ELSEVIER

Journal of Organometallic Chemistry 533 (1997) 201–212

Journal of Organometallic Chemistry

Cationic methyl–palladium(II) complexes containing bidentate N ^ O and P ^ O ligands and a tridentate P ^ O ^ N ligand: synthesis, carbonylation and catalytic applications in the copolymerisation of carbon monoxide and ethene

George J.P. Britovsek [a], Kingsley J. Cavell [a,*], Melinda J. Green [a], Frank Gerhards [a], Brian W. Skelton [b], Allan H. White [b]

[a] *Department of Chemistry, University of Tasmania, GPO Box 252C, Hobart, Tas. 7001, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, W.A. 6907, Australia*

Received 10 September 1996; revised 11 October 1996

Abstract

Cationic methyl–palladium complexes, containing chelating N–O, P–O and P–O–N ligands, of the type {[PdMe(Y–O)L]BF_4} and {[PdMe(P–O–N)]BF_4} [Y–O = methylpicolinate, L = PPh_3, Ph_2PCH_2COOEt; Y–O = Ph_2PCH_2COOEt, L = PPh_3, 2,6-lutidine; P–O–N = diphenylphosphine-acetic acid-methyl-2-pyridylester ($Ph_2PCH_2CO_2CH_2(NC_5H_4$-2)$)$] have been synthesized. The crystal structure of the complex {[PdMe(N–O)PPh_3]BF_4} indicates distorted square-planar coordination around the palladium centre. The bite angle of the methylpicolinate ligand is small [74.8(4)°] and the Pd–N [2.141(9) Å] and Pd–O [2.180(7) Å] bonds to the ligand are somewhat elongated. The complexes react readily with CO to give the corresponding acyl complexes, and with the exception of {[PdMe(N–O)Ph_2PCH_2COOEt]BF_4} catalyse the reaction between CO and ethene at room temperature to give polyketone.

Keywords: Copolymerisation; Methylpalladium complexes; Carbon monoxide; Ethylene; Polyketone; Chelating ligands

1. Introduction

There has recently been increased interest in the alternating copolymerisation of olefins with carbon monoxide to form polyketones [1–3]. A terpolymer formed by the co-reaction of the ethene, propene and CO (Carilon®) is of particular economic interest, as recently production on a pilot-plant scale has been announced by Shell [4]. Propene and other olefins have been studied with special attention given to the synthesis of optically active polyketones [5–8].

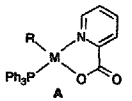
Diphosphine-containing cationic palladium catalysts have been found to be extremely active catalysts for this copolymerisation reaction [2]. N ^ N ligands have also received much attention, especially in studies on the mechanism of the copolymerisation reaction [2,9–12].

As part of our ongoing investigation into the catalytic activation of small molecules through d^8 transition metal complexes, we investigated ligand influences on the carbonylation reaction and the intramolecular olefin insertion reaction of hydrocarbyl–palladium(II) and platinum(II) complexes [13–16]. The complexes studied contained potentially hemilabile anionic bidentate N ^ O ligands, such as pyridine-2-carboxylate (pyca) (**A**). Subsequent to these modelling studies, a number of nickel(II) analogues were prepared and found to be active single component catalysts for ethene oligomerisation and polymerisation as well as ethene–CO copolymerisation [17]. Interestingly, these complexes **A** bear a resemblance to the neutral nickel(II) complexes, such as **B** with anionic bidentate P ^ O ligands developed by

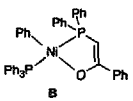
* Corresponding author.

PII S0022-328X(96)06841-6

Keim and coworkers [18,19], which are active olefin oligomerisation catalysts.



A

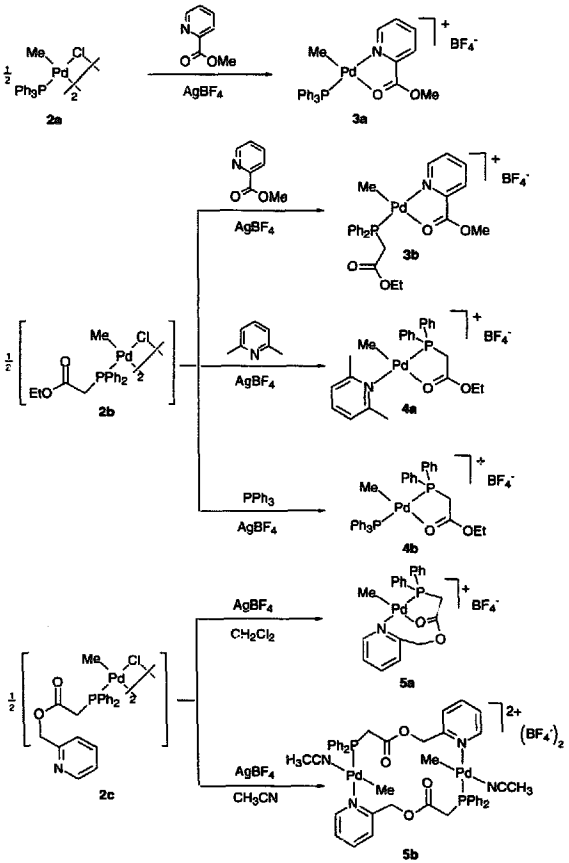


B

M = Ni; R = o-tolyl
M = Pd; R = Me, Ph
M = Pt; R = Me, Et

Cationic transition metal alkyl complexes have been found to be much more reactive than neutral complexes in olefin or CO insertion reactions [20]. Therefore we were interested in cationic analogues to the complexes mentioned above. In this paper we present the synthesis of novel cationic methylpalladium(II) complexes (**3a–4b**) with potentially hemilabile N ^ O and P ^ O ligands (Scheme 1). The reaction of the complexes **3a–4b** with carbon monoxide is described and the catalytic properties in the co-reaction of ethene with carbon monoxide have been investigated.

Tridentate ligands with three different donors P, N and O are currently receiving attention in coordination chemistry [21–23] and catalysis [24–26]. However, there



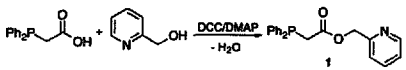
Scheme 1.

are no examples in which complexes containing such ligands have been applied as catalysts in polyketone formation. Consequently, in addition to complexes **3a**, **3b** and **4a** with P, N ^ O and N, P ^ O ligand systems, we synthesized complex **5a**, with a novel, potentially tridentate, P ^ O ^ N ligand diphenylphosphino acetic acid methyl-2-pyridylester (**1**) (Scheme 1). The ordering of donor atoms in the tridentate ligand was selected as this follows exactly that order (NOP) present in the previous neutral complexes **A** [13–17] and cationic compounds of type **3a** and **3b**.

2. Results and discussion

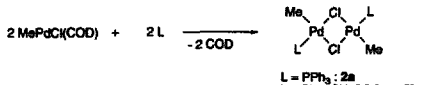
2.1. Preparation of ligands and complexes

Diphenylphosphinoacetic acid methyl-2-pyridylester $Ph_2PCH_2CO_2CH_2(NC_5H_4\text{-}2)$ **1** was prepared from diphenylphosphino acetic acid and 2-pyridylcarbinol using the DCC/DMAP (DCC = dicyclohexylcarbodiimide; DMAP = 4-dimethylaminopyridine) method [27]:



(1)

The dimeric chloro-bridged methylpalladium-(II) complexes **2a–c** were prepared according to reaction (2), as described by Ladipo and Anderson [28]. MePdCl(COD) was reacted with one equivalent of phosphine ligand in CH_2Cl_2. In the case of PPh_3 and $Ph_2PCH_2CO_2CH_2(NC_5H_4\text{-}2)$ **1**, the resulting complexes (**2a** and **2c** respectively) precipitated after stirring for half an hour. These two complexes are insoluble in apolar solvents and only sparingly soluble in CH_2Cl_2, $CHCl_3$, acetone or CH_3CN, in contrast to the solubilities of **2a** stated elsewhere [28,29]. Complex **2b** with Ph_2PCH_2COOEt as the ligand is very soluble in CH_2Cl_2 and $CHCl_3$. In spite of the different solubility observed, we propose a similar dimeric structure for **2b**; NMR and IR data do not support coordination of the carbonyl oxygen (vide supra).



(2)

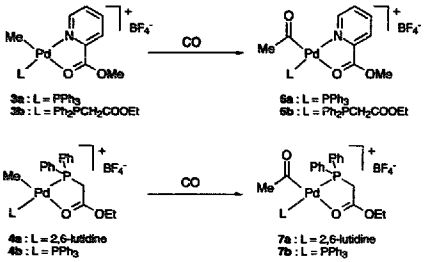
The addition of two equivalents of methylpicolinate to a suspension of the dimeric complex $[MePdPPh_3Cl]_2$ (**2a**) in CH_2Cl_2 at room temperature did not resuk in bridge-splitting as found for other ligands [30]. Abstraction of the chloro ligand to allow coordination of the methylpicolinate ligand was necessary and was achieved by addition of $AgBF_4$ (Scheme 1). NMR spectra revealed that only one isomer of complex **3a** was obtained. This isomer was shown by an X-ray diffraction study to have the triphenylphosphine ligand *trans* to the pyridyl moiety (Section 2.4).

The same procedure described for the formation of complex **3a** was used to prepare complexes **3b** and **4a–b** starting from the compound $[MePdCl(Ph_2PCH_2COOEt)]_2$ (**2b**) (Scheme 1). Addition of 2,6-lutidine or methylpicolinate to **2b** in CH_2Cl_2 caused a colour change from orange to yellow. After the addition of $AgBF_4$, complexes **3b** and **4a** were isolated as yellow solids. Addition of PPh_3 to a solution of **2b** in CH_2Cl_2 resulted in an off-white precipitate, probably $[MePdPPh_3Cl]_2$ **2a**, due to a phosphine exchange reaction [30]. Subsequent reaction of the slurry with $AgBF_4$, however, gave complex **4b** as a deep red solid in almost quantitative yield.

The reaction of $AgBF_4$ with a suspension of complex **2c** in CH_2Cl_2 gave, after filtration to remove AgCl, a clear pale yellow solution of complex **5a**. After removal of the solvent, however, the resulting off-white precipitate could only be partly redissolved. This is probably due to the formation of dimeric or oligomeric species, with the tridentate ligand acting as a bridging ligand. Only the monomeric species **5a** dissolves. From NMR, IR, MS and microanalysis data the structure drawn in Scheme 1 is proposed for **5a**. When the reaction of **2c** with $AgBF_4$ was conducted in CH_3CN complex, **5b** having one CH_3CN ligand coordinated per palladium was obtained. Complex **5b** is insoluble in CH_2Cl_2 or $CHCl_3$ but can be dissolved in warm CH_3CN. A monomeric complex with ligand **1** adopting a bidentate coordination mode is possible. However, such a structure would have an eight-membered ring. More likely is the proposed dinuclear complex as depicted in Scheme 1, with **1** acting as a bridging P ^ N ligand. Similar observations have been made for other phosphine–pyridine and diphosphine ligands which form large rings on coordination to a single metal [23,31,32].

2.2. Carbonylation reactions of methylpalladium complexes 3a–4b

The methylpalladium(II) complexes **3a–4b** are readily carbonylated at room temperature to give the corresponding acetyl complexes **6a–7b** (Scheme 2). Carbon monoxide was bubbled for 5 min through a solution in $CDCl_3$ in a NMR tube. The NMR and IR spectroscopic data for the resulting acetyl complexes were recorded and a selection of these data is given in Tables 1 and 2. Noteworthy is a broadening of some of the methylpicol-



Scheme 2.

inate ligand signals of the acetyl complex **6a** upon heating to 50 °C. The broadening can be explained by a fast exchange of the coordination positions on the NMR timescale, i.e. an isomerisation of the acetyl complexes. This process is known to occur for square-planar complexes [9,33].

For complex **3a** the carbonylation rate was determined by monitoring the formation of the acetyl complex from the decay of the PdCH_3 and increase of the PdCOCH_3 ^{1}H NMR signals. Under the conditions used (T = 253 K, [**3a**] = 18 mmol l^{-1} in $CDCl_3$, P(CO) = 1 bar) the rate constant observed was $k' = 9.5 \times 10^{-4}$ s^{-1} ($t_{1/2}$ = 12 min). The rate constant for the carbonylation of the related neutral palladium(II) complex MePdPPh$_3$(pyca) (pyca = 2-pyridine carboxylate) was also determined under the same conditions and found to be faster, i.e. $k' = 25.9 \times 10^{-4}$ s^{-1} ($t_{1/2}$ = 4.5 min). Similar observations and comparative reaction rates have been reported for neutral and cationic methylpalladium(II) complexes containing bidentate pyridyl–imine ligands [34]. The fact that the neutral complex MePdPPh$_3$(pyca) does not catalyse the copolymerisation of ethene and CO, whereas the cationic analogue does, indicates that the carbonylation step has little bearing on the overall catalytic activity, i.e. carbonylation is a facile process compared with the coordination and insertion of ethene. Moreover, the carbonylation rate for complex **4b** was too fast to be determined under the conditions used ($t_{1/2}$ < 3 min), whereas the catalytic activity in the copolymerisation reaction is lower than for complex **3a**.

2.3. Spectroscopic studies

2.3.1. IR spectroscopy (Table 1)

In the IR, coordination of the ester moiety of a carboxylic acid ester ligand results in a shift of ν(C=O) to lower wavenumbers. For phosphinocarboxylic acid ester ligands $\Delta\nu$(C=O) = 80–100 cm^{-1} [35]. From the IR data for free ligand [36] and for the complex **3a**, the resulting shift $\Delta\nu$(C=O) for the methylpicolinate ligand is 50–60 cm^{-1} upon chelation. IR data in Table 1 show that in complexes **4a** [$\Delta\nu$(C=O) = 94 cm^{-1}] and **4b** [$\Delta\nu$(C=O) = 97 cm^{-1}] the P ^ O ligand acts as a bidentate ligand. In complex **3b**, however, the methylpicolinate ligand is the stronger chelating ligand, leaving the P ^ O ligand as a monodentate ligand.

The difference between the IR stretching frequency [$\Delta\nu$(C=O)] for complex **5a** and the free ligand **1** is 76 cm^{-1}, indicating that the carbonyl oxygen is coordinated to the palladium centre in **5a**. For complex **5b**, with $\Delta\nu$(C=O) = −5 cm^{-1}, it is apparent that the carbonyl oxygen remains uncoordinated. The negative value is ascribed to the different solvent effects of CH_2Cl_2 and CH_3CN.

2.3.2. NMR spectroscopy (Table 2)

With the exception of complex **4b**, the ^{1}H NMR spectra of complexes **2b–5b** show the palladium methyl

Table 1
IR data [ν(C=O)] for complexes **2b–7b** [a]

Compound	ν(C=O)/cm^{-1} (free ligand)	ν(C=O)/cm^{-1} (complex)	$\Delta\nu$(C=O)/cm^{-1}	ν(C=O)/cm^{-1} (PdCOMe)
2b	1732	1728	4	
3a	1726	1671	55	
3b	1726 (COOMe)	1669	57	
	1732 (COOEt)	1731	1	
4a	1732	1638	94	
4b	1732	1635	97	
5a	1731	1655	76	
5b	1731	1736 [b]	−5	
6a	1726	1673	53	1721
6b	1726 (COOMe)	1673	53	1715
	1732 (COOEt)	1726	6	
7a	1732	1641	91	1710
7b	1732	1639	93	1714

[a] In CH_2Cl_2 solution.
[b] In CH_3CN solution.

Table 2
Selected ^{1}H, ^{13}C and ^{31}P NMR data for complexes **2b–7b** [a]

Compound	^{1}H NMR $\delta(PdC\underline{H}_3$ or $PdCOC\underline{H}_3)$ (J_{HP} in Hz)	^{13}C NMR $\delta(Pd\underline{C}H_3$ or $PdCO\underline{C}H_3)$ (J_{HP} in Hz)	^{13}C NMR $\delta(C{=}O)$ $PdCOCH_3$	^{13}C NMR $\delta(C{=}O)$ COOR (J_{CP} in Hz)	^{31}P NMR δ (J_{PP} in Hz)
2b	0.65 (d, 2.5)	6.70		168.3	27.7
3a	1.09 (d, 1.4)	5.74		171.3	35.8
3b	1.02 (d, 1.8)	4.26		170.1 (R = Me) 167.9 (R = Et)	26.3
4a	0.40 (d, 3.3)	−0.07		173.9	24.2
4b	0.70 (t, 5.8)	0.56		181.6 (15)	24.5, 16.6 (381)
5a	0.68 (d, 2.1)	0.42		180.2 [b]	27.7 [b]
5b	0.52 (d, 3.0) [c]	0.21 [c]		170.3 [c]	32.1 [c]
6a	2.25 (d, 1.7)	35.6 (d, 9.8)	221.0	170.3	24.2
6b	2.24	36.2 (d, 15)	221.3	168.8 (R = Me) 168.0 (R = Et)	14.5
7a	1.80	37.0 (d, 24)	222.5	172.7	12.4
7b	1.70 (t, 1.7)	36.6 (d, 18)	219.4	179.1 (13)	17.6, 6.61 (245)

[a] In $CDCl_3$.
[b] In CD_2Cl_2.
[c] In CD_3CN.

resonance, which appears between 0.4 and 1.1 ppm, as a doublet due to coupling with the phosphorus atom in the *cis* position. For complex **4b** this signal appears as a virtual triplet, which can be explained by assuming similar coupling constants with both phosphorus atoms. The σ-methyl signals of complexes **3a** and **3b** which contain the chelating N ^ O ligand are shifted downfield by 0.5 ppm compared with complexes **4a** and **4b**, and also when compared with complex **5a** which has the chelating P ^ O ligand. A similar shift of ca. 5 ppm is observed in the ^{13}C NMR spectrum. Interestingly, the ^{13}C NMR signals for the σ-methyl ligand appear as a singlet with no phosphorus coupling, whereas the acyl methyl group in the acetyl complexes appears as a doublet.

^{31}P NMR resonances for the phosphine ligands are shifted downfield by ca. 40 ppm when coordinated *trans* to a pyridyl ligand. For complex **4b** the shift for each phosphine ligand is less (ca. 30 ppm), which must be ascribed to the different *trans* influence of phosphines. Carbonylation of the alkyl complexes to give acetyl complexes results in a general upfield shift of ca. 10 ppm, indicating significantly different *cis* effects of the alkyl and acetyl ligands.

2.4. Solid-state structure of complex 3a

Crystals of complex **3a** suitable for an X-ray structure determination were obtained by slow diffusion of diethylether into a chloroform solution of **3a**. Table 3 lists selected bond distances and bond angles and Table 4 provides non-hydrogen atom coordinates. The structure of the cation **3a** is presented in Fig. 1.

The complex has the expected square-planar coordination around the palladium metal. The methyl group is *trans* to the oxygen donor [O(21)] and *cis* to the phosphine ligand and the pyridyl nitrogen donor. Comparison of the cationic complex **3a** with the analogous neutral complex $MePdPPh_3$(pyca) (pyca = 2-pyridine carboxylate) shows some interesting differences [37]. The neutral methylpicolinate ligand has a relatively small bite angle of 74.8(4)° compared with the anionic picolinate ligand [78.22(7)°]. In addition, the Pd–N and Pd–O distances of 2.141(9) and 2.180(7) Å respectively are elongated compared with the neutral complex [2.114(2) Å for Pd–N and 2.134(2) Å for Pd–O]. This indicates a weaker interaction between the N ^ O ligand and the metal centre for complex **3a**. In particular, the Pd–O bond, which is believed to be the weakest in the complex, is significantly longer. The weaker Pd–O bond does not appear to impact significantly on the

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

Pd–P(1)	2.208(3)	C(2)–C(21)	1.48(2)
Pd–N(1)	2.141(9)	C(2)–C(3)	1.34(2)
Pd–O(21)	2.180(7)	C(3)–C(4)	1.33(2)
Pd–C(0)	2.02(1)	C(21)–O(21)	1.22(2)
N(1)–C(2)	1.31(2)	C(21)–O(22)	1.30(2)
N(1)–C(6)	1.33(2)	O(22)–C(22)	1.49(2)
P(1)–Pd–N(1)	174.7(3)	Pd–N(1)–C(2)	117.0(8)
P(1)–Pd–O(21)	99.9(2)	N(1)–C(2)–C(21)	112(1)
P(1)–Pd–C(0)	88.3(3)	C(2)–C(21)–O(21)	122(1)
N(1)–Pd–O(21)	74.8(4)	Pd–O(21)–C(21)	113.8(9)
N(1)–Pd–C(0)	96.9(4)	Pd–N(1)–C(6)	129.5(9)
O(21)–Pd–C(0)	171.5(4)	O(21)–C(21)–O(22)	121(1)

Table 4
Non-hydrogen positional and isotropic displacement parameters

Atom	x	y	z	U_{eq} Å^2
Pd	0.66630(4)	0.54205(4)	0.56314(6)	0.062(3)
P(1)	0.7381(1)	0.5431(2)	0.6830(2)	0.058(1)
C(111)	0.7135(6)	0.5940(6)	0.7866(8)	0.063(5)
C(112)	0.6585(5)	0.6386(5)	0.7818(7)	0.059(4)
C(113)	0.6367(6)	0.6763(6)	0.863(1)	0.074(5)
C(114)	0.6681(7)	0.6674(6)	0.9468(9)	0.075(5)
C(115)	0.7245(6)	0.6227(7)	0.9527(8)	0.080(5)
C(116)	0.7457(6)	0.5845(6)	0.8727(9)	0.073(5)
C(121)	0.8220(5)	0.5686(5)	0.6493(8)	0.058(4)
C(122)	0.8607(7)	0.6166(6)	0.7020(8)	0.076(5)
C(123)	0.9255(7)	0.6352(7)	0.668(1)	0.095(6)
C(124)	0.9485(7)	0.6034(9)	0.584(1)	0.111(8)
C(125)	0.9092(8)	0.5579(8)	0.5335(9)	0.103(7)
C(126)	0.8473(6)	0.5420(7)	0.5662(9)	0.091(5)
C(131)	0.7442(6)	0.4548(6)	0.7319(7)	0.056(4)
C(132)	0.6886(6)	0.4274(6)	0.7793(8)	0.068(5)
C(133)	0.6873(6)	0.3557(8)	0.8085(8)	0.084(6)
C(134)	0.7409(8)	0.3113(6)	0.785(1)	0.082(6)
C(135)	0.7941(7)	0.3361(7)	0.7384(9)	0.080(6)
C(136)	0.7967(6)	0.4099(6)	0.7107(7)	0.067(5)
N(1)	0.5958(4)	0.5306(6)	0.4491(7)	0.076(4)
C(2)	0.5681(6)	0.4679(8)	0.4381(9)	0.070(5)
C(21)	0.5935(7)	0.4152(8)	0.507(1)	0.094(7)
O(21)	0.6324(4)	0.4319(4)	0.5708(6)	0.075(3)
O(22)	0.5724(6)	0.3501(6)	0.4984(7)	0.145(5)
C(22)	0.597(1)	0.2925(7)	0.562(1)	0.19(1)
C(3)	0.5225(6)	0.4494(8)	0.372(1)	0.092(6)
C(4)	0.4992(9)	0.498(1)	0.311(1)	0.122(8)
C(5)	0.5268(8)	0.560(1)	0.313(1)	0.123(9)
C(6)	0.5744(7)	0.5787(8)	0.387(1)	0.108(7)
C(0)	0.6915(6)	0.6445(6)	0.5365(9)	0.097(6)
B *	0.516(2)	0.774(2)	0.637(2)	0.146(9)
F(1)	0.5371(7)	0.7651(8)	0.725(1)	0.283(9)
F(2)	0.5393(8)	0.8363(7)	0.6236(8)	0.257(9)
F(3)	0.4542(5)	0.7731(7)	0.6437(7)	0.215(7)
F(4)	0.5419(5)	0.7386(7)	0.576(1)	0.31(1)

* Isotropic thermal parameter.

trans Pd–CH_3 bond, as it is of similar length in both complexes [2.02(1) Å in the cationic complex versus 2.021(3) Å in the neutral complex]. The metal to phosphorus distance is significantly shorter in the cationic complex [2.208(3) Å] compared with that in the neutral complex [2.2303(6) Å].

2.5. Copolymerisation of ethene and carbon monoxide

Copolymerisation reactions of ethene with carbon monoxide were carried out in CH_2Cl_2 or $CHCl_3$ under 20 bar each of CO and ethene (40 bar total pressure). In CH_2Cl_2 each of the complexes **3a–5a**, with the exception of **3b**, catalyses the copolymerisation of ethene and CO to alternating polyketone. Similar results are obtained in $CHCl_3$ (run 1 vs. run 2). Chloroform was used for experiments at higher temperature. After the given reaction time the polyketone was collected on a frit, dried and weighed. The alternating structure of the polyketone was confirmed by microanalysis, IR and ^1H and ^{13}C NMR. Keim et al. [38] have recently reported the formation of oligomeric products from CO and ethene. Analysis of the filtrate showed that no oligomeric products were obtained under the reaction conditions used here, possibly due to the higher ratio of CO to ethene (20:20 bar) employed in our work. In the absence of CO, dimerisation of ethene to butenes occurs. The presence of methanol inhibits the polymerisation reaction with these complexes (run 5), and trace amounts of methylpropionate were detected in the reaction solution. Methylpropionate has also been observed in the presence of methanol, for catalysis with palladium(II) complexes containing monodentate ligands [39].

Catalytic results are listed in Table 5. Catalytic activities are expressed in terms of the turnover number (TON), the total number of moles of substrate (CO and ethene) converted per mole of catalyst during the experiment. Results are also expressed in the unit gram polyketone per gram palladium, g(PK)/g(Pd).

Complex **3a**, with PPh_3 and the pyridyl ligand in *trans* positions, gives the best results regarding activity and catalyst stability. Substitution of PPh_3 by the more basic alkyldiphenylphosphine Ph_2PCH_2COOEt, complex **3b**, results in an inactive catalyst. At higher temperatures (60 °C) only traces of polyketone are formed with complex **3b**. This result follows the trend observed in the carbonylation of neutral Pd(II) complexes $MePdPR_3(pyca)$ (pyca = 2-pyridine carboxylate). These complexes do not catalyse the copolymerisation reaction, however they can be carbonylated to give acetyl complexes. The carbonylation rate decreases as the basicity of the phosphine ligand is increased, e.g. from PPh_3 to PEt_3 and PCy_3 [16].

When the pyridyl ligand is not part of a chelate but a monodentate ligand and the P ^ O ligand Ph_2PCH_2COOEt takes on the bidentate coordination mode as in complex **4a**, catalytic activity is resumed. A further increase in catalytic activity is obtained when the monodentate pyridyl ligand is replaced by PPh_3, as in complex **4b**. However, comparison of complex **3a** and **4b** shows that the N ^ O ligand yields a better catalyst than the P ^ O ligand, which may be explained in terms of increased stability of complex **3a** provided by a stronger chelating N ^ O ligand.

All three ligand donor types are combined in the tridentate P ^ O ^ N ligand **1** in complex **5a**. The complex shows a catalytic activity somewhere between complex **3a** and **4b** and is one of the first examples of a complex with a tridentate ligand demonstrating activity for polyketone formation. However, from runs 14 and 15 it can be seen that the instability of the complex leads to a fast decomposition and catalysis ceases at an early stage. As mentioned previously, in solution complex **5a** forms oligomeric species which are insoluble in CH_2Cl_2.

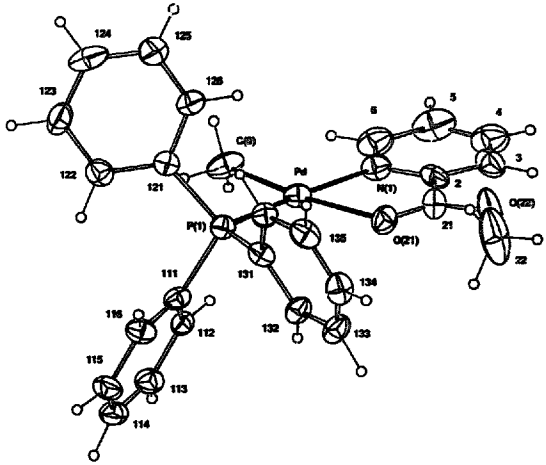


Fig. 1. Projection of the cation of **3a** oblique to the coordination plane about the palladium atom. 20% thermal ellipsoids are shown for the non-hydrogen atoms having arbitrary radii of 0.01 Å.

Compared with cationic palladium catalysts with bidentate P ^ P ligands, activities of these complexes for polyketone formation are low. However several conclusions can be drawn from these studies which may contribute to a better understanding of the copolymerisation reaction.

Table 5
Ethene/CO copolymerisation results for complexes **3a–5a**

Run	Catalyst	*n* (mmol)	Reaction conditions [a]		Results	
			Temperature (°C)	Time (h)	TON	g(PK)/ g(Pd)
1	**3a**	0.097	20	1	41	21
2	**3a** [b]	0.093	20	1	42	22
3	**3a**	0.093	20	20	115	60
4	**3a** [b]	0.093	80	1	163	86
5	**3a** [c]	0.087	20	1	0	0
6	**3b**	0.051	20	1	0	0
7	**3b** [b]	0.051	60	1		traces of PK
8	**4a**	0.054	20	1	7	3
9	**4a**	0.049	60	1	14	6
10	**4a**	0.237	20	20	22	11
11	**4b**	0.103	20	1	18	9
12	**4b** [b]	0.093	60	1	35	18
13	**4b**	0.109	20	20	72	38
14	**5a**	0.018	20	1	30	16
15	**5a**	0.10	20	20	40	21

[a] Conditions: 40 ml CH_2Cl_2; initial $p(CO) = 20$ bar; initial $p(ethene) = 20$ bar.
[b] 40 ml $CHCl_3$.
[c] 20 ml CH_2Cl_2 /20 ml MeOH.

For catalytic systems using bidentate ligands it is generally agreed that the catalytic species in the copolymerisation reaction can be represented by structure **I**, containing a chelate (L ^ L), the growing polymer chain (**P**) and a 'vacant' coordination site usually occupied by a monomer ligand, i.e. CO or ethene. In the absence of monomer this 'vacant' position may be occupied by a weakly coordinating solvent molecule. The growing polymer chain and the monomer are always *cis* to each other, which is the most favourable position for migratory insertion reactions.

Complexes **3a–4b** do not contain strongly coordinating bidentate ligands. The hemilabile N ^ O and P ^ O ligands have one weakly coordinating oxygen donor, which can dissociate during the course of the reaction. There is also evidence to suggest that the monodentate ligand L may also dissociate [14]. Accordingly, the structure of these complexes becomes similar to that of Pd–alkyl complexes with monodentate ligands and can be represented by structure **II**. A *trans* orientation of the phosphine/pyridine ligands is preferred, probably

primarily for electronic reasons in that it avoids the unfavourable situation of phosphorus *trans* to an alkyl group. Consequently, the growing polymer chain and the incoming monomer are also *trans* to each other. Under catalytic conditions a *cis / trans* isomerisation is therefore necessary to place the growing chain and monomer *cis* to each other. Recently we have presented strong evidence for such a mechanism [40].

3. Experimental section

3.1. General remarks

All reactions and manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques. All solvents were dried and purified by standard methods and freshly distilled before use. N,N'-dicyclohexylcarbodiimide (DCC) was distilled before use. The starting materials MePd(COD)Cl [41], Ph_2PCH_2COOH [42], Ph_2PCH_2COOEt [43], were synthesized according to known methods and fully characterized by multinuclear NMR and IR spectroscopy.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-300 or a Varian Gemini-200 NMR spectrometer. Chemical shifts (δ) are reported in parts per million relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P). Infrared (IR) spectra were recorded on a Bruker IFS-66 FTIR spectrometer. CH_2Cl_2 solutions were used in the mid-IR range (4000–400 cm^{-1}). Liquid secondary ion mass spectroscopy (LSIMS) measurements were recorded on a Kratos Concept ISQ spectrometer using 10 kV caesium ions as the primary beam, 5.3 kV accelerating voltage and scanning m/z of 1400 to 100 at 2 s/decade (resolution 1000). Samples were dissolved in m-nitrobenzyl alcohol. Microanalyses were performed by the Central Science Laboratory, University of Tasmania on a Carlo Erba CHNS-O EA elemental analyzer. Gas chromatography analyses were performed on a Hewlett Packard 5890 gas chromatograph fitted with an SGE 50QC3/BP1-0.5 capillary column.

3.2. Structure determinations

A unique room-temperature diffractometer data set (T ~ 295 K; Enraf–Nonius CAD-4 instrument, monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å; $2\theta/\theta$ scan mode; $2\theta_{max} = 50°$) as measured yielding 4252 independent reflections, 2019 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement ($n_v = 321$) after Gaussian absorption correction and solution of the structure by the heavy atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms (B excepted), $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals on $|F|$ at convergence $(\Delta/\sigma)_{max} = 0.04$; $|\rho|_{max} = 0.49$ e Å^{-3}; R and R_w both 0.053; 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 Hall [44]. Pertinent results are given in the figures and tables; material deposited comprises structure factor amplitudes, thermal and hydrogen atom parameters and full molecular geometry. Apparent thermal motion was high in the vicinity of the anion but no disorder was resolvable.

3.2.1. Crystal / refinement data

[Pd(Me)(Me–picolinate)(PPh_3)]BF_4 = $C_{26}H_{25}BF_4NO_2PPd$, $M = 607.68$. Orthorhombic, space group $Pbca$, $a = 19.934(3)$, $b = 18.788(6)$, $c = 14.033(4)$ Å, $V = 5255(2)$ Å^3, $D_c(Z = 8) = 1.536$ g cm^{-3}; $F(000) = 2448$. $\mu_{Mo} = 8.2$ cm^{-1}; specimen $0.20 \times 0.40 \times 0.43$ mm^3; $A^*_{min,max} = 1.15, 1.25$.

3.3. Ligand synthesis

3.3.1. Diphenylphosphinoaceticacid-2-picolylester, $Ph_2PCH_2COOCH_2NC_5H_4$ (1)

To a solution of Ph_2PCH_2COOH (2.00 g, 8.2 mmol) in 10 ml CH_2Cl_2 were added 4-dimethylaminopyridine (DMAP) (30 mg) and 2-pyridylmethanol (0.89 g, 8.2 mmol). After the addition of N,N'-dicyclohexylcarbodiimide (DCC) (1.75 g, 8.5 mmol) at 0 °C the reaction mixture was stirred for 5 min at 0 °C after which a white precipitate formed. The mixture was stirred for another 12 h at room temperature. The precipitated urea was filtered off and the solvent removed in vacuo. The residue was treated once more with cold CH_2Cl_2 and filtered a second time to remove further precipitated urea. The ester (1) was obtained as a white to pale yellow oil. ^1H NMR (200 MHz, $CDCl_3$): δ 8.54 (d, 1H, $J = 4.0$ Hz, 6-pyr-*H*), 7.65–7.05 (m, 14H, $H_{arom} + H_{pyr}$), 5.16 (s, 2H, OCH_2), 3.25 (s, 2H, PCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8 (d, $J = 7.9$ Hz, $C{=}O$), 156.2–122.1 ($C_{arom} + C_{pyr}$), 67.8 (OCH_2), 35.8 (d, $J = 22$ Hz, PCH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ −18.3. IR (CH_2Cl_2): ν(C=O) 1731 cm^{-1}. Mass spectrum: m/z 335 $[M]^+$, 126 $[Ph_2PCH_2CO]^+$.

3.4. Synthesis of alkyl complexes

3.4.1. $[MePd(PPh_3)Cl]_2$ (2a)

To a solution of MePd(COD)Cl (1.19 g, 4.49 mmol) in 10 ml CH_2Cl_2 was added one equivalent of triphenylphosphine (1.18 g, 4.46 mmol). The mixture was stirred for 0.5 h at room temperature, during which time a white precipitate formed. The yellow product was filtered off, washed with CH_2Cl_2 and dried in vacuo.

No suitable solvent was found to dissolve the product. Yield 93%. Anal. Found: C, 54.52; H, 4.43. $C_{19}H_{18}PPdCl$ Calc.: C, 54.44; H, 4.33%.

3.4.2. [MePd(Ph$_2$PCH$_2$COOEt-κ^1-P)Cl]$_2$ (2b)

To a solution of MePd(COD)Cl (1.45 g, 5.5 mmol) in 10 ml CH_2Cl_2 was added one equivalent of Ph_2PCH_2COOEt (1.49 g, 5.5 mmol). The mixture was stirred for 0.5 h at room temperature, during which time the colour changed from yellow to orange–red. The volume of the solution was reduced to ca. 3 ml. After addition of 20 ml hexane, the product was separated and washed with hexane. The orange product is soluble in CH_2Cl_2, in contrast to the corresponding complexes of PPh_3 or diphenylphosphinoaceticacid-2-picolylester. Yield 99%. Anal. Found: C, 48.02; H, 4.86. $C_{17}H_{20}PO_2PdCl$ Calc.: C, 47.57; H, 4.70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82–7.40 (m, 10H, Ar*H*), 3.86 (q, 2H, J = 7.1 Hz, OCH_2), 3.55 (d, 2H, J = 9.7 Hz, PCH_2), 1.01 (t, 3H, J = 7.1 Hz, CH_2CH_3), 0.65 (d, 3H, J = 2.5 Hz, PdCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3 (*C*O), 134.5–129.0 (Ar*C*), 61.8 (OCH_2), 35.6 (d, J = 22 Hz, PCH_2), 14.5 (CH_2CH_3), 6.7 (PdCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 27.7. IR (CH_2Cl_2): ν(C=O) 1728 cm^{-1}.

3.4.3. [MePd(Ph$_2$PCH$_2$COOCH$_2$NC$_5$H$_4$-κ^1-P)Cl]$_2$ (2c)

To a solution of MePd(COD)Cl (0.58 g, 2.21 mmol) in 10 ml CH_2Cl_2 was added one equivalent of diphenylphosphinoaceticacid-2-picolylester (0.74 g, 2.21 mmol). The mixture was stirred for 0.5 h at room temperature giving a white precipitate. The mixture was filtered and washed with CH_2Cl_2. No suitable solvent was found to dissolve the white product. Yield 67%. Anal. Found: C, 46.19; H, 3.96; N, 2.46. $[C_{21}H_{21}O_2PNPdCl]_2 \cdot 2CH_2Cl_2$ Calc.: C, 45.78; H, 4.02; N, 2.43%.

3.4.4. [MePdPPh$_3$(2-NC$_5$H$_4$COOMe-κ^2-N,O)]BF$_4$ (3a)

To a suspension of $[MePd(PPh_3)Cl]_2$ (2a) (1.62 g, 1.93 mmol) in 20 ml CH_2Cl_2 was added two equivalents of methylpicolinate (0.53 g, 3.86 mmol). The mixture was stirred for 0.5 h at room temperature and then added to a suspension of $AgBF_4$ (0.81 g, 4.16 mmol) in 10 ml CH_2Cl_2 at room temperature. After stirring for 1 h at room temperature the AgCl was filtered off through Celite yielding a pale yellow solution. The solvent was evaporated and the product washed twice with hexane and dried in vacuo to give a yellow solid. Yield 91%. Anal. Found: C, 51.58; H, 4.16; N, 2.45. $C_{26}H_{25}PNO_2PdBF_4$ Calc.: C, 51.39; H, 4.15; N, 2.30%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.72 (d, 1H, J = 5.0 Hz, pyr-*H*^{6}), 8.30 (br s, 2H, pyr-*H*^{4,5}), 8.01 (br s, 1H, pyr-*H*^{3}), 7.63–7.42 (m, 15H, Ar*H*), 3.93 (s, 3H, OCH_3), 1.09 (d, 3H, J = 1.4 Hz, PdCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3 (*C*O), 148.5, 146.0, 141.3, 131.6, 128.1 (pyridyl carbons), 134.2–128.7 (Ar*C*), 55.8 (OCH_3), 5.74 (PdCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 35.8. IR (CH_2Cl_2): ν(C=O) 1671 cm^{-1}. MS (LSIMS) for the cation: m/z 520 $[M]^+$, 383 $[M\text{-}NC_5H_4COOMe]^+$, 277 $[Ph_3PMe]^+$.

3.4.5. [MePdPh$_2$PCH$_2$COOEt(2-NC$_5$H$_4$COOMe-κ^2-N,O)]BF$_4$ (3b)

To a solution of $[MePd(Ph_2PCH_2COOEt\text{-}\kappa^1\text{-}P)Cl]_2$ (2b) (0.30 g, 0.35 mmol) in 10 ml CH_2Cl_2 was added two equivalents of methylpicolinate (0.096 g, 0.70 mmol). After stirring for half an hour the colour changed from orange to yellow. This solution was then added to a suspension of $AgBF_4$ (0.17 g, 0.87 mmol) in 10 ml CH_2Cl_2 at room temperature. After 5 min the mixture was filtered through Celite and the solvent reduced in vacuo and the yellow product precipitated with hexane. Yield 79%. Anal. Found: C, 46.54; H, 4.70; N, 2.50. $C_{24}H_{27}PNO_4PdBF_4$ Calc.: C, 46.67; H, 4.41; N, 2.27%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.70 (d, 1H, J = 4.8 Hz, pyr-*H*^{6}), 8.30–7.80 (m, 3H, pyr-*H*^{3,4,5}), 7.78–7.46 (m, 10H, Ar*H*), 4.04 (s, 3H, OCH_3), 4.03 (q, 2H, J = 7.1 Hz, OCH_2), 3.65 (d, 2H, J = 11 Hz, PCH_2), 1.08 (t, 3H, J = 7.1 Hz, CH_2CH_3), 1.02 (d, 3H, J = 1.8 Hz, PdCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1 (*C*OOMe), 167.9 (*C*OOEt), 149.6–128.1 (Ar*C* and pyr-*C*), 62.4 (OCH_2), 55.6 (OCH_3), 34.7 (d, J = 27 Hz, PCH_2), 14.4 (CH_2CH_3), 4.26 (PdCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 26.3. IR (CH_2Cl_2): ν(*C*=O) 1731 cm^{-1} (*C*OOEt), 1669 cm^{-1} (*C*OOMe).

3.4.6. [MePd(2,6-lutidine)(Ph$_2$PCH$_2$COOEt-κ^2-P,O)]BF$_4$ (4a)

To a solution of $[MePd(Ph_2PCH_2COOEt\text{-}\kappa^1\text{-}P)Cl]_2$ (2b) (0.30 g, 0.35 mmol) in 10 ml CH_2Cl_2 was added two equivalents of 2,6-lutidine (0.075 g, 0.70 mmol). After stirring for half an hour the colour had changed from orange to yellow. This solution was then added to a suspension of $AgBF_4$ (0.17 g, 0.87 mmol) in 10 ml CH_2Cl_2 at room temperature. After 5 min the mixture was filtered through Celite and the solvent reduced in vacuo and the product precipitated with hexane to give a yellow solid. Yield 83%. Anal. Found: C, 48.85; H, 5.19; N, 2.50. $C_{24}H_{29}PNO_2PdBF_4$ Calc.: C, 49.05; H, 4.97; N, 2.38%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.74–7.31 (m, 11H, Ar*H* and pyr-*H*^{4}), 7.18 (d, 2H, J = 7.8 Hz, pyr-*H*^{3,5}), 4.05 (q, 2H, J = 7.1 Hz, OCH_2), 3.62 (d, 2H, J = 11 Hz, PCH_2), 2.95 (s, 6H, pyr-CH_3), 1.14 (t, 3H, J = 7.1 Hz, CH_2CH_3), 0.40 (d, 3H, J = 3.3 Hz, PdCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9 (*C*OOEt), 159.1–123.7 (Ar*C* and pyr-*C*), 63.9 (OCH_2), 37.2 (d, J = 28 Hz, PCH_2), 27.0 (pyr-*C*H_3), 14.4 (CH_2CH_3), −0.07 (PdCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.2. IR (CH_2Cl_2): ν(C=O) 1638 cm^{-1}.

3.4.7. [MePdPPh$_3$(Ph$_2$PCH$_2$COOEt-κ^2-P,O)]BF$_4$ (4b)

To a solution of [MePd(Ph$_2$PCH$_2$COOEt-κ^1-P)Cl]$_2$ (**2b**) (0.89 g, 1.04 mmol) in 10 ml CH_2Cl_2 was added two equivalents of PPh_3 (0.54 g, 2.08 mmol). After a few minutes a precipitate started to form. This mixture was then added to a suspension of $AgBF_4$ (0.41 g, 2.10 mmol) in 5 ml CH_2Cl_2 at room temperature. After 5 min the mixture was filtered through Celite and the solvent removed in vacuo to give a red–brown solid. Yield 96%. Anal. Found: C, 54.52; H, 4.55. $C_{35}H_{35}P_2O_2PdBF_4 \cdot 0.5CH_2Cl_2$ Calc.: C, 54.30; H, 4.62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71–7.48 (m, 25H, Ar*H*), 4.04 (dd, 2H, J = 1.3 Hz, J = 10.2 Hz, PCH_2), 3.95 (q, 2H, J = 7.1 Hz, OCH_2), 1.11 (tr, 3H, J = 7.1 Hz, CH_2CH_3), 0.70 (tr, 3H, J = 5.8 Hz, PdCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.6 (d, J = 15 Hz, *C*O), 135.6–127.1 (Ar*C*), 66.6 (OCH_2), 38.8 (d, J = 28 Hz, PCH_2), 14.1 (CH_2CH_3), 0.56 (PdCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.5, 16.6 (2d, J_{PP} = 381 Hz). IR (CH_2Cl_2): ν(C=O) 1635 cm^{-1}.

3.4.8. [MePd(Ph$_2$PCH$_2$COOCH$_2$NC$_5$H$_4$-κ^3-P,N,O)]BF$_4$ (5a)

A suspension of [MePd(Ph$_2$PCH$_2$COOCH$_2$NC$_5$H$_4$-κ^1-P)Cl]$_2$ · 2CH_2Cl_2 (0.24 g, 0.42 mmol) in 10 ml CH_2Cl_2 was added to a suspension of $AgBF_4$ (0.09 g, 0.46 mmol) in 80 ml CH_2Cl_2 at −10 °C. After stirring for 0.5 h the AgCl was filtered off through Celite yielding a clear pale yellow solution. The volume was reduced to 10 ml. After complete removal of the solvent in vacuo the resulting off-white solid product could only be partly redissolved in CH_2Cl_2. Yield 93%. Anal. Found: C, 44.17; H, 3.75; N, 2.56. $C_{21}H_{21}O_2PNPdBF_4 \cdot 0.5CH_2Cl_2$ Calc.: C, 44.06; H, 3.78; N, 2.39%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, 1H, J = 5.3 Hz, 6-pyr-*H*), 7.85–6.90 (m, 14H, $H_{arom} + H_{pyr}$), 5.87 (s, 2H, OCH_2), 4.16 (d, 2H, J = 11 Hz, PCH_2), 0.68 (d, 3H, J = 2.1 Hz, PdCH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 180.2 (*C*=O), 156.5–123.6 ($C_{arom} + C_{pyr}$), 70.4 (OCH_2), 39.7 (d, J = 32 Hz, PCH_2), 0.42 (PdCH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 27.7. IR (CH_2Cl_2): ν(C=O) 1655 cm^{-1}. MS (LSIMS) for the cationic part: m/z 456 $[M]^+$, 441 $[M - CH_3]^+$, 347 $[H_3CPdPPh_2CH_2CO]^+$.

3.4.9. [MePd(Ph$_2$PCH$_2$COOCH$_2$NC$_5$H$_4$-κ^2-P,N)(CH$_3$CN)]BF$_4$ (5b)

A suspension of [MePd(Ph$_2$PCH$_2$COOCH$_2$NC$_5$H$_4$-κ^1-P)Cl]$_2$ · 2CH_2Cl_2 (0.35 g, 0.61 mmol) in 5 ml CH_3CN was added to a solution of $AgBF_4$ (0.14 g, 0.71 mmol) in 5 ml CH_3CN at room temperature. After stirring for 0.5 h the AgCl was filtered through Celite yielding a clear pale yellow solution. The solvent was removed in vacuo leaving a white solid. The product is insoluble in CH_2Cl_2 but can be dissolved in warm CH_3CN. Yield 75%. Anal. Found: C, 47.07; H, 4.05; N, 4.89. $C_{21}H_{21}O_2PNPdBF_4 \cdot CH_3CN$ Calc.: C, 47.25; H, 4.14; N, 4.79%. ^{1}H NMR (300 MHz, CD_3CN): δ 8.82 (s, 1H, 6-pyr-*H*), 8.07 (s, 1H, pyr-*H*), 7.85–7.50 (m, 14H, $H_{arom} + H_{pyr}$), 5.86 (s, 2H, OCH_2), 3.99 (d, 2H, J = 10 Hz, PCH_2), 0.52 (d, 3H, J = 3.0 Hz, PdCH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 170.3 (*C*=O), 157.2–124.1 ($C_{arom} + C_{pyr}$), 68.0 (OCH_2), 34.8 (d, J = 34 Hz, PCH_2), 0.21 (PdCH_3). ^{31}P NMR (121 MHz, CD_3CN): δ 32.1. IR (CH_3CN): ν(C=O) 1736 cm^{-1}.

3.5. Synthesis of acetyl complexes

The corresponding acetyl complexes of complexes **3–4** were prepared in situ by bubbling carbon monoxide through a solution of the methyl palladium complex in $CDCl_3$ in an NMR tube. The carbonylation was followed by ^{1}H NMR and was usually complete within 5 min.

3.5.1. [MeCOPdPPh$_3$(2-NC$_5$H$_4$COOMe-κ^2-N,O)]BF$_4$ (6a)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (br s, 1H, pyr-*H*), 7.70–7.43 (m, 15H, Ar*H*), 3.99 (br s, 3H, OCH_3), 2.25 (d, 3H, J = 1.7 Hz, PdCOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.0 (PdC*O*CH$_3$), 170.3 (*C*OOMe), 150.2–127.7 (pyridyl carbons + Ar*C*), 55.5 (OCH_3), 35.6 (d, J = 9.8 Hz, PdCOCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.2. IR (CH_2Cl_2): ν(C=O) 1721 cm^{-1} (PdCOCH$_3$), 1673 cm^{-1} (COOMe).

3.5.2. [MeCOPdPh$_2$PCH$_2$COOEt(2-NC$_5$H$_4$COOMe-κ^2-N,O)]BF$_4$ (6b)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52, 8.26, 8.14 (br s, 4H, pyr-*H*), 7.81–7.50 (m, 10H, Ar*H*), 4.03 (s, 3H, OCH_3), 3.97 (q, 2H, J = 7.1 Hz, OCH_2), 3.59 (br s, 2H, PCH_2), 2.24 (br s, 3H, PdCOCH_3), 1.04 (tr, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.3 (PdC*O*CH$_3$), 168.8 (*C*OOMe), 168.0 (*C*OOEt), 150.7–127.6 (pyr-*C* and Ar*C*), 62.4 (OCH_2), 55.3 (OCH_3), 36.2 (d, J = 15 Hz, PdCOCH_3), 34.7 (d, J = 21 Hz, PCH_2), 14.5 (CH_2CH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 14.5. IR (CH_2Cl_2): ν(C=O) 1726 cm^{-1} (COOEt), 1715 cm^{-1} (PdCOCH$_3$), 1673 cm^{-1} (COOMe).

3.5.3. [MeCOPd(2,6-lutidine)(Ph$_2$PCH$_2$COOEt-κ^2-P,O)]BF$_4$ (7a)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67–7.26 (m, 11H, Ar*H* and pyr-*H*^{4}), 7.15 (d, 2H, J = 7.3 Hz, pyr-*H*^{3,5}), 4.09 (q, 2H, J = 6.9 Hz, OCH_2), 3.46 (d, 2H, J = 9.3 Hz, PCH_2), 3.04 (s, 6H, pyr-CH_3), 1.80 (s, 3H, PdCOCH_3), 1.15 (t, 3H, J = 6.9 Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 222.5 (PdC*O*CH$_3$), 172.7 (*C*OOEt), 159.7, 140.1, 123.8 (pyr-*C*), 133.7, 132.2, 129.7 (Ar*C*), 63.8 (OCH_2), 37.0 (d, J = 24 Hz, PdCOCH_3), 36.3 (d, J = 30 Hz, PCH_2), 26.7 (pyr-CH_3), 14.5 (CH_2CH_3). ^{31}P NMR (121 MHz, $CDCl_3$):

δ 12.4. IR (CH_2Cl_2): ν(C=O) 1710 cm^{-1} ($PdCOCH_3$), 1641 cm^{-1} (COOEt).

3.5.4. [MeCOPd(PPh$_3$)(Ph$_2$PCH$_2$COOEt-κ^2-P,O)]BF$_4$ (7b)

^1H NMR (300 MHz, $CDCl_3$): δ 7.80–7.43 (m, 25H, Ar*H*), 4.08 (d, 2H, J = 11.0 Hz, PCH_2), 3.85 (q, 2H, J = 7.1 Hz, OCH_2), 1.70 (t, 3H, J = 1.7 Hz, $PdCOCH_3$), 1.06 (t, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 219.4 ($PdCOCH_3$), 179.1 (d, J = 13 Hz, *C*OOEt), 135.2–127.4 (Ar*C*), 65.3 (OCH_2), 36.6 (d, J = 18 Hz, $PdCOCH_3$), 36.2 (d, J = 26 Hz, PCH_2), 13.6 (CH_2CH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 17.6, 6.61 (2d, J_{PP} = 245 Hz). IR (CH_2Cl_2): ν(C=O) 1714 cm^{-1} ($PdCOCH_3$), 1639 cm^{-1} (COOEt).

3.6. Determination of reaction rates for the carbonylation reaction

A 10 ml sample tube containing 0.08 mmol of palladium complex and a magnetic stirrer bar was affixed to the inside of a 250 ml round bottom flask. The flask was flushed with a steady stream of CO for 30 min. $CDCl_3$ (3 ml) containing TMS and presaturated with CO was injected into the sample tube at t_0. Concentrations of palladium complexes were 0.018 M. Aliquots of 0.3 ml were taken at regular time intervals and analysed by ^1H NMR. For the duration of the experiment all experimental apparatus, reagents/solvents and the NMR spectrometer were maintained at 253 K.

3.7. Copolymerisation of carbon monoxide and ethene

A solution of the complex (0.05–0.1 mmol) in CH_2Cl_2 (40 ml) was transferred via a syringe into a 350 ml steel autoclave, which was equipped with a glass inlet and a magnetic stirring bar. The autoclave was pressurised first with carbon monoxide (20 bar), then ethene (20 bar) was introduced and the mixture stirred for the given reaction time. Except for the reactions at room temperature the autoclave was heated in an oil bath. After the appropriate time the excess ethene/CO was released. The reaction mixture was filtered on a frit, the solid residue was dried and weighed. The alternating structure of the polyketone obtained was confirmed by microanalysis, IR and ^{13}C NMR in CF_3COOH. The filtrate was analysed by gas chromatography.

Acknowledgements

We would like to acknowledge the support of the Australian Research Council, in particular for the salary of G.J.P.B. We would also like to acknowledge Johnson Matthey for their generosity in providing a loan of palladium chloride.

References

[1] A. Sen and T.-W. Lai, *J. Am. Chem. Soc., 104* (1982) 3520.
[2] E. Drent and P. Budzelaar, *Chem. Rev., 96* (1996) 663.
[3] A. Sen, *Acc. Chem Res., 26* (1993) 303.
[4] D. Medema and A. Noordam, *Chemisch Magazine, March* (1995).
[5] Z. Jiang and A. Sen, *J. Am. Chem. Soc., 117* (1995) 4455.
[6] S. Bronco, G. Consiglio, R. Hutter, A. Batistini and U.W. Suter, *Macromol., 27* (1994) 4436.
[7] S. Bronco, G. Consiglio, S. Di Benedetto, M. Fehr, F. Spindler and A. Togni, *Helv. Chim. Acta, 78* (1995) 883.
[8] M. Brookhart, M.I. Wagner, G.G.A. Balavoine and H.A. Haddou, *J. Am. Chem. Soc., 116* (1994) 3641.
[9] B.A. Markies, D. Kruis, M.H.P. Rietveld, K.A.N. Verkerk, J. Boersma, H. Kooijman, M.T. Lakin, A.L. Spek and G. van Koten, *J. Am. Chem. Soc., 117* (1995) 5263.
[10] R. van Asselt, E.E.C.G. Gielens, R.E. Rülke, K. Vrieze and C.J. Elsevier, *J. Am. Chem. Soc., 116* (1994) 977.
[11] F.C. Rix and M. Brookhart, *J. Am. Chem. Soc., 117* (1995) 1137.
[12] F.C. Rix, M. Brookhart and P.S. White, *J. Am. Chem. Soc., 118* (1996) 4746.
[13] H. Jin and K.J. Cavell, *J. Chem. Soc., Dalton Trans.*, (1994) 415.
[14] H. Jin, K.J. Cavell, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1995) 2159.
[15] K.J. Cavell and H. Jin, *J. Chem. Soc., Dalton Trans.*, (1995) 4081.
[16] J.L. Hoare, K.J. Cavell, R. Hecker, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1996) 2197.
[17] S.Y. Desjardins, K.J. Cavell, H. Jin, B.W. Skelton and A.H. White, *J. Organomet. Chem., 515* (1996) 233.
[18] W. Keim, F.H. Kowalt, R. Goddard and C. Krüger, *Angew. Chem., Int. Ed. Engl., 17* (1978) 466.
[19] W. Keim, *Angew. Chem., Int. Ed. Engl., 29* (1990) 235.
[20] A. Yamamoto, *J. Organomet. Chem., 500* (1995) 337.
[21] M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc., Dalton Trans.*, (1994) 2755.
[22] K.K. Hii, S.D. Perera and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1994) 3589.
[23] K. Tani, M. Yabuta, S. Nakamura and T. Yamagata, *J. Chem. Soc., Dalton Trans.*, (1993) 2781.
[24] H. Yang, M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, (1995) 1721.
[25] Y. Kataoka, Y. Tsuji, O. Matsumoto, M. Ohashi, T. Yamagata and K. Tani, *J. Chem. Soc., Chem. Commun.*, (1995) 2099.
[26] H.-J. Haupt and U. Ortmann, *Z. Anorg. Alg. Chem., 619* (1993) 1209.
[27] B. Neises and W. Steglich, *Angew. Chem., Int. Ed. Engl., 17* (1978) 522.
[28] F.T. Ladipo and G.K. Anderson, *Organometallics, 13* (1994) 303.
[29] A. Singhal and V.K. Jain, *J. Chem. Soc., Dalton Trans.*, (1993) 1515.
[30] Y. Hayashi, K. Isobe, Y. Nakamura and S. Okeya, *J. Organomet. Chem., 310* (1986) 127.
[31] N.A. Al-Salem, H.D. Empsall, R. Markham, B.L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, (1979) 1972.
[32] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze and P.W.N.M. van Leeuwen, *Organometallics, 11* (1992) 1598.
[33] G.K. Anderson and R.J. Cross, *Chem. Soc. Rev., 9* (1980) 185.
[34] R.E. Rülke, J.G.P. Delis, A.M. Groot, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, K. Goubitz and H. Schenk, *J. Organomet. Chem., 508* (1996) 109.
[35] G.J.P. Britovsek, W. Keim, S. Mecking, D. Sainz and T. Wagner, *J. Chem. Soc., Chem. Commun.*, (1993) 1632.

[36] G.J.P. Britovsek, K.J. Cavell and W. Keim, *J. Mol. Catal.*, in press.
[37] K.E. Frankcombe, K.J. Cavell and B.F. Yates, unpublished data, 1996.
[38] W. Keim, H. Maas and S. Mecking, *Z. Naturforsch., 50b* (1995) 430.
[39] E. Drent, J.A.M. van Broekhoven and M.J. Doyle, *J. Organomet. Chem., 417* (1991) 235.
[40] M.J. Green, G.J.P. Britovsek, K.J. Cavell, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1995) 1563.
[41] R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen and K. Vrieze, *Inorg. Chem., 32* (1993) 5769.
[42] J.A. van Doorn and N. Meijboom, *Phosphorus, Sulfur and Silicon, 42* (1989) 211.
[43] B. Demerseman, C. Renouard, R. Le Lagadec, M. Gonzalez, P. Crochet and P.H. Dixneuf, *J. Organomet. Chem., 471* (1994) 229.
[44] S.R. Hall, H.D. Flack and J.M. Stewart (eds.), *The XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland, 1992.