DALTON

Carbonylation of hydrocarbylpalladium(II) complexes containing substituted pyridinecarboxylate chelating ligands. Steric and electronic manipulation of the CO-insertion mechanism †

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Organopalladium(II) complexes of general formula [PdR(N–O)L] [R = Ph, N–O = pyridinecarboxylate (pyca), L = $P(C_6H_{11})_3$; R = Ph, N–O = 6-methylpyridinecarboxylate (mpyca), L = PPh_3, $PMePh_2$, $P(C_6H_{11})_3$ or PEt_3; R = Ph, N–O = 4-nitropyridinecarboxylate (npyca), L = $P(C_6H_{11})_3$; R = Ph, N–O = 6-methyl-4-nitropyridinecarboxylate, L = $P(C_6H_{11})_3$; R = Me, N–O = mpyca, L = PPh_3, $P(CH_2Ph)_3$ or $P(C_6H_{11})_3$; R = Me, N–O = npyca, L = PPh_3, $PMePh_2$ or $P(C_6H_{11})_3$] have been prepared, and their carbonylation reactions studied in detail. Kinetic studies of the CO-insertion process have indicated that the rate of reaction decreases as the basicity of the phosphine, L, increases. Complexes containing the highly basic phosphine $P(C_6H_{11})_3$ only undergo carbonylation if hemilability of the chelating ligand is promoted (by substitution of the N–O chelate). Substitution of the N–O ligand modifies the carbonylation pathway and provides an alternative route from that generally observed for palladium(II) and platinum(II) hydrocarbyl complexes of pyca. A mechanism for insertion of CO involving partial dissociation of the N–O chelate is proposed for these complexes. The crystal stucture of [PdMe(mpyca)(PPh_3)] has been determined. The complex has square-planar co-ordination with the nitrogen of pyca *trans* to the phosphorus. Considerable distortion of the inner co-ordination sphere is evident, caused by steric interactions betwen the σ-methyl ligand and the methyl group on the N–O ligand.

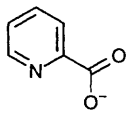
The recent revival in interest in carbonylation reactions has largely been driven by the desire to develop suitable catalysts for carbon monoxide–ethylene copolymerisation, leading to the formation of polyketones.[1,2] Much of the current work has concentrated on complexes of d^8 metals, in particular palladium(II) and platinum(II), containing chelating ligands. Several groups have reported studies using neutral P–P,[3] P–N,[4] N–N,[5] N–N–N[6] and P–N–N[7] chelates.

Examples of complexes resulting from successive CO–ethylene insertions have been characterised[5d–g] and the isolation of a number of such complexes has been reported.[5f,g] These studies have provided valuable information about the mechanism of polyketone formation. The copolymerisation reaction is thought to proceed by a series of alternating, sequential insertions of CO and alkene into the metal–carbon bond.[1b] Very recently Rix and Brookhart[8] reported the first observation of migratory insertion of an olefin acylpalladium complex. These authors have identified and characterised ethylene alkyl- and acyl-palladium complexes and their insertion products, providing clear evidence that in palladium systems insertion generally occurs from a four-co-ordinate intermediate which contains the reacting substrate *cis* to the metal–carbon bond. In forming this intermediate the substrate (CO or alkene) displaces a substitution-labile ligand in the original complex. The labile ligand may be one part of the chelate (hence the term 'hemilabile' has been adopted), or one of the monodentate ligands may be displaced. The actual active species have not been identified, although evidence suggests that initial insertion may occur into a metal–hydride or –alkyl bond.[8] However, in an alcohol solvent, a metal alkoxide may be the initiating species in some instances.[1b]

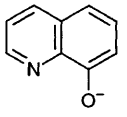
Our interest in this area has been concentrated on the insertion/elimination behaviour of a series of palladium and platinum hydrocarbyl complexes containing bidentate, anionic ligands.[9a,10–14] From a background in catalyst development we have undertaken a systematic assessment of the role of the chelate ligand in controlling and modifying the insertion process. Emphasis has been on insertion of CO (carbonylation). Initially, complexes containing chelates of the β-diketonate type were studied and we were able to monitor the effect of changing the co-ordinating atom and of altering moieties attached to the chelate backbone on rates of carbonylation.[10–12] More recently our studies have focused on hydrocarbyl complexes of pyridinecarboxylate (pyca) **A** and related (N–O) anions, **B**–**E**.[13,14] The hemilability of a number of these ions when co-ordinated to palladium(II) and platinum(II) has been demonstrated.[14] However, our studies to date have suggested that the initial and possibly rate-determining step in the carbonylation of these complexes is not dissociation of one arm of the hemilabile chelate, although this may be an important step in the overall carbonylation process, but rather it is the displacement of the monodentate ligand L, which is present in the four-co-ordinate hydrocarbyl complexes.

We have now investigated the effect of adding substituents to the pyridine ring of pyca on the carbonylation behaviour of the palladium complexes. Alkyl- and aryl-palladium phosphine complexes **1**–**13** of anions, **A** and **C**–**E** have been prepared and their carbonylation activity studied. Pyridinecarboxylate can be considered as a prototypic N–O type chelating ligand; **C**–**E** modify pyca sterically, electronically, or both. In comparison with our previous studies on complexes containing the pyca ligand, it has been found that substitution of the N–O ligand has a marked effect on both the carbonylation rate and the carbonylation mechanism. A solid-state structural study has been carried out on the complex [PdMe(mpyca)(PPh_3)] in an attempt to correlate reactivity patterns with structural aspects. The structure clearly shows the distortions caused by steric interactions between neighbouring methyl groups and in general the behaviour of the complexes containing the mpyca ligand can be understood in terms of the observed structural features.

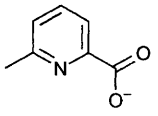
† *Non-SI units employed:* bar = 10^5 Pa, atm = 101 325 Pa.



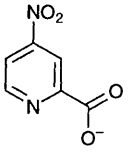
pyridinecarboxylate, pca, A



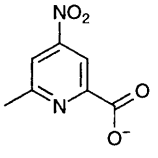
quinolin-8-olate, B



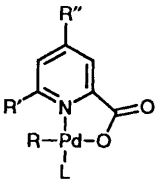
6-methylpyridinecarboxylate, mpyca, C



4-nitropyridinecarboxylate, npyca, D



6-methyl-4-nitropyridinecarboxylate, mnpyca, E



	R	L	R′	R″
1	Me	PPh_3	Me	H
2	Me	$P(CH_2Ph)_3$	Me	H
3	Me	$P(C_6H_{11})_3$	Me	H
4	Me	PPh_3	H	NO_2
5	Me	$PMePh_2$	H	NO_2
6	Me	$P(C_6H_{11})_3$	H	NO_2
7	Ph	PPh_3	Me	H
8	Ph	$PMePh_2$	Me	H
9	Ph	$P(C_6H_{11})_3$	Me	H
10	Ph	$P(C_6H_{11})_3$	H	NO_2
11	Ph	$P(C_6H_{11})_3$	Me	NO_2
12	Ph	$P(C_6H_{11})_3$	H	H
13	Ph	PEt_3	Me	H
14	C(O)Ph	PPh_3	Me	H

Experimental

Reagents

Solvents were dried and purified by the methods described in Perrin *et al.*[15] and distilled under purified nitrogen immediately prior to use. Glassware was dried overnight in an oven at 120 °C. High-purity nitrogen was further dried and purified over 4 Å molecular sieves and BASF R 3-11 catalyst at 135 °C. Experimental manipulations were carried out using standard vacuum-line and Schlenk techniques under a dry nitrogen atmosphere. Tetramethyltin,[16] $[PdCl_2(cod)]$,[17] [PdMe(Cl)(cod)] (cod = cycloocta-1,5-diene),[18] $[Pd(dba)_2]$ (dba = dibenzylidineacetate)[19] and [PdPh(I)(tmen)] (tmen = $Me_2NCH_2CH_2NMe_2$),[20] were prepared by literature methods. Other reagents were used as received.

Nuclear magnetic resonance (NMR) spectra were recorded at 22 °C on a Brüker AM-300 spectrometer at 300.13 (^1H), 75.48 (^{13}C) and 121.50 MHz (^{31}P) and a Varian Gemini 200 spectrometer at 199.98 MHz (^1H only). [$^2H_1$]Chloroform was used as the solvent unless specified. Chemical shifts are expressed in parts per million (ppm) relative to internal $SiMe_4$ (^1H, ^{13}C) or to external H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz and peaks are labelled as singlet (s), doublet (d), triplet (t) or multiplet (m). Unlabelled peaks may be assumed to be singlets. Infrared (IR) spectra were recorded in absorbance units on a Brüker IFS 66 FTIR spectrometer as KBr discs or $CDCl_3$ solutions in the range 400–4000 cm^{-1}. Absorption bands are described as very strong (vs), strong (s), medium (m) or weak (w) in intensity. Mass spectra were recorded on a Kratos Concept ISQ mass spectrometer using the liquid secondary ion mass spectrometry (LSIMS) technique in a *m*-nitrobenzyl alcohol matrix, or the methane desorption chemical ionisation method. A range m/z of 50–1500 was scanned with an 8 kV probe. Gas chromatography (GC) was performed on a Hewlett-Packard 5890A gas chromatograph, employing a SGE 50 m Qc3/BP1 1.0 μm capillary column, with an initial temperature of 30 °C and a heating rate of 4 °C min^{-1}. Data manipulations were performed using Data Acquisition, Plotting and Analysis (DAPA) software from DAPA Scientific Pty. Ltd. Microanalyses were performed by the Central Science Laboratory, University of Tasmania, using a Carlo Erba EA1108 elemental analyser.

Crystallography

A unique data set was measured at ≈295 K within the limit $2\theta_{max} = 50°$ using an Enraf-Nonius CAD-4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.71073$ Å); 4054 independent reflections were obtained, 3429 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at appropriate trigonal or tetrahedral sites. Conventional residuals R,R' on F were 0.042, 0.052, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.2 program system implemented by S. R. Hall;[21] neutral-atom complex scattering factors were employed.[22]

Crystal data. $C_{26}H_{24}NO_2PPd$, $M = 519.9$, monoclinic, space group $P2_1/c$, $a = 9.579(7)$, $b = 19.789(6)$, $c = 14.512(4)$ Å, $\beta = 123.10(5)°$, $U = 2305(3)$ Å^3, D_c ($Z = 4$) = 1.50 g cm^{-3}, $\mu_{Mo} = 9.0$ cm^{-1}; specimen 0.65 × 0.18 × 0.55 mm; $A^*_{min,max} = 1.15, 1.37$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/16.

Synthesis

The synthesis of 4-nitropyridinecarboxylic acid has been reported elsewhere.[23] 6-Methyl-4-nitropyridinecarboxylic acid was prepared in a three-step synthesis adapting methods developed by Krohnke and Schafer[24] and Matsumura *et al.*[25]

2-Methyl-4-nitropyridine *N*-oxide. 2-Methylpyridine *N*-oxide (24.00 g, 0.220 mol) was dissolved in concentrated sulfuric acid (66 cm^3) at 0 °C and a mixture of concentrated nitric acid (79 cm^3) and concentrated sulfuric acid (66 cm^3) was added slowly. The reaction mixture was heated at 160 °C for approximately 2 h, until evolution of NO_2 had ceased. The pH was adjusted to approximately 7.5 with 10 mol dm^{-3} NaOH solution, with initial cooling followed by gentle heating to prevent inorganic salt precipitation. During this neutralisation the yellow-orange product precipitated and was filtered off. It was recrystallised

from chloroform and dried *in vacuo* (yield: 98%). ^{1}H NMR ($CDCl_3$): δ 8.33 (d, J = 7.2), 8.16 (d, J = 3.0 Hz), and 8.01 (m) (3 H, aromatic protons) and 2.58 (s, 3 H, 2-Me).

2-Cyano-6-methyl-4-nitropyridine. This compound was prepared under an atmosphere of nitrogen. 2-Methyl-4-nitropyridine *N*-oxide (9.58 g, 0.068 mol) and dimethyl sulfate (7.5 cm^3, 0.08 mol) were stirred at 65–70 °C for 2 h. Upon cooling a salt crystallised and was dissolved in water (30 cm^3). A solution of potassium cyanide (5.6 g in 20 cm^3 water) was added dropwise with vigorous stirring, at −7 to −8 °C. After standing overnight the precipitates were filtered off (yield: 61%). ^{1}H NMR ($CDCl_3$): δ 8.23 (s, 1 H, aromatic proton) 8.12 (s, 1 H, aromatic proton) and 2.81 (s, 3 H, 6-Me).

6-Methyl-4-nitropyridinecarboxylic acid monohydrate. A solution of 2-cyano-6-methyl-4-nitropyridine (4.18 g, 0.026 mol) in 90% sulfuric acid (40 g) was heated at 120 °C for 2 h. A solution of sodium nitrite (5 g in 10 cm^3 water) was added dropwise, with stirring, at 20–25 °C. The mixture was stirred at 20–25 °C for another hour, then at 80 °C for 1 h. The resulting solution was poured onto cracked ice (50 g) and adjusted to pH 1.6 with solid sodium carbonate. The pale yellow product precipitated, was filtered off and recrystallised from methanol (yield: 72%). ^{1}H NMR [$(CD_3)_2SO$]: δ 8.35 (d, 1 H, J = 2.20, aromatic proton), 8.28 (d, 1 H, J = 1.80 Hz, aromatic proton) and 2.71 (s, 3 H, 6-Me). The acidic proton was not observed due to rapid exchange with trace moisture in the solvent. FTIR: 1705s and 1308s [ν(O–C=O)]; 1545s and 1359s [ν(O–N=O)]; 850m cm^{-1} [ν(C–N)].

Thallium salts. Thallium salts of the pyca type anions were prepared in near-quantitative yield as described previously.[13]

Complexes: general method. When R = Ph, [PdPh(I)(tmen)][20] (1.6 mmol) was dissolved in dry tetrahydrofuran (thf) (20 cm^3). Solid pyca-type salt (10% excess) was added slowly with stirring, and the suspension stirred for 30 min. Phosphine (1.6 mmol) was added slowly with stirring, and the reaction mixture stirred overnight at room temperature. The reaction mixture was filtered through Celite, and the solvent removed *in vacuo*. The solid residue was washed with hexane, then recrystallised from CH_2Cl_2–hexane or thf–hexane. The recrystallised complex was washed with cold diethyl ether (−15 °C) and dried *in vacuo*. When R = Me, the procedure described above was repeated using [PdMe(Cl)(cod)][18] as the precursor complex. These complexes were recrystallised from CH_2Cl_2–ether or benzene–ether.

[PdMe(mpyca)(PPh_3)] **1**: white, air-stable solid (yield: 49%) (Found: C, 62.65; H, 5.05; N, 2.50. Calc. for $C_{26}H_{24}NO_2PPd{\cdot}0.5C_6H_6$: C, 62.75; H, 4.80; N, 2.50%), presence of benzene in the sample detected in the ^{1}H NMR spectrum. NMR ($CDCl_3$, 268 K): ^{1}H, δ 8.2 (d), 7.7 (t), 7.4 (d) (3 H, pyridyl); 7.6 (m), 7.4 (m) (15 H, PPh_3); 2.70 (3 H, 6-Me); 0.62 (d) and 0.48 (d) (3 H, J_{PH} = 2.6 Hz, two isomers, PdMe); ^{31}P-{^{1}H}, δ 37.5 and 36.1 (two isomers). IR (KBr): 1354s, 1644vs (br) [ν(O–C=O)]; 1600s cm^{-1} [ν(C=C)]. High-resolution mass spectrum: m/z 519.065 (Calc. for $C_{26}H_{24}NO_2PPd$: 519.060).

[PdMe(mpyca){$P(CH_2Ph)_3$}] **2**: white, air-stable solid, 35% yield (Found: C, 62.05; H, 5.60; N, 2.55. Calc. for $C_{29}H_{30}NO_2PPd$: C, 62.00; H, 5.40; N, 2.50%). NMR ($CDCl_3$): ^{1}H (298 K), δ 8.2 (d), 7.8 (t), 7.4 (d) (3 H, pyridyl); 7.4 (m), 7.2 (m) [15 H, $P(CH_2C_6H_5)_3$], 3.28 (m) [6 H, $P(CH_2C_6H_5)_3$]; 2.64 (3 H, 6-Me); 0.64 (d) and 0.26 (d) (3 H, J_{PH} = 2.6 Hz, two isomers, PdMe); ^{31}P-{^{1}H}, (243 K), δ 29.3 and 27.2. IR (KBr): 1640vs and 1358s [ν(O–C=O)]; 1600s cm^{-1} [ν(C=C)]. High-resolution mass spectrum: m/z 561.117 (Calc. for $C_{29}H_{30}NO_2PPd$: 561.105).

[PdMe(mpyca){$P(C_6H_{11})_3$}] **3**: air-stable white solid (yield: 40%) (Found: C, 58.15; H, 7.50; N, 2.85. Calc. for $C_{26}H_{42}NO_2PPd$: C, 58.05; H, 7.85; N, 2.60%). NMR ($CDCl_3$): ^{1}H, δ 8.2 (d), 7.7 (t), 7.3 (d) (3 H, pyridyl); 2.69 (3 H, 6-Me); 1.3–2.2 (m) [33 H, $P(C_6H_{11})_3$]; 0.62 (d) and 0.42 (d) (3 H, J_{PH} = 1.4 Hz, two isomers, PdMe); ^{31}P-{^{1}H}, δ 46.4 and 44.5. IR (KBr): 1358s, 1642vs (br) [ν(O–C=O)]; 1598s cm^{-1} [ν(C=C)]. High-resolution mass spectrum: m/z 537.205 (Calc. for $C_{26}H_{42}NO_2PPd$: 537.199).

[PdMe(npyca)(PPh_3)] **4**. The complex was obtained as a yellow, air-sensitive solid (yield: 41%) (Found: C, 55.20; H, 4.30; N, 4.80. Calc. for $C_{25}H_{21}N_2O_4PPd{\cdot}0.5C_4H_8O$: C, 55.25; H, 4.30; N, 4.75%), presence of thf detected in the ^{1}H NMR spectrum. NMR ($CDCl_3$): ^{1}H, δ 0.71 (d) (major) and 0.94 (d) (minor isomer) (3 H, J_{PH} = 4.6, PdMe); 7.34–7.73 (m) (15 H, PPh_3); 8.32 and 8.79 (d, 1 H, J = 1.2; d, 1 H, J = 4.8 Hz, $H^{3,5}$ of pyca); 9.04 (br, 1 H, H^6 of pyca); ^{31}P-{^{1}H}, (298 K), δ 33.95 (major) and 38.91 (minor); (253 K) 34.13 (major) and 38.99 (minor isomer). IR (KBr): 1333s, 1656vs [ν(O–C=O)]; 1590s [ν(C=C)]; 1543m cm^{-1} [ν(NO_2)].

[PdMe(npyca)($PMePh_2$)] **5**: yellow, air-sensitive solid (yield: 33%) (Found: C, 48.95; H, 4.00; N, 5.75. Calc. for $C_{20}H_{19}N_2O_4PPd$: C, 49.15; H, 3.90; N, 5.75%). NMR ($CDCl_3$): ^{1}H, δ 9.04 (d, ^{1}H, J = 2.2, H^6 of pyca); 8.72 (m) and 8.30 (m) (2 H, $H^{3,5}$ of pyca); 7.72–7.43 (m) [10 H, $PMe(C_6H_5)_2$]; 2.14 (d, 3 H, J_{PH} = 10.6, P*Me*Ph_2); 0.61 (d) (major) and 0.69 (d) (minor isomer) (3 H, J_{PH} = 19.0 Hz, PdMe); ^{31}P-{^{1}H}, (298 K), δ 20.83 (major) and 22.12 (minor isomer). IR (KBr): 1331s, 1658vs [ν(O–C=O)]; 1587m [ν(C=C)]; 1536s cm^{-1} [ν(NO_2)].

[PdMe(npyca){$P(C_6H_{11})_3$}] **6**: air-sensitive yellow solid (yield: 73%) (Found: C, 50.65; H, 6.65; N, 5.10. Calc. for $C_{25}H_{39}N_2O_4PPd{\cdot}0.4CH_2Cl_2$: C, 50.60; H, 6.65; N, 4.65%). NMR ($CDCl_3$): ^{1}H, δ 9.02 (d, 1 H, J = 2.2 Hz, H^6 of pyca); 8.70 (m) and 8.27 (m) (2 H, $H^{3,5}$ of pyca); 2.26–1.19 [m, 33 H, $P(C_6H_{11})_3$]; 0.58 (3 H, PdMe); ^{31}P-{^{1}H}, (298 K), δ 45.53 (major) and 43.73 (minor isomer). IR (KBr): 1327s and 1652vs [ν(O–C=O)]; 1585m [ν(C=C)]; 1543s cm^{-1} [ν($NO)_2$]. The presence of CH_2Cl_2 in the sample was detected in the ^{1}H NMR spectrum.

[PdPh(mpyca)(PPh_3)] **7**: air-stable white solid (yield: 65%) (Found: C, 64.00; H, 4.60; N, 2.30. Calc. for $C_{31}H_{26}NO_2PPd$: C, 64.00; H, 4.50; N, 2.40%). NMR ($CDCl_3$): ^{1}H, δ 1.67 (d, 3 H, J_{PH} = 2, 6-Me); 7.17 (d, 1 H, J = 3.6, H^5 of pyca); 7.80 (t, 1 H, J = 7.6, H^4 of pyca); 8.27 (d, 1 H, J = 7.8 Hz, H^3 of pyca); 7.03–6.97 (m) and 6.71–6.57 (m) (5 H, PdPh); 7.15–7.58 (m) (15 H, PPh_3); ^{13}C-{^{1}H}, δ 171.9 ($C_5H_3NCO_2$), 149.6 (*ipso*-C of PdPh) and 26.0 (6-Me); ^{31}P-{^{1}H} (298 K), δ 29.42 (major) and 29.28 (minor isomer). IR (KBr): 1355s, 1648vs [ν(O–C=O)]; 1595s cm^{-1} [ν(C=C)].

[PdPh(mpyca)($PMePh_2$)] **8**: air-stable white solid (yield: 65%) (Found: C, 59.75; H, 4.75; N, 2.80. Calc. for $C_{26}H_{24}NO_2PPd$: C, 60.05; H, 4.65; N, 2.65%). NMR ($CDCl_3$): ^{1}H, δ 1.67 (3 H, 6-Me); 1.61 (d, J_{PH} = 10.8, major) and 1.49 (d, 3 H, J_{PH} = 10.2, minor isomer, P*Me*Ph_2); 7.70 (t, 1 H, J = 7.8, H^4 of pyca); 8.14 (d, 1 H, J = 7.8, H^3 of pyca); 7.09–7.03 (m) and 6.76–6.67 (m, 6 H, PdPh and H^5 of pyca); 7.24–7.59 (m) [10 H, $PCH_3(C_6H_5)_2$]; ^{31}P-{^{1}H}, (298 K), δ 15.55 (major) and 14.56 (minor isomer); ^{13}C-{^{1}H}, (298 K), δ 14.2 (d, J = 36.6, P*Me*Ph_2), 25.4 (6-Me), 147.7 (d, J = 10.2 Hz, PMe*Ph*$_2$) and 171.4 ($C_5H_3NCO_2$). IR (KBr): 1356s, 1646vs [ν(O–C=O)]; 1596s cm^{-1} [ν(C=C)].

[PdPh(mpyca){$P(C_6H_{11})_3$}] **9**: air-stable white solid (yield: 77%) (Found: C, 62.05; H, 7.55; N, 2.40. Calc. for $C_{31}H_{44}NO_2PPd$: C, 62.05; H, 7.40; N, 2.35%). NMR ($CDCl_3$): ^{1}H, δ 8.12 (d, 1 H, J = 7.8, H^3 of pyca); 7.67 (t, 1 H, J = 7.8, H^4 of pyca); 7.05 (d) (1 H, J = 7.8 Hz, H^5 of pyca); 7.38–7.32 (m) and 6.87–6.84 (m) (5 H, PdPh); 2.18–0.93 (m) [36 H, $P(C_6H_{11})_3$ and 6-Me]; 1.67 (6-Me); ^{31}P-{^{1}H}, (298 K), δ 36.44 (major) and 36.09 (minor isomer). IR (KBr): 1358s, 1649vs [ν(O–C=O)]; 1596s cm^{-1} [ν(C=C)].

[PdPh(npyca){P(C_6H_{11})$_3$}] **10**: air-sensitive yellow solid (yield: 66%) (Found: C, 57.20; H, 7.05. Calc. for $C_{30}H_{41}N_2O_4PPd$: C, 57.10; H, 6.55%). NMR ($CDCl_3$): ^{1}H, δ 8.96 (d, 1 H, J = 2.6, H^6 of pyca); 8.02–7.98 (m) (2 H, H^{3,5} of pyca); 7.13–7.07 (m) and 7.49–7.43 (m) (5 H, PdPh); 2.14–1.03 (m) [33 H, P(C_6H_{11})$_3$]; ^{31}P-{^{1}H}, (253 K), δ 36.87; ^{13}C-{^{1}H}, (298 K), δ 151.10 (C^3 of pyca) and 37.5 (d) [J = 24.4 Hz, *ipso*-C of P(C_6H_{11})$_3$]. IR (KBr): 1345s, 1650vs [ν(O–C=O)]; 1565m [ν(C=C)]; 1382m, 1542s cm^{-1} [ν(NO_2)]. High-resolution mass spectrum: m/z 630.193 [Calc. for $C_{30}H_{41}N_2O_4P^{105}Pd(H)^+$: 630.193].

[PdPh(mnpyca){P(C_6H_{11})$_3$}] **11**: air-sensitive yellow solid (yield: 26%) (Found: C, 54.25; H, 6.30; N, 4.10. Calc. for $C_{31}H_{43}N_2O_4PPd\cdot0.6CH_2Cl_2$: C, 54.20; H, 6.35; N, 4.00%). NMR ($CDCl_3$): ^{1}H, δ 8.89 (d, 1 H, J = 2.4, H^3 of pyca); 7.85 (d, 1 H, J = 2.6 Hz, H^5 of pyca); 7.44–7.36 (m) and 6.98–6.92 (m) (5 H, PdPh); 2.14–0.97 (m) [36 H, P(C_6H_{11})$_3$ and 6-Me]; 1.82 (6-Me); ^{31}P-{^{1}H}, (253 K), δ 37.82. IR (KBr): 1344s, 1647vs [ν(O–C=O)]; 1564s [ν(C=C)]; 1382s, 1541m cm^{-1} [ν(NO_2)]. The presence of CH_2Cl_2 in the sample was shown in the ^{1}H NMR spectrum.

[PdPh(pyca){P(C_6H_{11})$_3$}] **12**: white air-stable solid (yield: 57%) (Found: C, 61.30; H, 7.45; N, 2.30. Calc. for $C_{30}H_{42}NO_2PPd$: C, 61.50; H, 7.20; N, 2.40%). NMR ($CDCl_3$): ^{1}H, δ 8.25 (d, 1 H, J = 5.2 Hz, H^6 of pyca); 7.85 (m) and 7.46 (m) (3 H, H$^{3-5}$ of pyca); 7.28–7.19 (m) and 7.07–6.96 (m) (5 H, PdPh); 2.09–1.07 (m) [33 H, P(C_6H_{11})$_3$]; ^{13}C-{^{1}H}, δ 171.9 ($C_5H_4NCO_2$) and 147.6 (*ipso*-C of PdPh); ^{31}P-{^{1}H}, (253 K), δ 35.6. IR (KBr): 1339s, 1644vs [ν(O–C=O)]; 1565s cm^{-1} [ν(C=C)].

[PdPh(mpyca)(PEt_3)] **13**: white, air-stable solid (yield: 61%) (Found: C, 51.55; H, 6.10; N, 3.35. Calc. for $C_{19}H_{26}NO_2PPd$: C, 52.10; H, 6.00; N, 3.20%). NMR ($CDCl_3$, 253 K): ^{1}H, δ 8.20 (d, 1 H, J = 7.6, H^3 of pyca); 7.80 (t, 1 H, J = 7.7, H^4 of pyca); 7.18 (d, 1 H, J = 7.5, H^5 of pyca); 7.41 (m) and 6.98 (m) (5 H, PdPh); 1.71 (3 H, 6-Me); 1.66 [dq, 6 H, J_{HH} = 7.56, J_{PH} = 10.20, P(CH_2CH_3)$_3$]; 1.21 [dt, 9 H, J_{HH} = 7.43, J_{PH} = 17.28 Hz, P(CH_2CH_3)$_3$]; ^{31}P-{^{1}H}, (253 K), δ 26.75. IR (KBr): 1357s and 1648vs [ν(O–C=O)]; 1596s cm^{-1} [ν(C=C)].

[Pd{C(O)Ph}(mpyca)(PPh_3)] **14**: quantitative yield, air-sensitive crystalline yellow solid by bubbling CO through a $CDCl_3$ solution of [PdPh(mpyca)(PPh_3)] for 10 min (Found: C, 58.65, H, 4.10; N, 2.10. Calc. for $C_{32}H_{26}NO_2PPd\cdot0.67CH_2Cl_2$: C, 58.85; H, 4.15; N, 2.10%). The presence of CH_2Cl_2 was detected in the ^{1}H NMR spectrum. NMR ($CDCl_3$): ^{1}H, δ 8.28 (d, 1 H, J = 6.9, H^3 of pyca); 7.85–7.78 (m), 7.66–7.60 (m) and 7.36–7.12 (m) (22 H, PPh_3, PdPh and H^{4,5} of pyca); 2.11 (d) (3 H, J_{PH} = 19.8 Hz, 6-Me); ^{13}C-{^{1}H}, δ 229.3 [Pd*C*(O)Ph], 171.3 ($C_5H_3NCO_2$) and 27.0 (6-Me); ^{31}P-{^{1}H}, (253 K), δ 25.8. IR ($CDCl_3$): 1367s, 1629vs (br) {ν(O–C=O) and 1680s ν[Pd–C(=O)Ph]}; 1599s cm^{-1} [ν(C=C)].

Kinetics of the carbonylation reaction

A sample tube (10 cm^3) containing typically 0.08 mmol of palladium complex and a magnetic stirrer bar was fixed to the inside of a round bottom flask (250 cm^3). The flask was flushed with a steady stream of CO, then sealed with a rubber septum. Deuteriated chloroform (typically 3.0 cm^3) containing $SiMe_4$ as reference, and presaturated with CO, was injected into the sample tube in the flask at t = 0. The concentrations of alkyl- and aryl-palladium(II) complexes were in the range 0.0269–0.0283 mol dm^{-3}. Aliquots of about 0.3 cm^3 were taken at regular time intervals and injected into NMR tubes (diameter 5 mm) (preflushed with CO) and the tubes were then sealed. Proton NMR spectra were recorded as soon as possible after removing the sample, and the time of sampling was taken as that of the first acquisition in the NMR spectrometer. Pseudo-first-order rate constants, k', for the complexes were calculated from the relative integrals of NMR spectral peaks for related alkyl and acyl, or aryl and aroyl, complexes. For the duration of the experiments, all apparatus, reagents/solvents and the NMR spectrometer were maintained at constant temperature (see Table 2). Each kinetic run consisted of 4–10 data points. Carbonylation reactions with complexes **4**, **8** and **9** were also attempted in the presence of an excess of phosphine. Between 0.2 and 1.0 equivalent of an excess of the appropriate phosphine was added and the behaviour monitored by NMR spectroscopy.

Carbonylation reactions of complexes 3 and 13, using MeI as a phosphine trap

These experiments, which were monitored by ^{31}P NMR spectroscopy, were carried out to detect the presence of free phosphine during carbonylation reactions. To test the effectiveness of MeI as a trap for P(C_6H_{11})$_3$ and PEt_3 at 253 K, the phosphine (3 mmol) was stirred with MeI (3 mmol) in $CDCl_3$ (5 cm^3) for 10 min. The ^{31}P NMR spectrum was then recorded, and showed that the salt [PR_3Me$^+$I$^-$] formed quantitatively. Complexes **3** and **13** (0.15 mmol) were each stirred with 1.5 equivalents of MeI in $CDCl_3$ (5 cm^3) at 253 K for 10 min. The NMR spectra showed that no reaction had occurred, indicating that the complexes are stable in the presence of MeI. Finally, CO was bubbled through a solution of complex (0.15 mmol) and MeI (1.5 equivalents) in $CDCl_3$ (5 cm^3) at 253 K for 10 min. The ^{31}P NMR spectra were obtained.

Co-reaction of carbon monoxide and ethylene

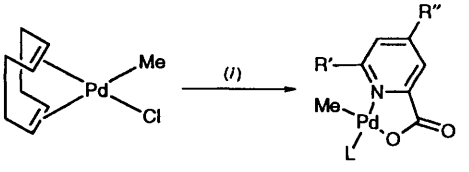
Complexes **1**, **3** and **9** were tested for their activity towards CO and ethylene. A autoclave (350 cm^3) with a spin bar was flushed with nitrogen, and a solution of complex (0.03 mmol in 20 cm^3 dry CH_2Cl_2) was transferred by cannula into the autoclave. The autoclave was then pressurised with CO (20 bar), followed by addition of ethylene (CP grade, 99% minimum) to give a total pressure inside the autoclave of 40 bar. The solution was stirred at 50 °C for 20 h. Analyses of the resultant red-brown solutions were performed by GC.

Results and Discussion

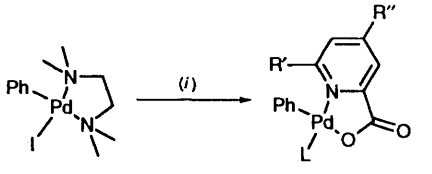
Preparation and characterisation of the complexes

The complexes were prepared from [PdMe(Cl)(cod)] and [PdPh(I)(tmen)] in moderate to high yield according to the reactions shown in Scheme 1. Complex **1** was made from *trans*-[PdMe(I)(PPh_3)$_2$] by reaction with Tl(mpyca). However, this approach was not applicable to phosphines more basic than PPh_3, as they could not be displaced by mpyca.

The alkyl and aryl complexes, which are white or yellow, were characterised by microanalysis and by spectroscopic means. Based on NMR and IR data, and verified by solid-state X-ray



L = PPh_3, P$MePh_2$, P(CH_2Ph)$_3$ or P(C_6H_{11})$_3$; R' = H; R'' = H or NO_2



L = PPh_3, P$MePh_2$, P(C_6H_{11})$_3$ or PEt_3; R' = H or Me; R'' = H or NO_2

Scheme 1 (*i*) Thallium salt of pyca derivative, L

crystallography, the complexes were found to be four-co-ordinate, square-planar, with the pyca-based ligands co-ordinating *via* the nitrogen and an oxygen, as previously found for related complexes;[13,14] pyca and mpyca gave the most stable complexes. Complexes of npyca and mnpyca are air sensitive. Microanalysis and ^{1}H NMR spectra for several of the complexes indicate the presence of solvent molecules of crystallisation.

In most cases, two isomers in varying ratios were observed, with the N-*trans*-P isomer always predominating. The isomerism is most clearly demonstrated by ^{31}P NMR spectroscopy, where the signals for the two isomers are separated by 1–5 ppm. The *cis*:*trans* ratio is dependent on both the basicity of the phosphine and the phosphine cone angle. The higher the basicity (and thus the greater the *trans* influence), and the larger the cone angle, the greater is the amount of the isomer N *trans* P (*i.e.* that in which the two highest *trans*-influence groups, phosphine and hydrocarbyl, are mutually *cis*). Complexes of the highly basic phosphines, $P(C_6H_{11})_3$ and PEt_3, exist almost exclusively as the *trans* isomer. Table 1 illustrates the effect of the phosphine on the isomer ratios for these complexes. A consideration of the pairs of complexes **4** and **5** and **7** and **8** indicates that the electronic factors may be more important than steric influences in directing the isomer structure (in each pair the phosphine with the smaller cone angle but larger pK_a gives the higher percentage of *trans* product).

At low temperature (−30 °C) in the solution containing [PdMe(mpyca){$P(CH_2Ph)_3$}] a small amount of a complex with two phosphines and a dangling pyca ligand was observed, **2***. A single phosphorus environment was noted in the ^{31}P NMR spectrum (^{31}P-{^{1}H}, δ 11.3) and in the ^{1}H NMR a triplet at δ −0.11 was observed for the σ-Me, due to splitting by the two adjacent phosphines.

The NMR data also provided evidence that the complex [PdMe(mpyca)(PPh_3)] **1** may be partially dissociated in solution. Both the ^{1}H and ^{31}P NMR spectra show considerable line broadening not apparent in the spectra of compounds **2** and **3**. In particular, ^{1}H NMR is very informative. Broad bands centred at approximately δ 2.7 (methyl protons of mpyca) and at approximately 0.5 (σ-Me group) are resolved at −30 °C to give a slightly broadened singlet at δ 2.7 and a pair of sharp doublets at δ 0.48 and 0.62. The appearance of two doublets is due to the *cis* and *trans* isomers being resolved and the signal splitting is due to phosphorus coupling. Similar behaviour for a palladium–triphenylphosphine complex has been observed before and it was concluded that the phosphine was partially dissociated in solution.[29] In this work it was not possible to differentiate unambiguously between equilibria involving phosphine dissociation and/or partial dissociation of the chelate ligand. However, attempts to undertake the carbonylation of complexes **4**, **8** and **9** in the presence of an excess of the appropriate phosphine provide clear evidence of hemilability of the chelate ligand. In each case displacement of the pyridine moiety of the chelate by the excess phosphine occurred and the *trans*-[PdR(*dangling*-pyca)(PR'_3)$_2$] complexes were characterised spectroscopically.

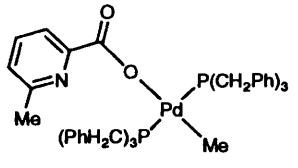


Table 1 Data correlating the properties of phosphines and the preferred structural isomer of palladium complexes

Phosphine	Cone angle/°	Basicity (pK_a)
PPh_3	145[a]	2.73[b]
$PMePh_2$	136[b]	4.57[b]
$P(CH_2Ph)_3$	165[b]	6.60[c]
PEt_3	132[b]	8.69[b]
$P(C_6H_{11})_3$	170[a]	9.65[b]

Complex		% *trans* isomer[d]
1	[PdMe(mpyca)(PPh_3)]	80
2	[PdMe(mpyca){$P(CH_2Ph)_3$}]	84
3	[PdMe(mpyca){$P(C_6H_{11})_3$}]	≈100
4	[PdMe(npyca)(PPh_3)]	80
5	[PdMe(npyca)($PMePh_2$)]	87
6	[PdMe(npyca){$P(C_6H_{11})_3$}]	≈100
7	[PdPh(mpyca)(PPh_3)]	69
8	[PdPh(mpyca)($PMePh_2$)]	91
9	[PdPh(mpyca){$P(C_6H_{11})_3$}]	100
13	[PdPh(mpyca)(PEt_3)]	100

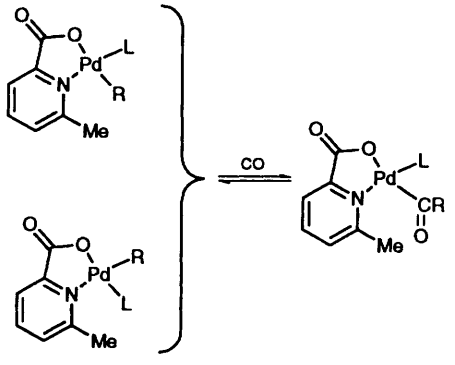
[a] Ref. 26. [b] Ref. 27. [c] Ref. 28. [d] Determined from relative integrals of ^{1}H NMR peaks corresponding to analogous signals of *cis* and *trans* complexes.

Reactions of the complexes with CO

Stirring solutions of the hydrocarbyl complexes in a polar solvent under an atmosphere of carbon monoxide produced, in almost quantitative yields, the corresponding acyl complexes. In general, the acyl compounds, which were obtained as red oils, were not stable and attempts to crystallise them invariably led to decomposition. The complexes were characterised in solution by spectroscopic techniques. However, the aroyl complex, **14**, could be isolated as a yellow solid, and was also characterised by microanalysis. Scheme 2 provides a summary of spectroscopic data. Whilst the alkyl and aryl compounds are obtained as *cis* and *trans* isomers, only one isomer of each acyl and aroyl complex is obtained (N *trans* P). This feature may be a function of the greater *trans* influence of the acyl compared with the alkyl group. The observed carbonylation product is also consistent with the proposed mechanism (see later), which predicts N *trans* P as the primary product.

Kinetic studies

Kinetic studies on the carbonylation process provided valuable information on the role of the ligands in directing the reaction,



Insertion product	IR/cm^{-1}	^{1}H NMR (δ)		^{31}P NMR (δ)
	Pd[CO(R)]	Pd(COR)	Me of pyca	
R = Me, L = PPh_3	1688s	2.0	2.3	26.8
R = Me, L = $P(CH_2Ph)_3$	1678s	1.9	2.4	26.2
R = Me, L = $(C_6H_{11})_3$	1690s	•	2.5	39.7
R = Ph, L = PPh_3	1680s	•	2.1	25.8

• Resonance obscured by signals from phosphine

Scheme 2

and hence on the mechanism for insertion of CO particularly when the rate data were compared with those previously obtained for carbonylation of pyca complexes of palladium.[14] Large excesses of CO were employed (> 100 fold) and hence pseudo-first-order rate constants, k', for the complexes active towards carbonylation were calculated and are given in Table 2. Straight lines were obtained in each case (plots for complexes **9**–**12** are shown in Fig. 1). As mentioned above attempts to follow carbonylation kinetics in the presence of an excess of phosphine were unsuccessful. Even small amounts of added phosphine (0.2 equivalent) led to formation of new bis(phosphine) complexes with a dangling N–O ligand.

Consideration of the relative activities of complexes **1** and **3**, **4**–**6** and **7**–**9**, **13** allows a comparison of the effect of the base strength and cone angle of the phosphine on the carbonylation rate. Other ligands are constant in each set. The trend in carbonylation rates with basicity is manifest: in general, the rate decreases as the donor strength of the phosphine increases. The trend in activity with cone angle is less obvious. However, comparison of complexes **4** and **5**, **7** and **8** (containing phosphines differing little in steric bulk, but significantly in basicity) and **9** and **13** (containing phosphines differing little in basicity, but significantly in steric bulk) suggests that the electronic influence of the phosphine ligand predominates over its steric influence in these carbonylation reactions.

An assessment of the relative steric and electronic influences of the N–O chelate on rates of carbonylation can be obtained by consideration of the activities of complexes **3** and **6**, **1** and **4**, and **9**–**12** (see Fig. 1 for kinetic plots) (within each set the phosphine and R group are constant). Activity decreases in the order mnpyca > mpyca > npyca > pyca. The steric effect of the *o*-methyl substituent has a greater effect on the activity than does the *p*-nitro substituent, and a combination of both generates the highest activity. The *o*-methyl group on the chelate increases the carbonylation activity of the methyl(triphenylphosphine)palladium complex to such an extent that it was not possible to measure k', even at 253 K (*cf.* ref. 14). The significant influence of substituents (in particular a Me group) in the *ortho* or 6 position of the pyridine ring in pyridine-based chelates has been noted before.[30] In keeping with our proposals, the key role of the 6-Me group in modifying reaction behaviour was attributed to steric rather than electronic factors.

Interestingly, the complex [PdMe(npyca){$P(C_6H_{11})_3$}] **6** is unreactive towards carbonylation at 253 K, whereas the phenyl analogue, **10**, showed some activity. More commonly, methyl complexes show greater carbonylation activity than their phenyl analogues (consider complexes **3** and **9** and see ref. 14). Temperature-dependent studies were undertaken to investigate further the reactivities of these two complexes. Although complex **6** became active at elevated temperatures, it consistently remained less kinetically active than the phenyl analogue. Preliminary analysis of kinetic data and Arrhenius parameters (**6**, E_{act} = 124 kJ mol^{-1}, $A = 1 \times 10^{17}$; **10**, E_{act} = 52 kJ mol^{-1}, $A = 1 \times 10^{5}$) indicates that the higher reactivity of the phenyl complex is attributable to a more favourable enthalpy rather than entropy of activation. This result is not unexpected since the two complexes can be assumed to react *via* intermediates with very similar transition-state geometries.

Carbonylation mechanism

It appears likely that carbonylation in these complexes occurs from a square-planar, four-co-ordinate intermediate as previously discussed.[8,14] Therefore, CO must obtain a co-ordination site by displacement of one of the ligands in the precursor complex. In previous studies on the carbonylation of alkyl-platinum and -palladium complexes of pyca it was suggested that the first step is displacement of the monodentate ligand L by CO (Scheme 3).[13,14] This step is favoured by weakly co-ordinating ligands such as L = PPh_3. With very basic, strongly bound phosphines [*e.g.* $P(C_6H_{11})_3$] the carbonylation reaction does not proceed, indicating that in such cases displacement of L (and by implication, the chelating ligand pyca) by CO probably does not occur. It was also found that it is not enough for L to be a good leaving group if effective carbonylation is to proceed. An intermediate (**I**, Scheme 3) in which a strong *trans* influence ligand occupies a position *trans* to the migrating σ-alkyl group also appears important.[31,32] Such an unfavourable intermediate will assist carbonylation by promoting the migration step.

Notwithstanding, the current study with hydrocarbylpalladium complexes of mpyca, npyca and mnpyca now shows that carbonylation can proceed (when the appropriate N–O ligand is used) even when L is a highly basic phosphine, $P(C_6H_{11})_3$ or PEt_3. In agreement with previous studies (in which pyca is the chelating N–O ligand) our phosphine-trapping studies (with mpyca as the chelate) demonstrate that displacement of $P(C_6H_{11})_3$ or PEt_3 by CO does not occur. These phosphines are too strongly co-ordinated to the palladium. Therefore, it is likely that in complexes with highly basic phosphines containing substituted pyca ligands the nitrogen of the pyca chelate is displaced to give a dangling N–O ligand. (The lability of the nitrogen was demonstrated by its ease of displacement with small amounts of excess of PPh_3.) Nitrogen

Table 2 Pseudo-first-order rate constants, k', for the carbonylation of complexes [PdMe(N–O)(PR_3)] (n.r = no reaction)

Complex		T/K	$10^{-4}\,k'$/s^{-1}	$t_{\frac{1}{2}}$/s
1	[PdMe(mpyca)(PPh_3)]	253	*	< 180
3	[PdMe(mpyca){$P(C_6H_{11})_3$}]	253	5.18	1 338
4	[PdMe(npyca)(PPh_3)]	253	2.24	3 092
5	[PdMe(npyca)($PMePh_2$)]	253	1.84	3 769
6	[PdMe(npyca){$P(C_6H_{11})_3$}]	253	n.r.	—
7	[PdPh(mpyca)(PPh_3)]	253	*	< 180
8	[PdPh(mpyca)($PMePh_2$)]	253	25.2	275
9	[PdPh(mpyca){$P(C_6H_{11})_3$}]	253	0.31	22 061
13	[PdPh(mpyca)(PEt_3)]	253	0.25	27 726
10	[PdPh(npyca){$P(C_6H_{11})_3$}]	253	0.17	43 842
11	[PdPh(mnpyca){$P(C_6H_{11})_3$}]	253	0.89	7 771
12	[PdPh(pyca){$P(C_6H_{11})_3$}]	298	n.r.	—
5		298	21.6	321
10		298	7.12	973
12		298	0.30	23 105
6		308	0.72	9 627
		323	1.21	5 728

* Reaction too fast to determine k'.

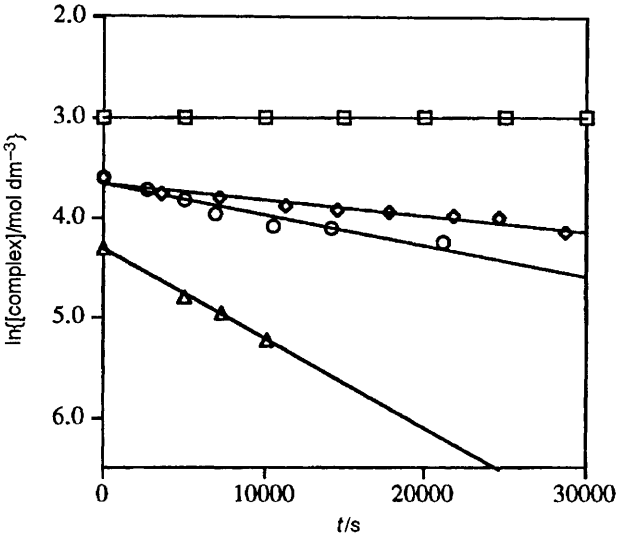
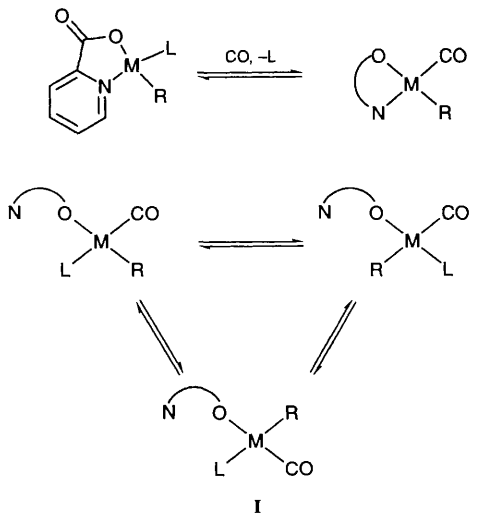


Fig. 1 Pseudo-first-order kinetic plots for the carbonylation of complexes **9** (○), **10** (◆), **11** (△) and **12** (□) at 253 K



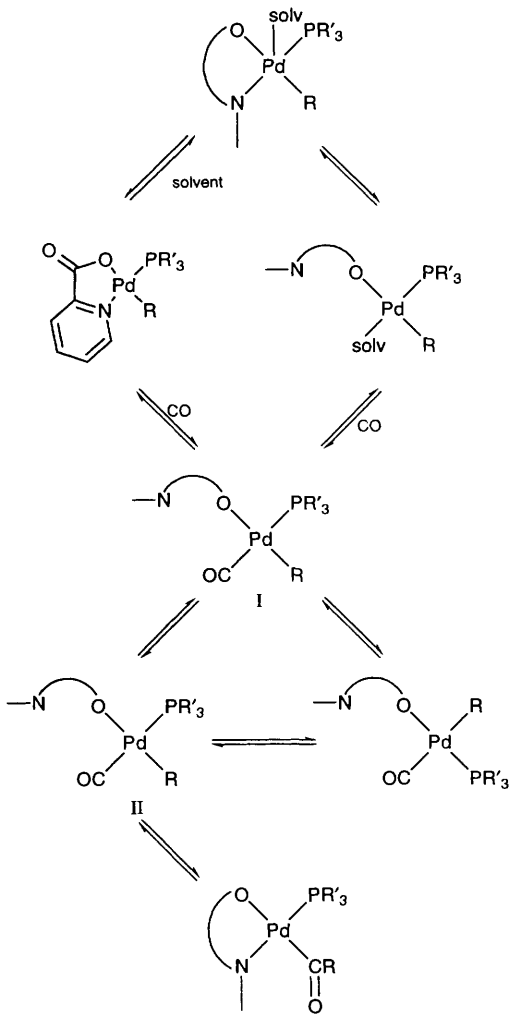
Scheme 3 Proposed reaction steps and intermediates in the carbonylation of complexes [PdR(pyca)(PR'_3)]. N–O = pyca

displacement is favoured by a weakened Pd–N bond, caused in mpyca by steric interactions between the methyl group on the chelate ligand and neighbouring ligands (see below). In complexes containing npyca bond weakening results from the electron-withdrawing effect of the nitro substituent, which reduces the electron density of the N atom to approximately one-fifth of its value in pyca and mpyca.[33] A combination of steric and electronic effects weakens the Pd–N bond to such an extent that only one stable complex containing mnpyca could be synthesised (see above). It is apparent that for complexes containing less basic phosphines such as PPh_3 and $PMePh_2$ carbonylation may occur by two concurrent routes, *i.e.* by displacement of the phosphine or *via* a dangling chelate. Consequently, a comparison of carbonylation rates for complexes containing these ligands with those containing more basic phosphines is complicated by this added possibility.

A significant solvent effect is observed for the carbonylation of these complexes. Insertion takes place rapidly in polar, co-ordinating solvents such as thf. In aromatic solvents no carbonylation takes place at all, even under more forcing conditions (5 atm CO). It is therefore probable that an initial equilibrium is established in which solvent co-ordinates to the palladium centre in an associative manner thereby promoting ligand displacement. The weakly co-ordinating solvent molecule is then easily displaced by CO prior to insertion. These observations are consistent with our recent studies on intramolecular alkene insertion in which it seems that a purely dissociative route may not occur.[34] In complexes containing highly basic phosphines a reaction pathway is provided by a solvent-stabilised intermediate with a dangling chelate ligand. As previously discussed, to promote facile migratory insertion, isomerisation will then give an intermediate in which the CO is *cis* and the phosphine is *trans* to the hydrocarbyl ligand.[4,13,31] A proposed, simplified mechanism for carbonylation is given in Scheme 4. Although evidence supports an initial solvent-promoted partial dissociation of the chelate ligand, the involvement of five-co-ordinate intermediates (not shown) involving weakly bound solvent and/or CO cannot be excluded.

Solid-state structure of [PdMe(mpyca)(PPh_3)]

In order to obtain structural evidence for our mechanistic proposal (that a weakening of the Pd–N bond, induced by steric and electronic modifications to the pyca ligand, promotes displacement of the pyridine moiety by CO) we undertook a full crystal-structure analysis of [PdMe(mpyca)(PPh_3)] **1**. Selected bond distances and angles are provided in Table 3. A comparison of metal-ligand distances in several pertinent



Scheme 4 Proposed carbonylation mechanism for complexes [PdR(N–O)(PR'_3)], containing hemilabile pyca-based ligands and a non-dissociating phosphine

[MR(chelate)(PR'_3)] complexes is provided in Table 4. A projection normal to the co-ordination plane is provided in Fig. 2.

Significant distortion from planarity is evident for the metal atom environment. Although the angle sum in the plane is 359.8° significant deviations from 90° for the individual angles are apparent. In particular, the C–Pd–N angle [99.3(2)°] has opened out markedly to relieve the steric strain between adjacent methyl groups; the N–Pd–O angle [78.8(1)°] is diminished by a corresponding amount. The remaining angles, P–Pd–O [92.4(1)°] and P–Pd–C [89.3(2)°], are not greatly changed from 90°. Significant out-of-plane bending, to relieve steric strain, is also clearly evident. The C–Pd–O [169.6(2)°] and P–Pd–N [171.2(1)°] angles are bent well away from the 180° required for a true planar structure. The bending gives the molecule a twisted structure with the two methyl groups inclined out of the co-ordination plane and away from each other. For a (weighted) least-squares plane through Pd, P, O, N, C the atom deviations are (respectively) 0.011(1), −0.003(2), −0.056(5), −0.018(5), −0.287(9) Å, C(0) being markedly deviated away from C(61), with the hydrogen atoms of the two methyl groups contacting at the van der Waals limit (*ca.* 2.4 Å). Atom C(61) in turn lies well out of the associated C_5N pyridine plane, as do Pd and C(201) [deviations, −0.14(1), 0.269(7), −0.127(8) Å respectively], the C_5N plane (χ^2 13.5) having a dihedral angle of 23.0(2)° to the co-ordination plane of 13.5(2)°, with the carboxylate C_2O_2 plane (χ^2 6) making dihedral angles of 11.1(2), 22.0(2)° respectively. Rings 1 and 3 of the phosphine

ligand straddle O(21) of the co-ordination plane, leaving C(21) quasi-coplanar [τ C(0)–Pd–P–C(21) −10.5(7)°], in consequence of which, among the Pd–P–C angles, Pd–P–C(21) is anomalously large. The Pd–P–C(21)-*o*-carbon torsion angles are unusual in having two values close to zero: −12.6(4), −65.9(5), −15.5(7)° (n = 1, 2, 3).

Palladium–ligand bond distances also provide some evidence for the proposed sterically induced weakening of the palladium–nitrogen bond. When compared to the structures of the related complexes [Pd(COMe)(pyca){$P(CH_2Ph)_3$}] and [Pt(COMe)(pyca)(PPh_3)][14] the Pd–P and the Pd–N distances, in particular, reflect this feature. The Pd–P distance in **1** [2.224(1) Å] is significantly shorter than that in [Pd(COMe)(pyca){$P(CH_2Ph)_3$}] by 0.024(2) Å (despite the more basic and smaller cone angle phosphine present in the latter complex), and the same length as that of the platinum complex. In general, Pt–P bond lengths are expected to be shorter than Pd–P for related complexes.[12,35] The Pd–N bond distance in **1** [2.140(3) Å] is significantly longer than that of [Pd(COMe)(pyca){$P(CH_2Ph)_3$}] by 0.024(4) Å and is likely to be a result of the sterically induced distortion in the structure of **1**. The lengthening of the Pd–N bond is consistent with the proposed weakening of the bond and displacement of the pyca N by CO. Further meaningful comparisons are limited by the lack of structural data for related complexes.

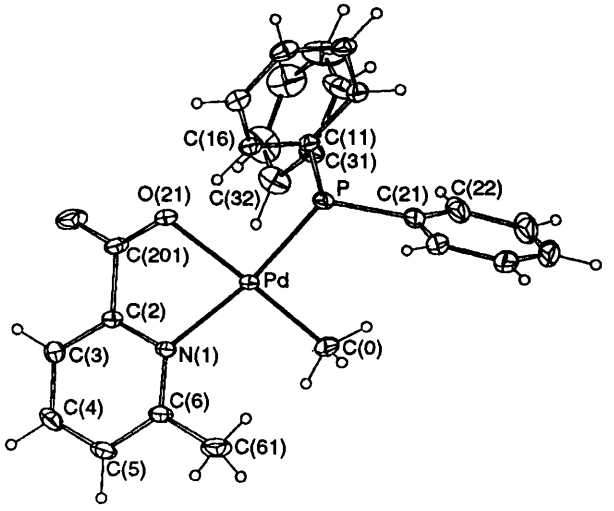


Fig. 2 View of [PdMe(mpyca)(PPh_3)] normal to the co-ordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Pd–P	2.224(1)	P–C(31)	1.825(5)
Pd–N(1)	2.140(3)	C(201)–O(21)	1.280(6)
Pd–O(21)	2.121(4)	C(201)–O(22)	1.220(6)
Pd–C(0)	2.033(7)	C(2)–C(201)	1.517(5)
P–C(11)	1.820(6)	N(1)–C(2)	1.349(6)
P–C(21)	1.815(7)	N(1)–C(6)	1.363(5)
P–Pd–N(1)	171.2(1)	C(21)–P–C(31)	106.5(3)
P–Pd–O(21)	92.4(1)	Pd–N(1)–C(2)	108.3(2)
P–Pd–C(0)	89.3(2)	Pd–N(1)–C(6)	132.9(3)
N(1)–Pd–O(21)	78.8(1)	C(2)–N(1)–C(6)	118.3(4)
N(1)–Pd–C(0)	99.3(2)	N(1)–C(2)–C(201)	117.3(4)
O(21)–Pd–C(0)	169.6(2)	N(1)–C(2)–C(3)	122.4(3)
Pd–P–C(11)	111.6(2)	C(201)–C(2)–C(3)	120.2(4)
Pd–P–C(21)	120.2(2)	C(2)–C(201)–O(21)	115.9(4)
Pd–P–C(31)	109.3(2)	C(2)–C(201)–O(22)	117.5(4)
C(11)–P–C(21)	102.4(3)	O(21)–C(201)–O(22)	126.5(4)
C(11)–P–C(31)	105.8(2)	Pd–O(21)–C(201)	110.2(3)

Coinsertion of CO and ethylene

Preliminary studies on the coinsertion of CO and ethylene into the palladium–carbon bond were undertaken. Reaction of complex **1** with CO and ethylene under mild conditions did not produce detectable amounts of polyketone or other oligomeric products. However, small amounts of methyl vinyl ketone were obtained, indicating that stoichiometric CO–ethylene coinsertion does occur. In contrast to the closely related [Ni(aryl)(pyca)(PR_3)] complexes[36] there was no evidence for any catalytic reaction occurring with the palladium complexes tested in these studies. Elimination rather than propagation is therefore the dominant reaction pathway. A β-elimination process for analogous alkylplatinum complexes of pyca has previously been observed; [PtEt(pyca)(PPh_3)] readily eliminates ethylene on warming to 60 °C to give rise to Pt–H complexes.[13] It was proposed that elimination proceeds *via* a vacant site provided by ligand dissociation from this very labile complex. In agreement with this proposal Vrieze and co-workers[5f] suggested that if a chelate or other ligand L present in a complex is too labile then a ready pathway for the elimination step is provided and polyketones will not form.

Subsequently, complexes **3** and **9** were tested for catalytic activity. It was expected that the presence of a non-dissociating phosphine $P(C_6H_{11})_3$ may limit the possibility of β-hydride elimination. However these complexes were also inactive. It is apparent that other factors such as lowering the activation energy for ligand displacement or stabilisation of a growing chain by chelating through the ketone oxygen may be important.[5g,29]

We have demonstrated that controlled manipulation of the carbonylation pathway is possible by selectively modifying the chelating N–O ligand. The predominantly steric influence of a methyl group placed in the *ortho* position of the ligand has led to significant enhancement of carbonylation reaction rates and some activity for stoichiometric CO–ethylene coinsertion. The electron-withdrawing effect of a nitro group in the *para* position of the ligand has also led to a change in the carbonylation mechanism. Development of our studies on chelating N–O ligands is continuing with investigations of changes in reaction behaviour when cationic complexes are tested. A balance of steric and electronic influences can be expected to control the relative rates of insertion and elimination processes in the reactions of interest and lead to catalyst development.

Table 4 Metal–ligand distances (Å) in some selected [PdR(chelate)(PR'_3)] complexes

Complex	M–P	M–N	M–C	M–O	Ref.
[PdMe(mpyca)(PPh_3)][a]	2.224(1)	2.140(3)	2.033(7)	2.121(4)	This work
[Pd(COMe)(pyca){$P(CH_2Ph)_3$}][a]	2.248(2)	2.116(5)	1.972(7)	2.141(4)	14
[PdMe(sacsac)(PPh_3)][b,c]	2.274(1)	—	2.033(7)	2.095(1)	12
[PdMe(acac)(PPh_3)][d]	2.209(2)	—	2.003(9)	2.083(4)	12
[Pt(COMe)(pyca)(PPh_3)][a]	2.223(7)	2.07(2)	1.99(3)	2.18(1)	14
[PtEt(sacsac)(PPh_3)][b,c]	2.247(1)	—	2.058(6)	2.105(4)	12
[PtEt(acac)(PPh_3)][d]	2.182(2)	—	2.013(9)	2.064(5)	12

[a] Atoms P and N are mutually *trans*, as are C and O in consequence. [b] sacsac = Dithioacetylacetonate. [c] Atom S is *trans* to P. [d] acac = Acetylacetonate.

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