Synthesis and Carbonylation Studies on Methylpalladium(II) Complexes containing Chelating Pyridinecarboxylate Ligands: Dynamic Behaviour of the Ligands and Implications for the Carbonylation Mechanism†

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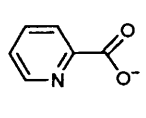
Methylpalladium complexes of the general formula [PdMe(pyca)(L)] [pyca = pyridine-2-carboxylate, L = PPh_3, $PMePh_2$, PMe_2Ph, $P(C_6H_4Me\text{-}p)_3$, $P(CH_2Ph)_3$, $P(C_6H_{11})_3$, PPr^i_3, $P(OMe)_3$, pyridine, 4-methylpyridine or NMe_2Ph] were synthesised and the dynamic behaviour of the ligands pyca and L studied in detail. The ligands were found to undergo readily a variety of exchange reactions, clearly demonstrating their lability under mild conditions. The ligand exchange behaviour and data on rates of carbonylation for the palladium complexes led to a dissociative mechanism, requiring lability in both the ligand L and the chelate, being proposed for the CO insertion process. The methylpalladium complexes exist in solution as a mixture of *cis* and *trans* isomers. However the acyl complexes were found to occur only in the geometry with the phosphine *cis* to the acyl group. X-Ray crystal structures were obtained for the complexes [Pd(COMe)(pyca){$P(CH_2Ph)_3$}] and [Pt(COMe)(pyca)-(PPh_3)]. The complexes have distorted square-planar geometry: for the palladium complex, which is highly distorted, P–Pd–O(21) 97.3(1), P–Pd–C(01) 88.9(2), N–Pd–O(21) 78.4(2) and N–Pd–C(01) 95.9(2)° and for the platinum complex P–Pt–O(21) 93.9(5), P–Pt–C(01) 95.1(9), N–Pt–O(21) 80.4(7) and N–Pt–C(01) 91(1)°.

Insertion of CO into metal–carbon bonds is a key process with widespread applications in catalysis. There has been increased interest in the CO insertion mechanism with the main attention being given to co-reaction of CO and ethylene to form polyketones.[1-5] The insertion process for d^8 transition-metal compounds containing monodentate ligands is considered to follow either a dissociative or an associative route depending on the base strength of the ligands.[6] The reaction of complexes containing chelate ligands is generally less well understood. However, earlier work suggested that a ligand with a flexible backbone and/or a weakly co-ordinating chelate ligand is important.[7] More recent studies in general agree with this view,[8-10] although it has been found that a hemilabile chelate is not essential for insertion.[4,11] Elsevier and co-workers have been able to use a rigid bidentate ligand to successfully isolate the complexes formed from the stepwise insertion of CO and ethylene during the formation of oligomeric ketones.[4] In agreement with our studies,[10] the vacant site for initial co-ordination of CO is thought to arise from the dissociation of a remaining monodentate ligand.[4] Dissociation of a monodentate ligand in chelated complexes may be a more important pathway than previously recognised. In all these studies however, it is implicit that a dissociative insertion mechanism is operating.[4,7,10] If the dissociative route is proposed as a mechanistic pathway ligand lability should be clearly demonstrable. Direct evidence of ligand lability and fluxional behaviour is limited in previous studies, although Vrieze and co-workers[12] have provided evidence of an intermediate with a dangling P–N chelate during carbonylation studies. To date studies with chelate species have concentrated primarily on complexes containing neutral chelate ligands, with particular emphasis given to phosphine based[7,8,12] and dinitrogen chelates.[11,13-16]



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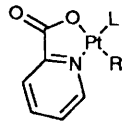

PtR(pyca)L

A number of recent studies have focused on complexes containing an anionic chelate and neutral monodentate ligands.[9,10,16-19] Many of these chelate ligands have been successfully used in homogeneous catalysts.[20] We previously reported the preparation of palladium and platinum hydrocarbyl complexes of triphenylphosphine bearing β-diketonate type ligands, and their reactions with CO to afford acyl complexes.[9,17,19] A comparison of rates of CO insertion for these complexes provided information on ligand influences, in particular on the effect of ligand moieties on the carbonylation process. In order to further investigate the role of the hemilabile chelate ligand (O–Y) and the neutral monodentate ligand (L) on the insertion pathway our research has been extended to complexes containing the anionic bidentate ligand, pyridine-2-carboxylate (pyca).

A group of unusually labile alkyl–platinum complexes containing pyca [PtR(pyca)(L)], have been investigated and their reactions with CO studied. The insertion/elimination processes for these complexes were found to depend on both the N–O ligand and the neutral monodentate ligand L. A mechanism was proposed that required both a hemilabile chelating ligand and a weakly co-ordinating, high *trans* influence ligand L.

In this paper we have studied the preparation and carbonylation behaviour of palladium complexes of pyca and

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Non-SI unit employed: atm = 101 325 Pa.

related ligands. Extensive spectroscopic investigations have been carried out unambiguously to demonstrate labile behaviour of the ligands. We were interested in correlating ligand lability and structure (and hence complex structure) with the mechanistic pathways followed during carbonylation. While the overall carbonylation process for the palladium complexes is similar to that proposed for the related platinum compounds, significant differences are apparent in the mechanistic detail and the requirements for active carbonylation differ in important aspects for the two metals. Results from this study provide insight into the electronic and steric requirements for CO insertion.

Stable acylpalladium complexes are relatively uncommon, consequently solid-state structural studies are rare. Here we report a structural analysis of the acyl complex [Pd(COMe)(pyca){P(CH_2Ph)$_3$}]. For comparative purposes we have also determined the structure of the related platinum complex [Pt(COMe)(pyca)(PPh_3)].[10] Our studies verify the proposed stereostructures of the complexes and provide information about the inner co-ordination sphere of the metals.

Experimental

Reagents.—Manipulations were generally carried out under dry, oxygen-free nitrogen in Schlenk apparatus using standard Schlenk techniques. Solvents were dried, purified by standard methods and freshly distilled before use. Chemical reagents were used as received and *trans*-[PdIMe(PPh_3)$_2$] and [{PdMe(SMe_2)(μ-I)}$_2$] were prepared by literature methods.[21,22] The synthesis of [Pt(COMe)(pyca)(PPh_3)] has been reported previously.[10] The salt Tl(pyca) was prepared by the reaction of Tl_2CO_3 with the corresponding pyridinecarboxylic acid in methanol. The phosphines were purchased from Strem Chemicals Inc. and used as received.

Nuclear magnetic resonance (NMR) spectra were recorded at 22 °C on a Bruker AM-300 NMR spectrometer at 300.13 (^{1}H), 75.48 (^{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). Unlabelled NMR peaks can be assumed to be singlets. Infrared (IR) spectra were recorded in absorbance units on a Digilab FTS 20E FT-IR spectrophotometer, KBr discs were used 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.

Kinetic Measurements.—The rates of carbonylation for the palladium(II) complexes were studied using ^{1}H NMR spectroscopy. Each sample for measurement was prepared according to the following procedure: the solid sample was placed in a N_2 filled 5 mm outside diameter NMR tube which was immersed in an ice–salt bath (−10 °C), and a CO flow passed continually over it for *ca.* 10 min, after which time $CDCl_3$, contaminated with a trace of grease, was added. Carbon monoxide was then bubbled through the solution for *ca.* 2 min. The NMR tube was quickly fitted with a septum cap and secured with Teflon tape. Sample solutions were made up to contain a concentration of between 0.01 and 0.02 mol dm^{-3} of complex for each run. The extent of conversion to the acyl complex with time was monitored by integration of the methyl absorption of the σ-methyl complexes (*ca.* δ 0.6) and comparing it to that of the external standard (grease, δ 0.1). A kinetic study of the carbonylation of [PdMe(pyca)(PPh_3)] in the presence of pyridine or PPh_3 was carried out in a similar manner, except that the $CDCl_3$ was mixed with the required amount of [$^2H_5$]pyridine or PPh_3. Each kinetic run consisted of four to eight data points.

Structure Determinations.—Unique room-temperature diffractometer data sets ($T \approx 295$ K; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; 2θ–θ scan mode, $2\theta_{max} = 50°$) were measured yielding *N* independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinements after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, (x, y, z, U_{iso})$_H$ being constrained at estimated values. Conventional residuals on $|F|$ at convergence, R,R' are quoted; statistical weights were derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system implemented by S. R. Hall.[23] Pertinent results are given in the Figures and Tables.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Crystal/Refinement Data.—[Pd(COMe)(pyca){P(CH_2-Ph)$_3$}], $C_{29}H_{28}NO_3PPd$, $M = 575.9$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 17.321(6)$, $b = 9.065(5)$, $c = 17.922(4)$ Å, $\beta = 113.16(2)°$, $U = 2587$ Å^3, D_c ($Z = 4$) = 1.48 g cm^{-3}, $F(000) = 1176$, $\mu_{Mo} = 8.1$ cm^{-1}, specimen 0.14 × 0.29 × 0.07 mm, $A^*_{min,max} = 1.05, 1.28$ (Gaussian correction), $N = 4396$, $N_o = 2693$; $R = 0.041$, $R' = 0.039$, $n_v = 316$. [Pt(COMe)(pyca)(PPh_3)], $C_{26}H_{22}NO_3PPt$, $M = 622.5$, monoclinic, space group Cc (C_s^4, no. 9), $a = 9.624(5)$, $b = 29.211(7)$, $c = 9.040(4)$ Å, $\beta = 112.54(4)°$, $U = 2347$Å^3, D_c ($Z = 4$) = 1.76 g cm^{-3}, $F(000) = 1208$, $\mu_{Mo} = 61$ cm^{-1}, specimen 0.31 × 0.22 × 0.28, $A^*_{min,max} = 1.14, 3.96$ (analytical correction), $N = 2077$, $N_o = 1631$; $R = 0.047$, $R' = 0.047$ (preferred chirality), $n_v = 282$.

Data for the platinum complex were weak, and the determination correspondingly less precise than that of the palladium derivative; anisotropic thermal parameter refinement for the nitrogen atom was unstable and the corresponding isotropic form was used.

Synthesis of Complexes.—[PdMe(pyca)(PPh_3)] **1**. A solution of *trans*-[PdIMe(PPh_3)$_2$] (0.2 g, 0.26 mmol) in tetrahydrofuran (thf) (15 cm^3) was treated with Tl(pyca) (0.084, 0.26 mmol) at room temperature overnight. The mixture was then refluxed under N_2 for 2 h. After cooling to room temperature, the yellow solution was evaporated to dryness leaving an oily residue. The residue was redissolved in CH_2Cl_2 (2–5 cm^3), and diethyl ether (*ca.* 20 cm^3) was added. The resulting solution was kept at −15 °C for about 2 h, during which time a small amount of white solid precipitated, which was removed by filtration. The solution was left under N_2 to evaporate slowly and a pale yellow solid precipitated. The precipitate was isolated by filtration and dried *in vacuo* to give a pale yellow solid (yield: 0.078 g, 60%) (Found: C, 57.6; H, 4.35; N, 2.75. $C_{25}H_{22}NO_2PPd·H_2O$ requires C, 57.3; H, 4.65; N, 2.65%). The presence of water in the molecule was detected by ^{1}H NMR and IR spectroscopy in CH_2Cl_2 solution. NMR($CDCl_3$): ^{1}H, two isomers δ 0.62 (d) and 0.83 (d) (3 H, $^3J_{PH}$ = 2.5 Hz, $PdCH_3$); ^{31}P-{^{1}H}, two isomers δ 40.0 (s), and 33.6 (s, major). IR(KBr): 1640vs [ν(C=O)], 1600vs [ν(C=C)] and 1340vs [ν(O–C=O)].

[PdMe(pyca){P(C_6H_{11})$_3$}] **2**. The complex was prepared by a similar method to that described for **3** (below). The complex was isolated as a pale yellow solid (yield: 67%). Mass spectrum: m/z 612 [M]$^+$ and 597 [$M - CH_3$]$^+$. NMR ($CDCl_3$): ^{1}H, two isomers δ 0.46 (d, J_{PH} = 1.0, **a**) and 0.56 (d, J_{PH} = 1.0 Hz, **b**); ^{31}P-{^{1}H}, δ 44.4 (s, major) and 45.6 (s). IR (KBr): 1640vs [ν(C=O)], 1600vs [ν(C=C) pyridyl], 2930vs, 2850s [ν(C–H)] and 1340s [ν(C–O)].

[PdMe(pyca)($PMePh_2$)] **3**. Solid Tl(pyca) (0.095 g, 0.29 mmol) was added to a brown-yellow solution of [{PdMe(SMe_2)(μ-I)}$_2$] (0.09 g, 0.15 mmol) in acetonitrile (15 cm^3) at 0 °C. The mixture was stirred for 10 min and then $PMePh_2$ (0.058 g, 0.29 mmol) was added. The mixture was

stirred for about 4 h, and allowed to slowly reach room temperature. The solution was evaporated to dryness and the residue was extracted with CH_2Cl_2 (2 × 10 cm^3). The solution was filtered to remove a dark green solid. The pale yellow filtrate was evaporated under reduced pressure. The resulting oily residue was redissolved in benzene (2 cm^3) and light petroleum (b.p. 40–60 °C) was added to precipitate a white solid. The solid was collected by filtration and dried *in vacuo* to give 0.1 g of white solid (yield: 69%) (Found: C, 60.9; H, 5.10; N, 2.55. $C_{25}H_{40}NO_2PPd$ requires C, 61.3; H, 5.15; N, 2.55%). NMR ($CDCl_3$): ^1H, two isomers δ 0.51 (d), 0.88 (d) (3 H, $^2J_{PH}$ = 2.4, $PdCH_3$) and 2.09 (d, 3 H, $^2J_{PH}$ = 3 Hz, PCH_3Ph_2); ^{13}C-{^1H}, δ 0.72 (d, $^2J_{PC}$ = 8.2, $PdCH_3$) and 14.3 (d, $^1J_{PC}$ = 30 Hz, PCH_3); ^{31}P-{^1H}, δ 20.9 (s, major) and 21.2 (s). IR (KBr): 1640vs, 1600vs and 1360s [ν(C=O), ν(C=C) and ν(C–O)].

[PdMe(pyca)(PMe_2Ph)] **4**. The complex was prepared by a method similar to that described for **3**, and was obtained at −10 °C from benzene–light petroleum (b.p. 40–60 °C) as a white to pale yellow solid (yield: 57%). The complex is moisture sensitive and became sticky upon contact with air (Found: C, 45.90; H, 4.95; N, 3.20. $C_{15}H_{18}NO_2PPd·0.8H_2O$ requires C, 45.55; H, 4.95; N, 3.55%). The presence of water in the sample was detected by IR spectroscopy in CH_2Cl_2 solution, which showed a broad band at 3500 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.51 (br s, 3 H, $PdCH_3$), 1.8 (d, 6 H, J_{PH} = 12 Hz, PCH_3) and 7.3–8.5 (m, 9 H, Ph and pyridyl); ^{13}C-{^1H}, δ −1.6 (s, $PdCH_3$), 14.3 (d, $^1J_{PC}$ = 38 Hz, PCH_3), 171.6 (s, O–C=O), 155 (s), 145 (s), 140 (s, pyridyl), 127 (d), 129 (d) and 132 (d, Ph). IR (KBr): 1640vs, 1360s [ν(O=C–O)] and 1600s [ν(C=C)].

[PdMe(pyca){$P(CH_2Ph)_3$}] **5**. The complex was prepared by a similar method to that described for **3**. The complex was obtained as a pale yellow solid (yield: 81%) (Found: C, 53.5; H, 4.50; N, 3.45. $C_{20}H_{21}NO_2PPd$ requires C, 54.0; H, 4.80; N, 3.15%). NMR ($CDCl_3$): ^1H, δ 0.3 (d, 3 H, $^3J_{PH}$ = 3, $PdCH_3$), 0.31 (d, 6 H, $^2J_{PH}$ = 12 Hz, PCH), 7.1–8.5 (m, 19 H, Ph and pyridyl); ^{13}C-{^1H}, δ −0.83 (d, $^2J_{PC}$ = 6, $PdCH_3$) and 30.7 (d, $^1J_{PC}$ = 26 Hz, PCH_2Ph); ^{31}P-{^1H}, δ 24.8 (s). IR (KBr): 1650vs (br), 1600vs and 1360vs [ν(C=O), ν(C=C) and ν(C–O)].

[PdMe(pyca)(PPr^i_3)] **6**. The complex was prepared by a similar method to that described for **3**. The complex was isolated as a pale yellow solid (yield: 75%). Mass spectrum: *m/z* 404 $[M + 1]^+$, 403 $[M]^+$ and 388 $[M - CH_3]^+$. NMR ($CDCl_3$): ^1H, δ 0.52 (d, 3 H, $^3J_{PH}$ = 3, $PdCH_3$), 1.32 (dd, 18 H, $^2J_{PH}$ = 6, $^3J_{HH}$ = 15 Hz, $PCHCH_3$) and 2.5 (m, 3H, PCH); ^{13}C-{^1H}, δ −0.46 (d, $^2J_{PC}$ = 7.5, $PdCH_3$), 20.0 (s, $PCHCH_3$), 24.0 (d, $^1J_{PC}$ = 52.9 Hz, PCH), 7.5 (t), 7.9 (t), 8.3 (d) and 8.4 (d) (pyridyl); ^{31}P-{^1H}, δ 55.8 (s). IR (KBr): 1640vs, 1340s [ν(O=C–O)] and 1600s [ν(C=C)].

[PdMe(pyca){$P(OMe)_3$}] **7**. The complex was prepared by a similar method to that described for **3**. The complex is a colourless oil at room temperature. NMR ($CDCl_3$): ^1H, two isomers δ 0.78 (s), 0.94 (s) (3 H, $PdCH_3$), 3.8 (d), 3.83 (d) (9 H, $^3J_{PH}$ = 15 Hz, $POCH_3$) and 7.5–8.7 (m, 4 H, pyridyl); ^{13}C-{^1H}, δ −3.1 (s), 1.8 (s) ($PdCH_3$), 52.9 (s), 53.1 (s) ($POCH_3$) and 153 [s, O–C(O)–]; ^{31}P-{^1H}, δ 116.4 (s) and 121.9 (s). IR (KBr): 1650vs, 1360vs [ν(O–C=O)] and 1020vs (br) [ν(P–O)].

[PdMe(pyca){$P(C_6H_4Me\text{-}p)_3$}] **8**. The complex was prepared by the method described for **3** and was isolated as a pale yellow solid (yield: 68%) (Found: C, 61.60; H, 5.30; N, 2.55. $C_{28}H_{28}NO_2PPd$ requires C, 61.40; H, 5.15; N, 2.55%). NMR ($CDCl_3$): ^1H two isomers, δ 0.58 (d), 0.76 (d) (3 H, $^3J_{PH}$ = 3 Hz, $PdCH_3$), 2.36 (s), 2.39 (s) (6 H, CH_3Ph); ^{31}P-{^1H}, δ 34.6 (s).

[PdMe(pyca)(py)] **9** (py = *pyridine*). Prepared by a similar method to that described for **3**. The complex was isolated as a yellow solid (yield: 91%) (Found: C, 45.05; H, 4.00; N, 8.20. $C_{12}H_{12}N_2O_2Pd$ requires C, 44.65; H, 3.75; N, 8.70%). NMR ($CDCl_3$): ^1H, 0.83 (s, 3 H, $PdCH_3$), 7.3 (t), 7.4 (t), 7.8 (t), 7.9 (t), 8.2 (d), 8.3 (d) and 8.7 (d), (9 H, pyridyl). IR (KBr): 1640vs, 1358s [ν(O–C=O)], 1600vs and 1568s [ν(C=C)].

[PdMe(pyca)(4Me-py)] **10** (4Me-py = 4-*methylpyridine*). The complex was prepared by a similar method to that described for **3** and was isolated as a white solid, (yield: 74%) (Found: C, 45.8; H, 4.20; N, 8.05. $C_{13}H_{14}N_2O_2Pd$ requires C, 46.4; H, 4.20; N, 8.30%). NMR ($CDCl_3$): ^1H δ 0.84 (s, 3 H, $PdCH_3$), 2.41 (s, 3 H, $NC_5H_4CH_3$), 7.1–8.5 (m, 8 H, pyridyl). IR (KBr): 1640vs, 1340s [ν(O–C=O)], 1600s and 1560m [ν(C=C)].

[PdMe(pyca)(NMe_2Ph)] **11**. The complex was prepared by the method described for **3** and was isolated as a yellow solid (Found: C, 49.40; H, 4.80; N, 7.25. $C_{15}H_{18}N_2O_2Pd$ requires C, 49.40; H, 4.95; N, 7.70%). NMR ($CDCl_3$): ^1H δ 0.68 (br s, $PdCH_3$), 2.58 (s, NCH_3) and 6.7–8.5 (m, Ph and pyridyl). IR (KBr): 1620s and 1360s [ν(O=C–O)].

[PdPh(pyca)(PPh_3)] **12**. The complex was prepared by a similar method to that employed for the preparation of the σ-methyl complexes, by treating *trans*-[PdIPh(PPh_3)$_2$] with Tl(pyca). The complex was obtained as a white solid (yield: 72%) (Found: C, 62.90; H, 4.25; N, 2.40. $C_{30}H_{24}NO_2PPd$ requires C, 63.45; H, 4.25; N, 2.45%). ^{31}P-{^1H} NMR ($CDCl_3$): δ 28.7 (s). IR (KBr): 1640vs and 1362vs [ν(O–C=O)].

[Pd(COMe)(pyca)(PPh_3)] **13**. Carbon monoxide (1 atm) was bubbled through a solution of [PdMe(pyca)(PPh_3)] (0.2 g, 0.40 mmol) in CH_2Cl_2 (*ca.* 10 cm^3) for *ca.* 1–2 min, after which the vessel was closed. Stirring was continued for 4 h, and the solution was then filtered through a Celite column and the solution was evaporated *in vacuo* to *ca.* 2 cm^3. The mixture was then treated with diethyl ether light–petroleum (b.p. 40–60 °C) (*ca.* 2:1) until a white solid precipitated. The mixture was kept at −15 °C for *ca.* 4 h, and the solution was removed by decantation. The residue was dried *in vacuo* to give an off-white solid (yield: 61%) (Found: C, 58.1; H, 4.20; N, 2.80. $C_{26}H_{22}NO_3PPd$ requires C, 58.5; H, 4.15; N, 2.60%). NMR ($CDCl_3$): ^1H, δ 2.06 (s, 3 H, $PdCOCH_3$); ^{13}C-{^1H}, δ 233 [s, *C*(O)Me], 171 [s, O*C*(O)R], 154 (s), 148 (s), 140 (s) (pyridyl) and 38 [d, J_{PC} = 17 Hz, C(O)*C*H_3]; ^{31}P-{^1H}, δ 24.4 (s). IR (KBr): 1710 s [ν(C=O) in acyl group], 1640vs and 1340s [ν(O–C=O)].

[Pd(COMe)(pyca)($PMePh_2$)] **14**. The complex was prepared by a similar method to that described for **13**, except that the reaction time was extended to overnight. The compound was isolated as a white crystalline solid (yield: 71%) (Found: C, 52.7; H, 4.10; N, 2.95. $C_{21}H_{21}NO_3PPd$ requires C, 53.3; H, 4.50; N, 2.95%). NMR ($CDCl_3$): ^1H, δ 2.06 (s, $PdCOCH_3$) and 2.1 (d, J_{PH} = 3 Hz, PCH_3); ^{31}P-{^1H}, δ 9.5 (s). IR (KBr): 1680s [ν(C=O) of acyl group] 1620vs and 1340vs [ν(O–C=O)].

[Pd(COMe)(pyca)(PMe_2Ph)] **15**. The complex was prepared by a similar method to that described for **14**. After crystallization from CH_2Cl_2–diethyl ether the complex was obtained as a white solid (Found: C, 46.55; H, 4.50; N, 3.40. $C_{16}H_{18}NO_3PPd$ requires C, 46.95; H, 4.40; N, 3.40%). NMR ($CDCl_3$): ^1H, δ 2.26 (s, 3 H, $PdCOCH_3$) and 1.8 (d, 6 H, $^2J_{PH}$ = 9 Hz, PCH_3); ^{31}P-{^1H}, δ 7.79 (s). IR (KBr): 1680s [ν(C=O) of acyl group], 1640vs and 1340s [ν(O=C–O)].

[Pd(COMe)(pyca){$P(CH_2Ph)_3$}] **16**. The complex was prepared by the method described for **14** and was obtained as a white solid (yield: 67%) (Found: C, 59.90; H, 4.75; N, 2.35. $C_{29}H_{28}NO_3PPd$: C, 60.50; H, 4.90; N, 2.45%). NMR ($CDCl_3$): ^1H, δ 1.96 (s, 3 H, $PdCOCH_3$), 3.20 (d, 6 H, J_{PH} = 9 Hz, PCH_2) and 7.1–8.5 (m, 19 H, pyridyl and Ph); ^{31}P-{^1H}, δ 22.9. IR (KBr): 1700 [ν(C=O) of acyl group], 1640vs and 1350s [ν(O=C–O)]. Crystals suitable for a crystal structure determination were obtained by slow crystallization from CH_2Cl_2–diethyl ether.

[PdMe(COMe)(pyca)(py)] **17**. A solution of [PdMe(pyca)(py)] (0.03 g) in $CDCl_3$ was treated with CO as described for **13**. However, the acyl complex is not stable in solution and decomposed to give a black solid during the carbonylation process. NMR ($CDCl_3$): ^1H, δ 2.4 (s, $PdCOCH_3$). IR (KBr): 1710s [ν(C=O) of acyl group], 1638vs and 1350s [ν(O=C–O)].

[PdMe(COMe)(pyca)(4Me-py)] **18**. The complex was prepared by a similar procedure to that described for **13**. The

acyl complex is not stable in solution and gradually decomposed to give a black solid during the carbonylation process. NMR ($CDCl_3$): ^1H, δ 2.3 (s, $PdCOCH_3$) and 2.42 (s, $NC_5H_4CH_3$). IR (KBr): 1710s [ν(C=O) of acyl group], 1640vs and 1350s [ν(O=C–O)].

Reaction of [PdMe(pyca){$P(C_6H_4Me$-*p*)$_3$}] **8** *with* [PdPh(pyca)(PPh_3)] **12**.—[PdMe(pyca){$P(C_6H_4Me$-*p*)$_3$}] (0.01 g, 0.018 mmol) and [PdPh(pyca)(PPh_3)] (0.01 g, 0.018 mmol) were mixed as solids and dissolved in $CDCl_3$ (0.5 cm^3). After standing at room temperature for 10 min, the solution was transferred to a N_2-filled NMR tube. The change in the NMR spectrum was monitored with time. NMR ($CDCl_3$): ^1H δ 0.58 (d, J_{PH} = 2, $PdCH_3$), 0.6 (d, J_{PH} = 2 Hz, $PdCH_3$), 2.32 (s) and 2.36 (s, *p*-$CH_3C_6H_4P$). These peaks are assigned to [PdMe(pyca){$P(C_6H_4Me$-*p*)$_3$}] **8**, [PdPh(pyca){$P(C_6H_4Me$-*p*)$_3$}] and [PdMe(pyca)(PPh_3)] **1**, based on the spectra of the individual complexes. ^{31}P-{^1H}, δ 26.9 (s), 28.8 (s), 32.7 (s), 34.6 (s), 37.9 (s) and 40.1 (s) (ratio: 1:1:1:1:0.2:0.2). The peaks are assigned to [PdPh(pyca){$P(C_6H_4Me$-*p*)$_3$}], [PdPh(pyca)(PPh_3)] **12**, [PdMe(pyca)(PPh_3)] **1** and [PdMe(pyca){$P(C_6H_4$-Me-*p*)$_3$}] **8**. The two smaller resonances were tentatively assigned to the *trans* (N *trans* to R) isomers of **1** and [PdPh(pyca){$P(C_6H_4Me$-*p*)$_3$}].

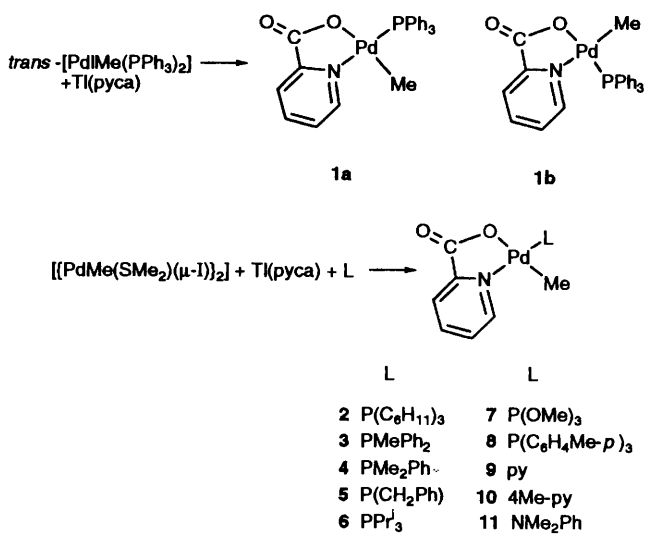
PPh_3 Exchange Reactions.—(1) [PdMe(pyca)(PPh_3)] **1** *with* [$^2H_5$]*pyridine*. [$^2H_5$]Pyridine (0.005 g, 0.06 mmol) was added by microsyringe to a solution of **1** (0.03 g, 0.06 mmol) in $CDCl_3$ (0.5 cm^3). A ^1H NMR spectrum ($CDCl_3$) was obtained within 5 min and showed no changes from that of **1**. Another 0.01–0.02 cm^3 of [$^2H_5$]pyridine was added sequentially and a further ^1H NMR spectrum recorded. Doublets at δ 0.61 and 0.81 became one singlet at 0.60. Doublets at δ 8.4 and 8.3, due to protons at the 6 and 3 positions of the pyridine ring in the pyca ligand, collapsed to one doublet at 8.3. When the solution was cooled to 231 K (−42 °C), a broad resonance at δ 8.4 reappeared and the singlet at δ 0.6 became a doublet at δ 0.61. These results indicate a rapid exchange process is taking place at room temperature.

(2) [PdMe(pyca)(PPh_3)] **1** *with* S. Complex **1** (0.02 g, 0.04 mmol) and an excess of sulfur powder were added to $CDCl_3$ (0.5 cm^3) in an NMR tube. The solution changed gradually from pale yellow to brown within 3 h. After centrifuging the solution a ^{31}P-{^1H} NMR spectrum was obtained *in situ*. The spectrum showed two new peaks at δ 29 and 43 in addition to those of complex **1**.

Results and Discussions

Syntheses and Characterization of the σ-Hydrocarbylpalladium Complexes [PdR(pyca)(L)].—The thallium(I) salt of pyridine-2-carboxylate, Tl(pyca), readily reacts with [$PdIMe(PPh_3)_2$] to yield the hydrocarbyl complex [PdMe(pyca)(PPh_3)] **1**. Attempts to synthesize the analogous complexes containing other tertiary phosphines, *e.g.* $P(C_6H_{11})_3$, $PMePh_2$, $P(CH_2Ph)_3$ *etc.*, by the same route were unsuccessful. This is presumably because of the inability of the pyridine of pyca to displace more strongly co-ordinating phosphines. However, as shown in Scheme 1, if [{$PdMe(SMe_2)(\mu$-I)}$_2$] is used as the precursor, complexes **2**–**11**, bearing a variety of monodentate ligands, L, may be synthesized. The yields from these reactions are normally high. Selected spectroscopic data for the complexes are recorded in Table 1.

The σ-methyl complexes generally appear in solution as a pair of isomers, *i.e. cis*-(pyridine, Me) **a** and *trans*-(pyridine, Me) **b**. The *cis* isomers are always preferred. This observation, consistent with previous results,[10] is probably due to the higher *trans* influence of the nitrogen than of oxygen.[24] Characterization of the two isomers is based mainly on spectroscopic methods, and on a comparison with the platinum analogues,[10] where the coupling constants of $^1J_{PtP}$ provide



Scheme 1 Preparation of palladium(II) σ-methyl complexes containing pyca; isomer **b** forms in some cases, see Table 1

important information about the atom *trans* to the phosphorus atom.[25]

As summarized in Table 1, the ratio of the two isomers, **a** (*cis*) and **b** (*trans*), in these σ-methyl complexes depends on the electronic and steric nature of the ligand, L. Normally, more basic ligands, *e.g.* $P(CH_2Ph)_3$ or PMe_2Ph, give higher selectivity to the *cis* isomer, in which the largest *trans* influence groups occupy mutually *cis* positions, while π-acidic ligands, such as $P(OMe)_3$, exhibit lower selectivity.

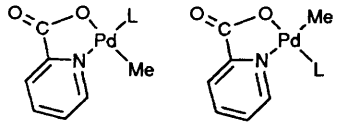
The methylpalladium(II) complexes containing the more basic trialkylphosphine ligands, for example, [PdMe(pyca)(PPr^i_3)] **6** and [PdMe(pyca){$P(C_6H_{11})_3$}] **2**, generally decompose slowly in $CDCl_3$ at room temperature, even under nitrogen, with the precipitation of metallic palladium. In contrast, [PdMe(pyca)(PPh_3)] **1** and [PdMe(pyca){$P(OMe)_3$}] **7** can be stored in solution, under nitrogen for one or two days without observable decomposition.

In the ^1H NMR spectra of these complexes the σ-methyl groups appear in the region δ 0.5–1 as doublets, due to coupling with the *cis* phosphine and, in general, the methyl protons in the *cis* isomers **a** are located at higher field than in the *trans* isomers **b**. The coupling constants of these protons with ^{31}P are typically ≈2–4 Hz. In contrast, the σ-methyl protons in the complex **7** containing trimethyl phosphite appear only as a singlet. The reason for the absence of an expected ^{31}P–^1H coupling is not clear. It may be attributed to a small coupling constant, or it may imply either a weaker interaction between palladium and phosphorus or a rapid dissociative/associative process occurring in solution.

Dynamic Behaviour of the Ligands in [PdMe(pyca)(PPh_3)].—One of the interesting features of these palladium complexes, as previously demonstrated for the alkylplatinum–pyca complexes,[10] is that they have potentially two labile sites, *i.e.* the pyridine in the pyridinecarboxylate chelate and the neutral ligand, L. A knowledge of the dynamic behaviour of these ligands would be invaluable in understanding the mode of reaction of the complexes towards carbon monoxide.

The complex [PdMe(pyca)(PPh_3)] **1** showed no reaction with 1 mol equivalent of [$^2H_5$]pyridine in $CDCl_3$. However, when excess pyridine (3–5 equivalents) was added, the two doublets due to the methyl resonances of **1a** and **1b** collapsed into one broadened doublet at δ 0.6, indicating that now only a single isomer is observable on the NMR timescale and that the σ-methyl protons are still coupled to the phosphorus of the PPh_3. In the aromatic region of the spectrum, a broad doublet

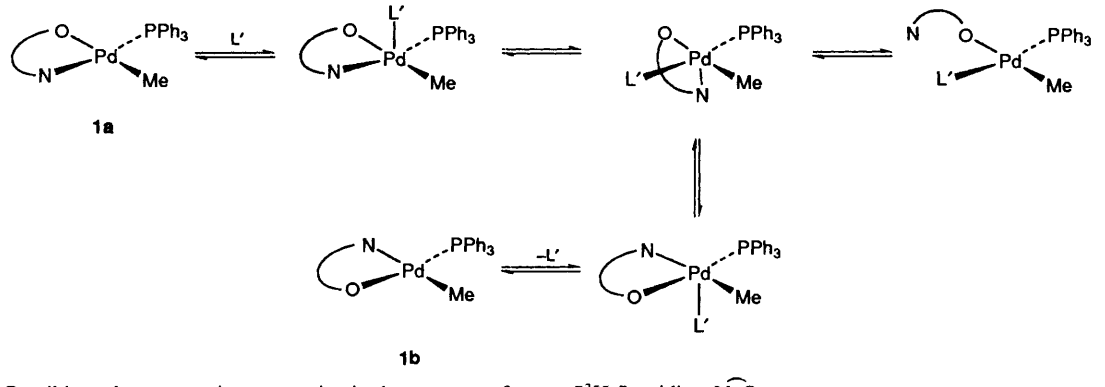
Table 1 Selected NMR spectroscopic data (δ, *J*/Hz) for the σ-methyl complexes [PdMe(pyca)(L)] and variation in isomer ratio with change of phosphine (L)



a **b**

Complex	L	^{1}H NMR $PdCH_3$	^{13}C NMR $PdCH_3$	^{31}P NMR	Isomer ratio **a**:**b**
1a	PPh_3	0.62 (d, J_{PH} = 2.5)		33.6	6:1
1b		0.83 (d, J_{PH} = 2.5)		40.0	
2a	$P(C_6H_{11})$	0.46 (d, J_{PH} = 1.0)	0.72 (d, J_{PC} = 8.2)	44.4	4:1
2b		0.56 (d, J_{PH} = 1.0)		45.6	
3a	$PMePh_2$	0.51 (d, J_{PH} = 2.4)	0.72 (d, J_{PC} = 8.2)	20.9	9:1
3b		0.88 (d, J_{PH} = 2.4)		21.2	
4*	PMe_2Ph	0.51 (d, J_{PH} = 3)	−1.60 (s)	2.33	1:0
5*	$P(CH_2Ph)_3$	0.3 (d, J_{PH} = 3)	−0.83 (d, J_{PC} = 6)	24.8	1:0
6*	PPr^i_3	0.52 (d, J_{PH} = 2.5)	−4.6 (d, J_{PC} = 7.5)	55.8	1:0
7a	$P(OMe)_3$	0.78 (s)	−3.1 (s)	116.4	2:1
7b		0.94 (s)	1.8 (s)	121.9	
8a	$P(C_6H_4Me\text{-}p)_3$	0.58 (d)	4.3 (d, J_{PC} = 6)	34.6	4:1
8b		0.76 (d)	5.4 (d, J_{PC} = 7.5)		
9*	py	0.83 (s)			
10*	4Me-py	0.84 (s)			
11*	NMe_2Ph	0.68 (s)			

* Isomer **a** only.



Scheme 2 Possible exchange reactions occurring in the presence of excess [$^2H_5$]pyridine; N⌒O = pyca

at δ 8.4 and a doublet at δ 8.3, due to protons at the 6 and 3 positions of the pyridine in the pyca ligand, became a doublet at δ 8.3, with a relative integral of two. (The proton in the 6 position is extremely sensitive to changes to the pyca co-ordination and/or the environment imposed by the other ligands and large upfield or downfield shifts are common.) Two separate, broad doublets for the protons in the pyridine 6 and 3 positions were only re-observed when the temperature was dropped to ≤ −30 °C and separate resonances (overlapping, broad singlets) for the σ-methyl group, at about δ 0.6 and 0.65 (**1a** and **1b**), appeared at −40 °C. These observations may be explained in terms of a series of complex exchange reactions between free pyridine and the pyridine of pyca and with PPh_3 (Scheme 2).

Exchange of free PPh_3 with co-ordinated phosphine in complex **1** is also observed in the ^{1}H and ^{31}P NMR spectra with ^{31}P-{^{1}H} NMR providing the clearest picture. In the presence of free PPh_3 the original sharp singlets at δ 35 and δ 40, in the ^{31}P-{^{1}H} NMR spectrum, due to **1a** and **1b**, were replaced by a very broad singlet at δ 10, which remains even at −40 °C. Although, a complex has not been characterized, the large change in the chemical shift indicates that a new complex may be formed, possibly by exchange of free PPh_3 with both co-ordinated phosphine and the pyridine of pyca, to give a single new phosphine environment, possibly *trans*-[PdMe(PPh_3)$_2$(pyca-*O*)] (containing a dangling chelate co-ordinated through O only).

Ligand lability was also demonstrated in an intermolecular exchange reaction. When [PdMe(pyca){$P(C_6H_4Me\text{-}p)_3$}] **8** and [PdPh(pyca)(PPh_3)] **12** (in equal molar amounts) were dissolved in $CDCl_3$, a new set of resonances were observed in the ^{1}H NMR spectrum, at δ 0.58 (d) and δ 2.3 (s). Similarly in the ^{31}P-{^{1}H} NMR spectrum, in addition to resonances due to the starting complexes, two new peaks, at δ 32.7 and δ 26.9, were noted. The new peaks were subsequently assigned to [PdMe(pyca)(PPh_3)] **1** and [PdPh(pyca){$P(C_6H_4Me\text{-}p)_3$}] [equation (1)]. Assignments were made by comparison of each spectrum with the spectra of the pure complexes.

$$[PdMe(pyca)(PPh_3)] + [PdPh(pyca)\{P(C_6H_4Me\text{-}p)_3\}] \longrightarrow [PdMe(pyca)\{P(C_6H_4Me\text{-}p)_3\}] + [PdPh(pyca)(PPh_3)] \quad (1)$$

As a probe, for the dissociation of the phosphine, complex **1** was treated with an excess of sulfur.[26] The *in situ* ^{31}P-{^{1}H}

NMR spectrum indicated formation of $S{=}PPh_3$ (δ 43), as may be expected if dissociated PPh_3 was present [equation (2)].

$$[PdMe(pyca)(PPh_3)] + S(excess) \longrightarrow [PdMe(pyca)(solvent)] + S{=}PPh_3 \quad (2)$$

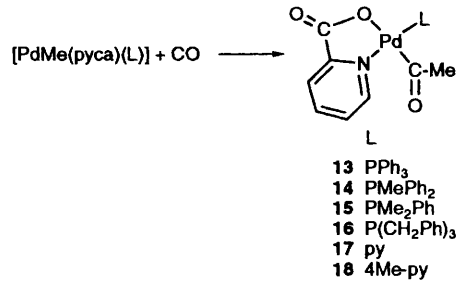
The above results clearly demonstrate the lability of the PPh_3 and pyca ligands in these palladium complexes. It is evident therefore that either or both dissociation processes may be reasonably invoked in any discussion of a dissociative carbonylation mechanism. However, a conclusive statement about the relative labilities of PPh_3 and pyca ligands should be treated with caution, because an unambiguous probe to distinguish the behaviour of the two ligands is lacking.

To some extent, the uncertainty in comparing ligand labilities can be alleviated by a consideration of the analogous platinum complex [PtMe(pyca)(PPh_3)].[10] In the ^1H NMR spectrum, the ^{195}Pt–^1H coupling, between ^{195}Pt and the *ortho* (or 6) proton of the pyridine in pyca provides an excellent probe for investigating the fate of the ligands. As observed for its palladium analogue **1**, [PtMe(pyca)(PPh_3)] appeared in $CDCl_3$ solution as a pair of *cis*/*trans* isomers. The isomers do not show any evidence of ligand lability even when treated with excess [$^2H_5$]pyridine (*ca.* 5–6 equivalents). Two sharp doublets at δ 0.65 and δ 0.73 ($^2J_{PtH}$ = 78 and 71 Hz respectively) due to the σ-methyl group and a doublet at δ 8.7 ($^3J_{PtH}$ = 35 Hz) due to the *ortho* proton of pyridine in pyca remain unaffected throughout the reaction. However, upon treatment with about $\frac{1}{8}$ equivalent of PPh_3, the two sharp doublets at δ 0.65 and 0.73 collapsed to two broad singlets at δ 0.63 and 0.71. The resonance at δ 8.7 became slightly broader, but the coupling with ^{195}Pt still remained. This result indicates that under the experimental conditions, exchange of free PPh_3 with the pyridine of pyca does not occur or at least is relatively slow, whilst exchange with co-ordinated PPh_3 does occur. Consequently it can be concluded that PPh_3 in [PtMe(pyca)(PPh_3)] is kinetically more labile than the pyridine-2-carboxylate. Exchange eventually occurred with both ligands when higher concentrations of free PPh_3 were used.

Carbonylation Reactions of the σ-Methyl Complexes.—When the σ-methyl complexes [PdMe(pyca)(L)] were treated with carbon monoxide (1 atm) at room temperature in CH_2Cl_2 or $CHCl_3$ solution they, in general, underwent carbonylation reactions to afford the corresponding acyl complexes [Pd(COMe)(pyca)(L)] **13**–**18** (Scheme 3). The stability of these complexes largely depends on the nature of the ligands, L. The acyl complexes with lower basicity ligands, such as pyridine or 4-methylpyridine, were not stable in solution. They decomposed rapidly even under CO and precipitated as black solids. Complexes with more basic ligands, such as PPh_3, $PMePh_2$, PMe_2Ph or $P(CH_2Ph)_3$, are normally stable in solution under CO, and can generally be isolated as pure complexes. The acyl complexes that have been isolated are surprisingly stable in the solid state, and can be stored under a nitrogen atmosphere for several weeks without observable decomposition.

Although their alkylpalladium precursors often exist as a pair of *cis* and *trans* isomers, the acyl complexes are observed only as the *cis* isomers, *i.e.* in which the acyl ligand is *cis* to the nitrogen of the pyridine. This selectivity may be attributed to either, the larger *trans* influence of the acyl group compared with the methyl group,[19,27] or as a result of the reaction mechanism discussed later. Selected spectroscopic data for the acyl complexes are recorded in Table 2.

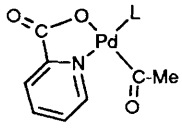
The methyl protons of the acyl groups in [Pd(COMe)(pyca)(PR_3)] appear at δ 2.0–2.4 as a singlet in the ^1H NMR spectra. The corresponding methyl carbons of the acyl ligands in ^{13}C-{^1H} NMR spectra normally appear as a doublet at about δ 40 due to coupling with the *cis* phosphine. In the IR spectra, all the acyl complexes show a characteristic, strong band in the region *ca.* 1680–1720 cm^{-1} (Table 2), which is at a slightly higher wavenumber than the carbonyl moiety of the pyca ligand. The intensity of the acyl band is normally lower than that of the pyca carbonyl.



13 PPh_3
14 $PMePh_2$
15 PMe_2Ph
16 $P(CH_2Ph)_3$
17 py
18 4Me-py

Scheme 3 Carbonylation of the σ-methyl complexes [PdMe(pyca)(L)]

Table 2 Selected spectroscopic data for the acyl complexes [Pd(COMe)(pyca)(L)]



Complex	L	^1H NMR $PdCOCH_3$	IR (KBr/cm^{-1})*	^{31}P NMR
13	PPh_3	2.06 (s)	1710	24.4
14	$PMePh_2$	2.06 (s)	1680	9.5
15	PMe_2Ph	2.26 (s)	1680	7.79
16	$P(CH_2Ph)_3$	1.96 (s)	1700	22.9
17	py	2.4 (s)	1710	
18	4Me-py	2.3 (s)	1710	

* ν(C=O) Of acyl group.

Unlike the decarbonylation of the platinum complex [Pt(COMe)(pyca)(PPh_3)],[10] the thermal decarbonylation of [Pd(COMe)(pyca)(PPh_3)] **13** is a complicated reaction from which only a small amount of the expected σ-methyl complex is obtained. The major product formed in this reaction is a white solid, which is not soluble in $CDCl_3$. The IR spectrum of the white solid shows strong and broad bands at 1720 and 1690 cm^{-1}, which is typical for ν(C=O) in acyl compounds. The bands due to pyridine and triphenylphosphine have also been located. The composition of this white solid has not yet been identified because of its poor solubility, but it was tentatively assigned as an oligomeric species formed possibly by pyridinecarboxylate acting as a bridging ligand. Such an oligomeric palladium–acyl compound has been proposed before.[8]

Early studies had shown that palladium complexes with monodentate phosphines tend to undergo carbonylation more readily than their chelate counterparts and of the complexes with chelate ligands, those containing weakly co-ordinating ligands generally undergo the reaction more easily.[7,12] In this study a somewhat unique system has been investigated, *i.e.* [PdMe(A–A′)(L)] (where A–A′ is a monoanionic chelate ligand, L is a neutral monodentate ligand).

It may be expected that a more basic donor ligand L could favour the pyridine dissociation pathway, whereas in contrast, a weak donor ligand L may facilitate a self-dissociation pathway. In either case, under the correct balance of ligand properties, dissociation can be anticipated. To compare the effects of the neutral ligands L, the kinetics of carbonylation of palladium complexes containing various L have been studied by ^1H NMR spectroscopy. The kinetics of carbonylation of [PdMe(pyca)(L)] under the conditions employed follow pseudo-first order behaviour. The reaction rates are summarized in Table 3.

Table 3 Reaction rates for the carbonylation reaction of [Pd(COMe)(pyca)(L)] under a variety of conditions

Complex	Conditions	$10^5 k/s^{-1}$	$t_{\frac{1}{2}}/s$
1 [PdMe(pyca)(PPh_3)]	CO (1 atm)	3.6	19 250
3 [PdMe(pyca)($PMePh_2$)]	CO (1 atm)	0.96	72 188
4 [PdMe(pyca)(PMe_2Ph)]	CO (1 atm)	0.01	6 930 000
2 [PdMe(pyca){$P(C_6H_{11})_3$}]	CO (1 atm)	No reaction	
5 [PdMe(pyca){$P(CH_2Ph)_3$}]	CO (1 atm)	0.17	407 647
9 [PdMe(pyca)(py)]	CO (1 atm)	1.6	43 312
10 [PdMe(pyca)(4Me-py)]	CO (1 atm)	2.4	28 875
11 [PdMe(pyca)(NMe_2Ph)]	CO (1 atm)	*	
1	CO (1 atm) + py	0.95	72 947
1	CO (1 atm) + PPh_3	1.8	38 500

* The complex decomposes immediately upon treatment with CO, precluding any possibility of monitoring in a kinetic NMR experiment.

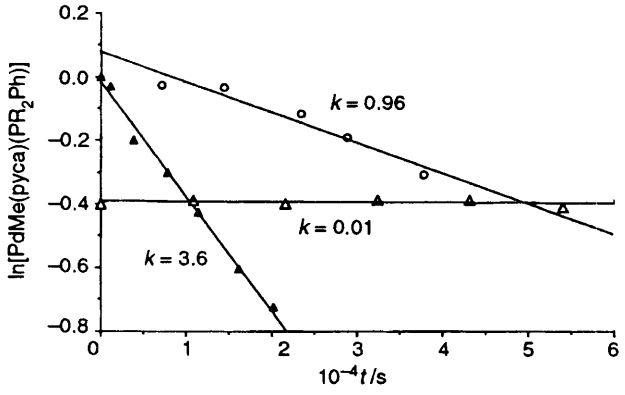


Fig. 1 Plots of carbonylation rates for the complexes [PdMe(pyca)(PPh_3)] (▲), [PdMe(pyca)($PMePh_2$)] (○) and [PdMe(pyca)(PMe_2Ph)] (△)

Results indicate that the ease of carbonylation is strongly dependent on the nature of L. Weakly co-ordinating ligands, L, favour CO insertion. For example, complexes containing the ligands, PPh_3, pyridine or 4-methylpyridine, undergo carbonylation smoothly. In contrast, the complex with $P(C_6H_{11})_3$ failed to give the acyl complex under the same conditions. This trend is most clearly demonstrated by consideration of the complexes with PR_2Ph ligands (Table 3 and Fig. 1). When R in PR_2Ph was changed gradually from Ph to the stronger donor group Me, *i.e.* from PPh_3 to $PMePh_2$ to PMe_2Ph, the reaction rate for the carbonylation of the complexes [PdMe(pyca)(PR_2Ph)] decreased dramatically. This result is in agreement with a previous study, which revealed that the rate of carbonylation of the complexes *trans*-[PtXR'(PR_nPh_{3-n})$_2$] (X = halide), generally decreases as the phenyl substituents on the phosphines are replaced by alkyl groups.[21] The inactivity of the complex containing $P(C_6H_{11})_3$ provides specific evidence that the dissociative mechanism for CO insertion is the route favoured by these complexes. Neither the $P(C_6H_{11})_3$ or the pyca dissociate or are displaced under the reaction conditions and hence no carbonylation activity is observed.

These observations strongly suggest that displacement/dissociation of L from palladium is an important step in the insertion process. Significantly, among the complexes containing more weakly co-ordinating ligands L, such as **1**, **9** and **10**, the complex with the larger *trans* influence ligand underwent carbonylation most rapidly (Table 3). This feature is consistent with the proposal which suggested that L does not act solely as a leaving ligand, but also assists the alkyl migration step during carbonylation, by activating the alkyl group in the *trans* position.[12,10,28]

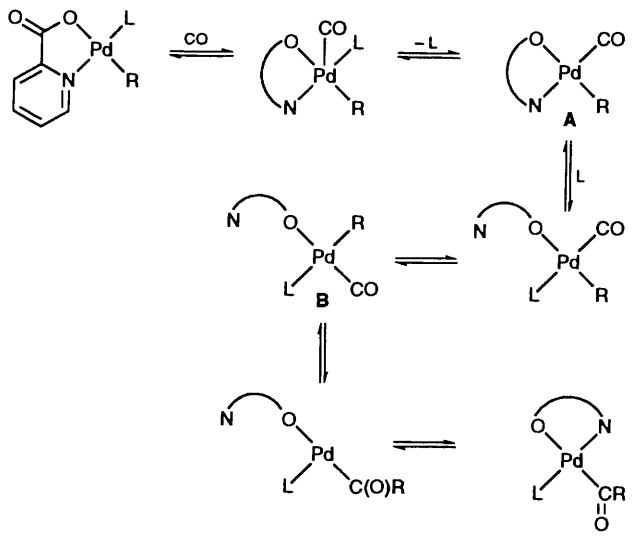
Adding 1 mol equivalent of [$^2H_5$]pyridine to the solution of [PdMe(pyca)(PPh_3)] decreases the carbonylation reaction rate four-fold (Table 3). This behaviour may be explained by assuming that the pyridine is competing directly with the CO for a binding site. Interestingly, the reaction rate for carbonylation of **1** in the presence of an equal molar amount of free PPh_3 differs only by a factor of two from that of pure **1** (Table 3). This relatively small effect may not be as surprising as first appears. As discussed earlier, the interaction of free PPh_3 with [PdMe(pyca)(PPh_3)] **1** possibly occurs at two sites, that of co-ordinated PPh_3 and also with the pyridine of pyca, forming an uncharacterized complex, possibly [PdMe(pyca)(PPh_3)$_2$], in which pyca is co-ordinated through the oxygen only. Therefore, we have an equilibrium of several complexes in solution, all of which contain a labile phosphine and we have already demonstrated that PPh_3 is readily displaced by CO. If the initial dissociation of L is the rate-determining step in the overall carbonylation process, then this step should be less affected by the addition of 1 mol equivalent of free phosphine.

The influence of the hemilabile chelate ligands in the carbonylation reaction is not straightforward to assess. Although there are significant differences in the nature of the chelate ligands we have studied,[9,10] in terms of the ring size and the co-ordinating atoms Y in the monoanionic chelate ligands O–Y, kinetic studies indicate that there is not a marked difference in the ease of carbonylation for the resulting complexes. For example, the reaction rate of [PdMe(pyca)(PPh_3)] **1** is 3.6×10^{-5} s^{-1}, which is close to the value of 4.0×10^{-5} found for [PdMe(acac)(PPh_3)] (Hacac = acetylacetone) and 3.0×10^{-5} for [PdMe(sacac)(PPh_3)] (Hsacac = 4-sulfanylpent-3-en-2-one).[9] Similarly, the recently reported complexes, [Pd(S_2CNMe_2)(alkyl)(PEt_3)], which contain a strongly bound dithiocarbamate chelate ligand, have also been reported to undergo a facile carbonylation reaction to yield the corresponding acyl complexes.[18]

Carbon monoxide insertion through a five-co-ordinate intermediate, in which the methyl group migrates directly to the carbon monoxide co-ordinated in the axial position, has been proposed as a possible mechanism.[21,27] However, recent studies on a number of square-planar palladium and platinum complexes suggest that a dissociative mechanism is more likely. From the previous studies and from the results presented in this paper a mechanism for carbonylation of the complexes [PdMe(pyca)(L)] is presented in Scheme 4.[10] The key intermediates in the proposed mechanism are **A**, in which the co-ordinating CO has displaced L and **B**, in which the methyl group is *trans* to L.

Intermediate **B**, as has been suggested, will promote the alkyl migration step.[12,27,29] Interestingly, insertion from this intermediate leads to the only acyl isomer we observe in the carbonylation reactions (*i.e.* that in which the acyl group is *trans* to the oxygen of the pyca ligand). Consistent with this observation, the palladium acyl complex [Pd(COMe)(pyca)(PPh_3)] **13** obtained from carbonylation of the mixture of isomers, **1a** and **1b**, could be partly decarbonylated thermally, regenerating complex **1** as two isomers in exactly the same ratio.

It is possible however, that co-ordination of CO is followed



Scheme 4 Proposed carbonylation mechanism for the complexes [PdMe(pyca)(L)]

Table 4 Co-ordination geometries for the palladium and platinum atoms in the complexes [M(COMe)(pyca)(PR_3)] (distances in Å, angles in °) (M = Pd, Pt)

M–P	2.248(2), 2.223(7)	M–O(21)	2.141(4), 2.18(1)
M–N	2.116(5), 2.07(2)	M–C(01)	1.972(7), 1.99(3)
P–M–N	171.5(2), 174.4(6)	O(21)–M–C(01)	173.2(3), 170.2(9)
P–M–O(21)	97.3(1), 93.9(5)	N–M–O(21)	78.4(2), 80.4(7)
P–M–C(01)	88.9(2), 95.1(9)	N–M–C(01)	95.9(2), 91(1)

'Right-angle' sums: 360.5, 360.4°

Table 5 Non-hydrogen positional parameters for [Pd(COMe)(pyca){$P(CH_2Ph)_3$}]

Atom	*x*	*y*	*z*
Pd	0.158 19(3)	0.328 80(5)	0.647 42(3)
P(1)	0.271 7(1)	0.465 5(2)	0.662 6(1)
C(110)	0.352 3(4)	0.341 2(7)	0.657 9(4)
C(111)	0.437 0(4)	0.403 3(7)	0.674 3(4)
C(112)	0.501 1(6)	0.397 4(8)	0.751 4(5)
C(113)	0.580 9(5)	0.451(1)	0.766 9(6)
C(114)	0.595 6(5)	0.513(1)	0.704 2(7)
C(115)	0.534 2(6)	0.522(1)	0.628 2(6)
C(116)	0.455 9(4)	0.463 5(9)	0.614 2(5)
C(120)	0.255 1(4)	0.603 1(7)	0.583 0(4)
C(121)	0.225 0(4)	0.544 5(7)	0.496 8(4)
C(122)	0.260 7(5)	0.597 9(9)	0.445 8(5)
C(123)	0.231 4(6)	0.551(1)	0.365 5(5)
C(124)	0.166 4(5)	0.452(1)	0.337 1(5)
C(125)	0.130 1(5)	0.400 3(8)	0.386 7(4)
C(126)	0.158 0(4)	0.446 7(8)	0.465 3(4)
C(130)	0.320 6(4)	0.583 1(7)	0.750 8(4)
C(131)	0.338 2(4)	0.524 6(7)	0.833 6(4)
C(132)	0.312 1(5)	0.391 6(9)	0.852 0(5)
C(133)	0.327 6(5)	0.348 2(9)	0.929 4(5)
C(134)	0.373 1(8)	0.435(1)	0.992 5(6)
C(135)	0.404 8(8)	0.566(1)	0.977 6(6)
C(136)	0.386 7(6)	0.610 1(9)	0.898 7(5)
N(1)	0.053 1(3)	0.187 4(5)	0.617 5(3)
C(2)	0.073 1(4)	0.042 9(7)	0.618 2(4)
C(21)	0.166 1(4)	0.008 1(8)	0.642 7(4)
O(21)	0.214 0(3)	0.117 0(5)	0.650 3(3)
O(22)	0.186 3(3)	−0.122 5(5)	0.654 2(3)
C(3)	0.012 1(4)	−0.064 9(7)	0.596 2(4)
C(4)	−0.070 7(4)	−0.024 4(8)	0.570 9(4)
C(5)	−0.090 3(4)	0.121 5(8)	0.569 3(4)
C(6)	−0.027 7(4)	0.224 1(7)	0.592 6(4)
O(01)	0.059 0(3)	0.579 9(5)	0.590 3(3)
C(01)	0.097 5(4)	0.511 9(7)	0.649 3(4)
C(02)	0.099 1(5)	0.550(1)	0.731 2(5)

by isomerisation of the five-co-ordinate intermediate before dissociation of the ligand L occurs. Isomerisation of a five-co-ordinate species, as depicted in Scheme 2 for pyridine exchange, may be an energetically preferred pathway. Extensive theoretical calculations to consider the energetics of these rearrangements and ligand-exchange processes are currently underway and will be reported in future papers.

Solid-state Structures of [Pd(COMe)(pyca){$P(CH_2Ph)_3$}] *and* [Pt(COMe)(pyca)(PPh_3)].—Selected bond distances and angles are provided in Table 4 and projections at selected angles to the co-ordination planes are given in Figs. 2(*a*)–(*d*). Atomic coordinates for the non-hydrogen atoms are given in Tables 5 and 6.

The solid-state structures of [Pd(COMe)(pyca){$P(CH_2Ph)_3$}] and [Pt(COMe)(pyca)(PPh_3)] demonstrate the expected planar four-co-ordinate array, with the preferred configuration being that in which the acyl group is *trans* to the oxygen of pyca. Significant deviations from square planarity are evident and are clearly seen for the palladium complex [Fig. 2(*a*)]. The N–Pd–O angle [78.4(2)°] subtended by the chelating ligand pyca is far short of the 90° expected for a regular square-planar structure. The angles, P–Pd–O [97.3(1)°] and N–Pd–C [95.9(2)°] between the ligands and metal centre are concomitantly much larger than 90°. There are surprisingly large differences in the metal–ligand bond angles for the two complexes. This may be a reflection of the steric requirements and bonding influences of the different phosphines.

Weighted least-squares planes calculated through the MPONC array shows significant non-coplanarity only for the palladium complex (χ^2 = 2001); deviations δ (M, P, O, N, C) being 0.013(1), −0.025(2), 0.050(7), −0.217(5), 0.083(9) Å; for the platinum complex χ^2 is 7.7 with deviations 0.000(1), 0.000(9), 0.03(3), 0.00(3), 0.11(4) Å, this result is a reflection of the limited precision of the study of the platinum atom as much as anything. The M–CO–C acyl planes (χ^2 = 12.9, 1.0) are at angles of 87.8(3), 75(1)°, *i.e.* quasi-normal to the metal environment planes of the complexes. The angle between the latter and the pyridine C_5N planes are 12.3(2), 4(1)°; the metal atoms deviate from the C_5N planes by 0.141(9), 0.08(4) Å. The carbonyl CCO_2 planes (χ^2 = 1, 0) are at angles of 11.5(2), 1.5(8)° to the metal environment planes of the complexes, and at 9.7(2), 5(1)° to the associated C_5N plane; metal atom deviations are 0.37(1), 0.03(4) Å. Although the statistics are fragile, there is a distinct impression that the (pyca MPC) array is not significantly distorted from planarity in the platinum complex, but appreciably so in the palladium, a result perhaps unexpected in the context of the replacement of phenyl by benzyl groups about similar atoms. Probably irrelevant to the consideration but nevertheless of interest are close contacts to the palladium atom by H(126, 132) at distances of 2.6, 2.8 Å [Fig. 2(*a*)]. Variations from regularity of the angular geometry about the phosphorus reinforce the impression that the interactions represented by the contacts may not be totally insignificant but, perhaps, agostic: Pd–P–C(*n*10) are 107.6(2), 114.8(2), 121.0(3) with C(110)–P–C(120, 130) 105.8(3), 107.4(3) and C(120)–P–C(130) 98.9(3)°. Rather smaller, less precisely determined excursions are found in the triphenylphosphine ligand of the platinum complex: Pt–P–C(*n*11) 109.0(8), 115(1), 119.9(8) with C(111)–P–C(121, 131) 106(1), 105(1) and C(121)–P–C(131) 101(1)°.

Few other structural studies of acyl complexes are reported in the literature, limiting the useful comparisons that can be made.

Comparisons with other structures are further restricted by the lower precision of the data obtained for the platinum complex in this study. However, from a comparison with structural data that have been reported the metal to ligand bond distances for these complexes fall within the range expected (see Table 7). The M–P distances in these complexes [Pt–P 2.223(7), Pd–P 2.248(2) Å] are at the shorter end of those reported [generally Pt–P 2.3(0.1) and Pd–P 2.28(0.08) Å]. As has been noted before[19,36] the Pt–P bond is somewhat shorter than the Pd–P bond, reflecting the greater affinity of platinum for phosphorus. The M–C(acyl) distances are also within the range generally observed for acyl complexes of palladium and platinum (Table 7). However, actual bond distances are very sensitive to the *trans* atom and this is particularly evident for the Pd–N(pyca) distances. In the complex $[PdI(COC_7H_{10}COC_7H_{10}COMe)(bipy)]$[34] the Pd–N distance for N *trans* to I is 2.098(4) Å, whilst that for N *trans* to sp^3-C is 2.161(4) Å (Table 7). In the present complex the Pd–N distance is 2.116(5) Å for N(pyca) *trans* to phosphorus.

Table 6 Non-hydrogen positional parameters for [Pt(COMe)(pyca)(PPh_3)]

Atom	*x*	*y*	*z*
Pt	0.0	0.411 98(3)	0.5
P(1)	0.136 7(7)	0.352 4(2)	0.482 6(7)
C(111)	0.110(2)	0.344 2(9)	0.274(3)
C(112)	0.060(3)	0.305(1)	0.196(3)
C(113)	0.036(3)	0.301(1)	0.033(3)
C(114)	0.065(3)	0.335(2)	−0.048(3)
C(115)	0.114(3)	0.376(1)	0.030(4)
C(116)	0.142(3)	0.382(1)	0.197(3)
C(121)	0.088(3)	0.299(1)	0.550(3)
C(122)	0.182(3)	0.263(1)	0.604(4)
C(123)	0.139(4)	0.222(1)	0.652(3)
C(124)	−0.001(4)	0.217(1)	0.643(3)
C(125)	−0.100(4)	0.252(1)	0.586(4)
C(126)	−0.056(4)	0.292(1)	0.539(4)
C(131)	0.345(2)	0.352 7(8)	0.595(3)
C(132)	0.389(3)	0.361(1)	0.762(3)
C(133)	0.540(3)	0.362(1)	0.855(3)
C(134)	0.640(3)	0.354(1)	0.785(4)
C(135)	0.595(4)	0.352(1)	0.627(5)
C(136)	0.441(3)	0.348(1)	0.522(4)
N(1)	−0.146(2)	0.463 9(8)	0.502(3)
C(2)	−0.299(3)	0.453(1)	0.413(4)
C(21)	−0.328(3)	0.407 1(9)	0.329(3)
O(21)	−0.213(2)	0.381 1(5)	0.347(2)
O(22)	−0.456(2)	0.396 1(6)	0.246(2)
C(3)	−0.412(3)	0.481(1)	0.414(3)
C(4)	−0.379(3)	0.522(1)	0.480(4)
C(5)	−0.233(4)	0.535(1)	0.558(4)
C(6)	−0.122(3)	0.504(1)	0.566(3)
C(01)	0.176(3)	0.450 3(9)	0.629(4)
O(01)	0.207(2)	0.454 2(7)	0.777(2)
C(02)	0.269(5)	0.469(1)	0.551(4)

Conclusion

The reaction of $[\{PdMe(SMe_2)(\mu\text{-}I)\}_2]$ with Tl(pyca) and L provides a convenient way to prepare the σ-methylpalladium(II) complexes, [PdMe(pyca)(L)], which contain a variety of neutral ligands, L. In a number of cases, two isomers are observed, the ratio of which depends on the nature of the neutral ligands, L. In general, the *cis* isomer in which the methyl group is *trans* to an oxygen atom is preferred. The reaction of σ-methyl complexes with carbon monoxide affords the corresponding acyl complexes, yielding in all cases studied the *cis* isomer only. The case of the carbonylation reaction also strongly depends on the nature of the neutral ligands, L, less basic ligands in general facilitating the reaction. The lability of L and pyca under a variety of conditions is clearly established in this study and the feasibility of the proposed dissociative mechanism is therefore demonstrated. Although we cannot rule out the possibility of an associative mechanism involving insertion from a five-co-ordinate intermediate, results suggest that the key or rate-determining step in the carbonylation of [PdMe(pyca)(L)] complexes could be the substitution of the neutral ligand L by CO.

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Table 7 Metal–ligand distances in some selected acyl complexes of platinum and palladium

Complex	Bond type	*r*/Å	Ref.
[Pt(COMe)(pyca)(PPh_3)]	Pt–C(*trans* pyca O)	1.99(3)	This work
	Pt–P(*trans* pyca N)	2.223(7)	
trans-[PtCl(COCOPh)(PPh_3)$_2$]	Pt–C	2.018(1)	30
	Pt–P	2.307(3)	
cis-[Pt(CO_2Me)(COPh)(PPh_3)$_2$]	Pt–C(CO_2Me)	2.031(4)	30
	Pt–C(COPh)	2.047(4)	
	Pt–P(*trans* CO_2Me)	2.313(1)	
	Pt–P(*trans* COPh)	2.359(4)	
trans-[PtCl(COPr)(PPh_3)$_2$]	Pt–C	2.002(19)	31
	Pt–P	2.317(6)	
trans-[PtCl(COC_6H_{13})(PPh_3)$_2$]	Pt–C	2.02(1)	32
	Pt–P	2.302(3)	
[Pd(COMe)(pyca){$P(CH_2Ph)_3$}]	Pd–C(*trans* pyca O)	1.972(7)	This work
	Pd–P(*trans* pyca N)	2.248(2)	
	Pd–N(*trans* P)	2.116(5)	
trans-[PdCl(COPr)(PPh_3)$_2$]	Pd–C	1.996(6)	31
	Pd–P	2.340(1)	
cis-[Pd{CO(Me)C_7H_{10}}(PPh_3)$_2$]$^+$	Pd–C	2.103(8)	33
	Pd–P(*trans* COR)	2.238(2)	
	Pd–P(*trans* alkyl C)	2.434(2)	
[PdI($COC_7H_{10}COC_7H_{10}$COMe)(bipy)]	Pd–C(*trans* py N)	1.952(5)	34
	Pd–N(*trans* alkyl C)	2.161(4)	
	Pd–N(*trans* I)	2.098(4)	
[Pd_2(COPh)$_2$(PPh_3)$_2$(μ-I)$_2$]	Pd–C(*trans* I)	1.986(7)	35
	Pd–P(*trans* I)	2.285(2)	

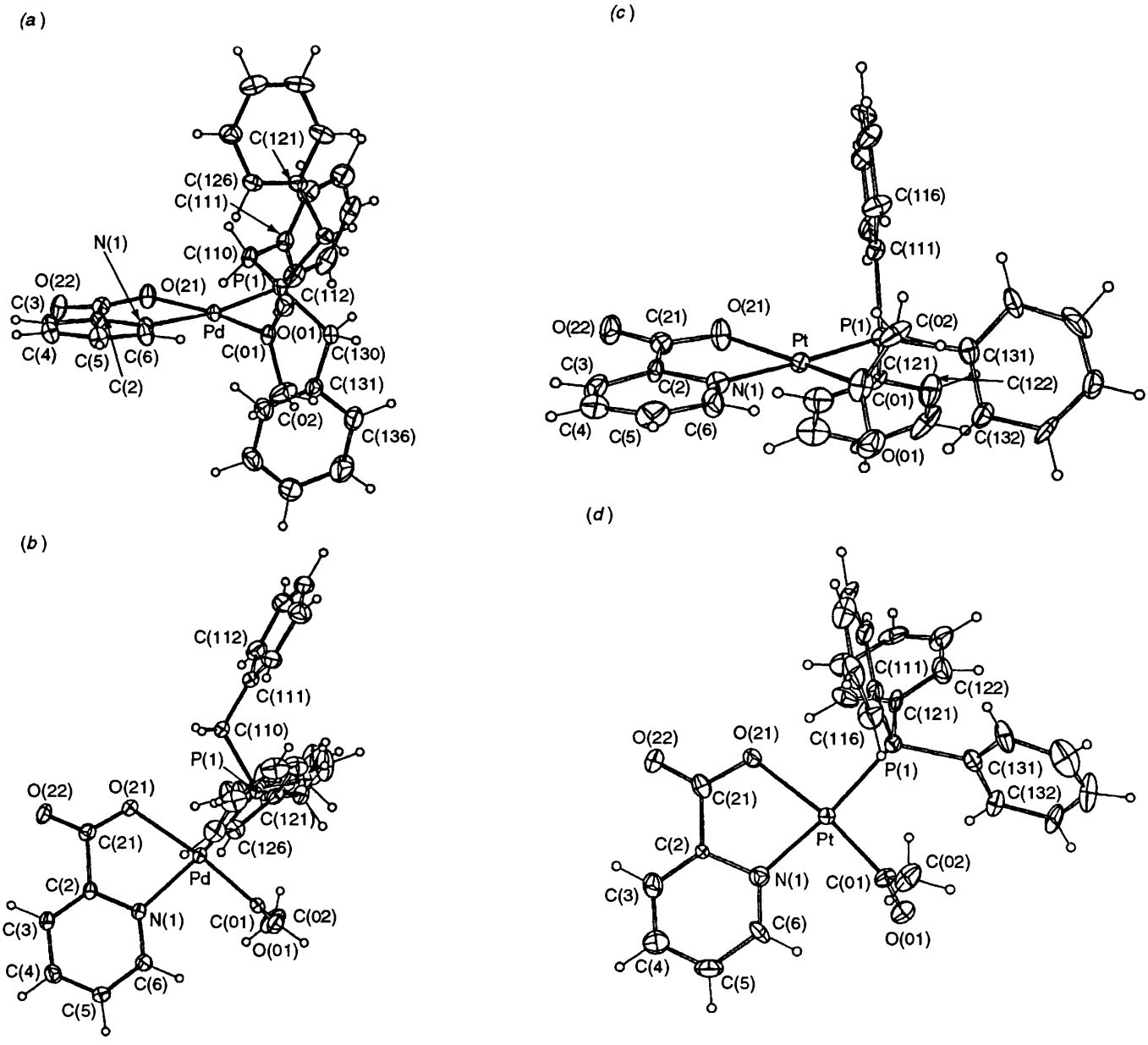

Fig. 2 Molecular projections oblique and normal to the co-ordination planes for the complexes $[Pd(COMe)(pyca)\{P(CH_2Ph)_3\}]$ (*a*), (*b*) and $[Pt(COMe)(pyca)(PPh_3)]$ (*c*), (*d*); 20% thermal ellipsoids are shown for the non-hydrogen atoms

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