh_3)] **6** was prepared from *trans*-[Pt(H)Cl(PPh_3)$_2$] in a 'one pot', multistage synthesis.[22,26] In this synthesis the chloride is first removed by reaction with silver ions, the resulting solvated platinum–hydride complex is then treated consecutively with ethylene and Tl(pyca) to give the desired product. Complexes were characterized by ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR and IR spectroscopy and microanalysis.

The σ-methyl groups of the complexes **1**–**3** and **8** appear in

* Collapsed quartet, which belongs to the A part of a complicated A_2C_3MX spin system, the values reported as coupling constants for these resonances are the separation between lines and do not necessarily reflect the true coupling constants.

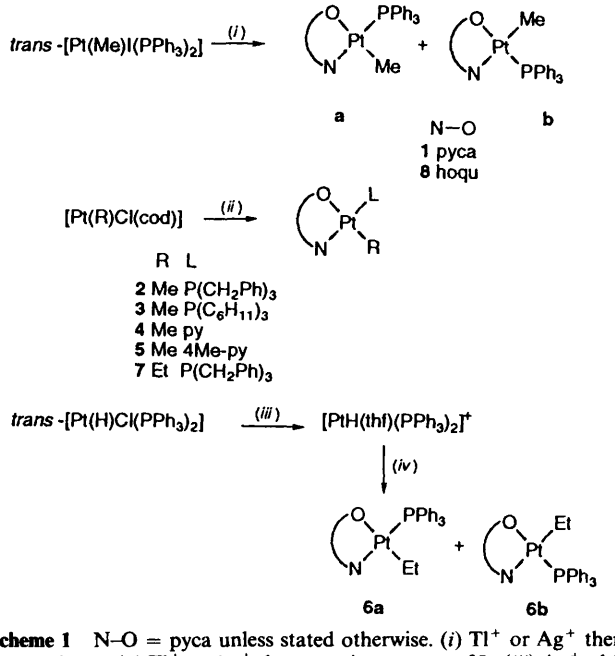
the ^1H NMR spectra in the region δ 0.5–1 as a doublet with ^{195}Pt satellites, due to couplings with the *cis* phosphine and the platinum atom. Coupling constants for these protons are typically 2–4 Hz. Ethyl groups in the σ-ethyl complexes **6** and **7** appear typically as a triplet and a collapsed quartet. Each set is flanked by platinum satellites. These resonances belong to a complicated A_2C_3MX spin system (A, C = ^1H; M = ^{195}Pt; X = ^{31}P), therefore the separations between lines of the resonances do not necessarily reflect the true coupling constants. The complexes **1** and **6** (L = PPh_3) exist in solution as a pair of isomers **a** and **b** (Table 1). In both cases the ratio of the isomers **a** and **b** is *ca.* 3 to 1 with **a** being the preferred isomer, *i.e.* in which the groups with the largest *trans* influence are *cis* to each other.[27] Where L = $P(CH_2Ph)_3$, py or 4Me-py only one isomer is observed (N *trans* to P or N *trans* to N respectively). Identification of the isomers is based on spectroscopic methods. The coupling constants $^1J_{PtP}$ and $^1J_{PtC}$ and ^{13}C NMR spectra usually provide important information about the atom *trans* to that being considered.[27] The coupling constants between ^{195}Pt and the σ-alkyl group in ^1H NMR spectra have also been used to distinguish the geometry of the complexes.[27b] In general, values of the ^{195}Pt–^{31}P coupling constants for isomers of type **a**, where the P atom is *trans* to N, are smaller than those in isomers of type **b**. The reverse trend is expected for values of the ^{195}Pt–^{13}C and ^{195}Pt–^1H (in Pt–CH_3) coupling constants.

Reactions of Complexes with CO.—The complexes **1** and **6** (L = PPh_3) readily undergo carbonylation in dichloromethane or chloroform at room temperature to generate almost quantitatively the respective acyl complexes [equation (1)]. Although **1** and **6** contain a mixture of *cis* and *trans* isomers only one isomer of each acyl complex is observed. Despite the large ^{195}Pt–^{31}P (J_{PtP} = 4685) coupling constant obtained for the acyl complex derived from **1**, we believe the isomer has the structure P *cis* to the acyl group, which is not surprising considering the large *trans* influences of the phosphine and acyl ligands.[27] In earlier carbonylation studies the preference of the acyl ligand to take up a position *cis* to a high-*trans* influence ligand, such as phosphine, was confirmed by a crystal structure.[17,22] In these same studies we also noted that the Pt–P coupling constant increased by approximately 300 Hz after carbonylation, which is in agreement with the changes observed in the current study of the pyca complexes. A recent crystal structure study of hydrocarbyl nickel pyca complexes has also shown that the phosphine ligand prefers a position *cis* to the hydrocarbyl ligand, which has a smaller *trans* influence than the corresponding acyl ligand.[28]



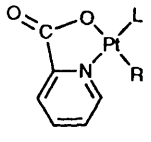
(1)

9

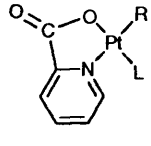


Scheme 1 N–O = pyca unless stated otherwise. (*i*) Tl^+ or Ag^+ then pyca or hoqu; (*ii*) Tl^+ or Ag^+ then pyca in presence of L; (*iii*) Ag^+, thf; (*iv*) C_2H_4 then pyca

Table 1 Selected NMR data (*J* in Hz) for the complexes [PtMe(N–O)(L)]



a



b

Complex	L	R	δ_H(Pt–R)	δ_C(Pt–R)	δ_P
1a	PPh_3	Me	0.65 (d, J_{PH} = 2.6, $^2J_{PtH}$ = 78)	−15.6 (d, J_{PC} = 8.2, $^1J_{PtC}$ = 720)	14.3 (s, $^1J_{PtP}$ = 4438)
1b	PPh_3	Me	0.73 (d, J_{PH} = 3.1, $^2J_{PtH}$ = 71)	−12.3 (d, J_{PC} = 7.5, $^1J_{PtC}$ = 654)	14.2 (s, $^1J_{PtP}$ = 4709)
2*	$P(CH_2Ph)_3$	Me	0.45 (d, J_{PH} = 3, $^2J_{PtH}$ = 81)	−19.8 (d, J_{PC} = 8.5, $^1J_{PtC}$ = 742)	−0.72 (s, $^1J_{PtP}$ = 4312)
3*	$P(C_6H_{11})_3$	Me	0.68 (d, J_{PH} = 1.2, $^2J_{PtH}$ = 89)	−23.1 (d, J_{PC} = 7.6, $^1J_{PtC}$ = 744)	19.9 (J_{PtP} = 4137)
4*	py	Me	1.02 (s, $^2J_{PtH}$ = 84)	−17.0 (s, $^1J_{PtC}$ = 846)	
5*	4Me-py	Me	1.02 (s, $^2J_{PtH}$ = 87)	−17.4 (s, $^1J_{PtC}$ = 850)	
6a	PPh_3	Et	0.59 (t, $^3J_{PtH}$ = 54), 1.2 (q, $^2J_{PtH}$ = 78)		14.7 ($^1J_{PtP}$ = 4678)
6b	PPh_3	Et	0.71 (t, $^3J_{PtH}$ = 36), 1.5 (q, $^2J_{PtH}$ = 69)		16.2 ($^1J_{PtP}$ = 5014)
7*	$P(CH_2Ph)_3$	Et	0.8 (t, $^3J_{PtH}$ = 57), 1.2 (q, $^2J_{PtH}$ = 75)	17.2 (d, $^2J_{PtC}$ = 40), −6.2 (d, $^1J_{PtC}$ = 731)	−0.49 ($^1J_{PtP}$ = 4502)

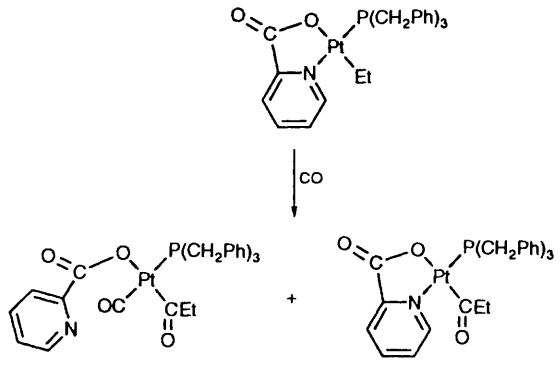
* Isomer **a** only.

The acyl complexes are clearly identified by ^1H and $^{31}P-\{^1H\}$ NMR spectroscopy and the complex [Pt(COMe)(pyca)(PPh_3)] **9** was isolated as a stable, white, crystalline solid and further characterized by microanalysis. Surprisingly no acyl complex is observed, under our conditions, in the reaction of the pyridine complex **4** or the 4-methylpyridine complex **5** with CO. This may indicate that the co-ordination strength of L in [PtR(pyca)L] may not be so crucial to the insertion step. The *in situ* ^1H NMR study shows that most of the [PtMe(pyca)(py)] remains unchanged (δ 1.0, s, $^2J_{PtH}$ = 84 Hz, $PtCH_3$). However, another σ-methyl resonance appears at δ 1.3 ($^2J_{PtH}$ = 72 Hz); this complex has been identified as a platinum carbonyl complex from the IR spectrum, which shows two strong peaks at 2050 and 1660 cm^{-1}. At this stage we have not been able to clearly differentiate between a four-co-ordinate complex in which the pyridine has been displaced by CO or a five-co-ordinate platinum carbonyl complex.

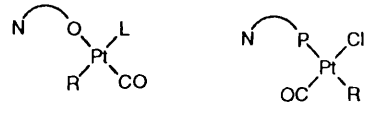
These systems offer an excellent opportunity to observe ligand influences on the insertion process and to assess the implications of these observations in terms of the carbonylation mechanism. In this respect, of particular interest is a comparison of the reaction of CO with the complexes [PtR(pyca)(PPh_3)], [PtR(pyca){$P(CH_2Ph)_3$}] and [PtMe(pyca){$P(C_6H_{11})_3$}], where a primary difference between the complexes is the donor capacity (and hence *trans* influence) of the phosphines or the R group attached to the platinum. Treatment of [PtMe(pyca)(PPh_3)] or [PtEt(pyca)(PPh_3)] with CO gives only the expected acyl complexes [Pt(COMe)(pyca)(PPh_3)] and [Pt(COEt)(pyca)(PPh_3)] in almost quantitative yield [equation (1)]. In contrast, [PtMe(pyca){$P(CH_2Ph)_3$}] and [PtMe(pyca){$P(C_6H_{11})_3$}] do not react with CO even over a prolonged reaction time (one week), or under a higher pressure of CO (5 atm). Complex [PtEt(pyca){$P(CH_2Ph)_3$}] on the other hand reacts with CO to give a mixture of products, with complexes of type [Pt(COEt)(pyca){$P(CH_2Ph)_3$}] **11** and [Pt(CO)(COEt)(pyca){$P(CH_2Ph)_3$}] **12** (Scheme 2) as the predominant species (accounting for approximately 25 and 50% of the product respectively; the remainder is unidentified at this stage). These compounds have been characterized by NMR and IR spectroscopy and their structures can be confidently assigned. No attempt has been made to isolate the complexes.

While we do not, at present, know the carbonylation mechanism for these platinum–alkyl complexes our results provide evidence that lability in the ligands attached to the platinum centre is important. Aspects of the above carbonylation behaviour suggest that the lability of the phosphine may be the dominant factor. For the σ-methyl complexes stronger donor or more basic phosphines such as $P(C_6H_{11})_3$ and $P(CH_2Ph)_3$ inhibit carbonylation, whereas a more acidic phosphine such as PPh_3 allows carbonylation to proceed. However the situation is evidently more complex than this simple explanation indicates. When the σ-ethyl complexes are considered, hemilabile behaviour in the pyca chelate appears to become more important and identification of the complex **12** provides evidence for a dangling pyca ligand. The formation of intermediates of the type **I** during the carbonylation reaction is therefore inferred. Further complicating the reaction behaviour is the lack of carbonylation activity of complexes containing pyridine and 4-methylpyridine. Neither complex gives an acyl species when treated with CO despite the expectation that these ligands would be more weakly bound to platinum than would phosphines. In agreement with this expected lability, reaction of the pyridine complexes with CO gave a species in which the CO appears to have displaced the pyridine. Hence it is evident that ligand lability is only one aspect in deciding reactivity in the carbonylation process and other factors such as appropriate *trans* influences may be of considerable importance.

Vrieze *et al.*[12] in their study of carbonylation reactions with complexes containing hemilabile P–N ligands have provided evidence for an intermediate **II** in which the phosphorus atom is *trans* to the alkyl group. This type of intermediate is a key



Scheme 2 Carbonylation of complex 7



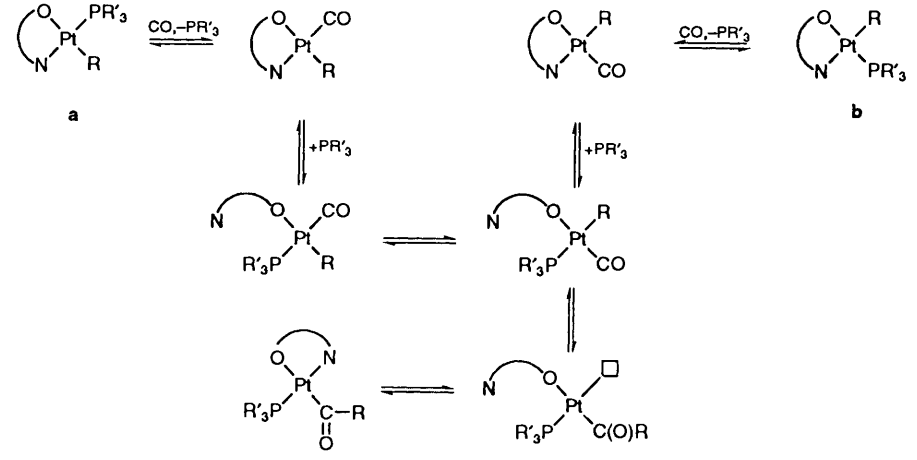
I **II**

species in the proposed carbonylation mechanism and was previously identified by Anderson and Cross[29] as being important for CO insertion in systems containing monodentate phosphine ligands. It is a reactive species in which two large *trans*-influence groups (the phosphorus and the alkyl group) are *trans* to each other and hence can be expected to promote the next step of the reaction, which is migration of the alkyl group to give the acyl compound. The inability to form such a key intermediate in the systems containing pyridine and 4-methylpyridine would explain their lack of activity in the carbonylation process. With these complexes there is no alternative high *trans*-influence ligand to promote the alkyl migration step.

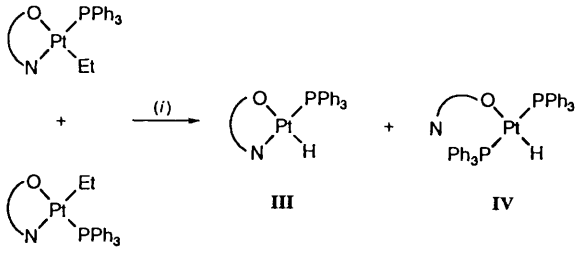
Further evidence for the importance of an available co-ordination site was obtained from the alternative preparation of [Pt(COMe)(pyca)(PPh_3)] **9**. Complex **9** could be synthesised from [PtCl(COMe)(PPh_3)$_2$] by reaction with Na(pyca), however, the actual nature of the product mix is dependent on the solvent used. Employing a weakly co-ordinating solvent such as thf a mixture of **9** and the σ-methyl complexes **1a** and **1b** was obtained. It is therefore apparent that decarbonylation of the acyl complex has occurred in thf. In the more strongly co-ordinating solvent MeCN only pure **9** was obtained *i.e.* no decarbonylation occurred in this solvent. These observations indicate that CO elimination probably proceeds *via* a vacant co-ordination site provided by the loss of ligand, and any species such as a solvent molecule which could successfully compete with CO for the vacant site would prevent decarbonylation. This is consistent with a previous observation[30] that an accessible co-ordination site provided by chloride abstraction facilitates decarbonylation.

The ease of decarbonylation of complex **9** is a significant feature as this is a rarely observed phenomenon in platinum chemistry,[20] especially in monomeric and neutral compounds. When **9** is heated at 60 °C in $CDCl_3$ for several hours, the σ-methyl compounds **1a** and **1b** are almost quantitatively regenerated [equation (1)]. The ratio of isomers, **1a** and **1b**, regenerated by CO elimination is also 3 to 1, suggesting that the same mechanism, but in reverse, is followed for both the insertion and elimination processes. This insertion and deinsertion process can be repeated several times without decomposition of the complexes. The decarbonylation of **9** is also observed in a variety of other solvents, at the same temperature, *e.g.* MeOH, dmso or pyridine, but not in benzene, indicating that a polar solvent is probably necessary for the decarbonylation process.

In order further to probe the mechanism for insertion–



Scheme 3 Proposed carbonylation-decarbonylation mechanism



Scheme 4 (*i*) β-Elimination, $CDCl_3$, 60 °C

deinsertion the complex [PtMe(hoqu)(PPh_3)] **8** was prepared. Complex **8** differs from **1** primarily in the rigidity of the chelating O–N ligand. The complex was prepared by a similar method to that employed for **1**, *i.e.* by reaction of the potassium salt of 8-hydroxyquinoline with [Pt(Me)I(PPh_3)$_2$] in the presence of $AgBF_4$. If in the mechanism for CO insertion, dissociation of the pyridine fragment of the chelate is an important step, then the rigid structure of the hydroxyquinolate chelate would be expected to inhibit reaction. Indeed, under the same carbonylation conditions as previously employed [PtMe(hoqu)(PPh_3)] does not give an insertion product, suggesting that the hoqu chelate is too rigid to allow partial dissociation as required by the mechanism. Similarly, decarbonylation of [Pt(COMe)(hoqu)(PPh_3)] {prepared from *trans*-[PtCl(COMe)(PPh_3)$_2$]} is very slow and initially generates only traces of the decarbonylated compound [PtMe(hoqu)(PPh_3)] although over a prolonged heating period (> 20 h) complete decarbonylation does eventually occur.

In conclusion, a possible carbonylation–decarbonylation mechanism for the platinum compounds studied in this work can be suggested. The overall process appears to be a complex one and it may well be that there are competing mechanisms and/or the rate-determining step may change under different conditions. However a mechanism, consistent with that suggested by Vrieze and co-workers,[12] is proposed and outlined in Scheme 3. The proposal, which is able to account for the apparently conflicting observations noted in this study, requires intermediates with a hemilabile or 'dangling' chelating ligand, as previously postulated,[12,17] and a key intermediate **I** in which a large *trans*-effect group or ligand (such a phosphine) is *trans* to the migrating alkyl species.[12,29] In those systems containing phosphines initial dissociation of the phosphine, or partial dissociation of the N–O chelate appear to be the likely rate-determining steps.

The foregoing discussion does not unambiguously preclude a mechanism involving the initial formation of a five-co-ordinate carbonyl intermediate, however, it is more difficult to explain the variable behaviour noted for these platinum–alkyl complexes if such a species is invoked.

Ethylene Elimination from [PtEt(pyca)(PPh_3)] **6**.—Because of the apparent lability of the pyca ligand and the ease of insertion–deinsertion of CO in examples of these complexes we were interested in investigating the behaviour of the platinum–ethyl complexes **6** and **7**. On warming complex **6** (a mixture of *cis* and *trans* isomers) to 60 °C ethylene is evolved and a mixture of mainly two hydrides **III** and **IV** (Scheme 4) is produced and can be identified *in situ* by ^{1}H NMR [**III** δ_H −26 (d, $^2J_{PH}$ = 20, $^1J_{PtH}$ = 1320 Hz), **IV** δ_H −16 (t, $^2J_{PH}$ = 9, $^1J_{PtH}$ = 1230 Hz)]. The complexes **III** and **IV** have not been isolated. The process is probably a β-elimination reaction, which possibly proceeds *via* an intermediate in which ligand dissociation provides a vacant site for elimination. The appearance of complex **IV** suggests that PPh_3 may dissociate to provide the vacant site. (However, it is possible that free PPh_3 arises from a small amount of decomposition. The free PPh_3 is then able to compete with the N of the pyca ligand for the co-ordination site.) In contrast, complex **7** which contains the more basic phosphine $P(CH_2Ph)_3$ does not undergo β-elimination under the same reaction conditions even after prolonged reaction times. Thus, if ligand dissociation is the preferred mechanism for ethylene elimination initial phosphine dissociation rather than a dangling pyca ligand would appear to be more in keeping with the observations.

Acknowledgements

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