Structurally characterized intermediates in the stepwise insertion of CO–ethylene or CO–methyl acrylate into the metal–carbon bond of Pd(II) complexes stabilized by (phosphinomethyl)oxazoline ligands†

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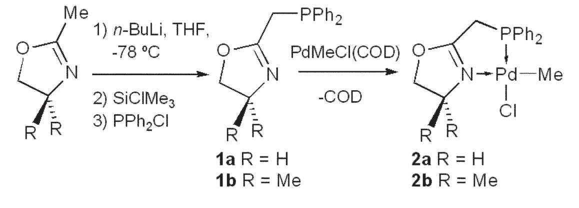
The initial CO–ethylene or CO–methyl acrylate insertion steps into the Pd–Me bond of methylpalladium(II) complexes with (phosphinomethyl)oxazoline ligands, leading to metallacycles, have been fully characterized, including by X-ray diffraction.

The palladium-catalyzed alternating copolymerisation of olefins and carbon monoxide, which leads to the formation of polyketones, has become a major field of research in both academic and industrial laboratories.[1]

Although the basic reaction mechanism of CO–olefin copolymerisation, which involves mutually *cis* sites of square-planar Pd(II) species, has been established,[1,2] detailed investigations on the early stages of the chain-growth process have mostly been carried out with strained alkenes owing to the difficulties often encountered in the isolation of intermediates. The first structural reports of an ethylene–CO coupling product by Green *et al.*, using monodentate PPh_3 and a N,O ligand,[3a] then by us using a P,O ligand[3b] or a diphosphine-bridged heterodimetallic Fe–Pd complex[3c] were followed by only a few examples with P,N,[3d,e] N,N[3f] and P,P[3g] chelating ligands. Furthermore, despite the considerable interest in the copolymerisation of olefins with polar monomers, such as methyl acrylate,[2e,4] only a few CO–methyl acrylate coupling products have been isolated and characterized.[2c,3b,c,5] Using a bidentate phosphine-imine (P,N) ligand, Reddy *et al.* have reported what appears to be the only structure of a CO–methyl acrylate coupling product.[3e] These authors used a large excess of olefin (33 to 67 equiv.) in CH_2Cl_2, with a reaction time between 1–3 h.

Following the synthesis of the ligands **1a,b** and of the Pd(II) methyl complexes **2a,b** (Scheme 1), we investigated the catalytic activity of Ni(II) complexes with **1b** in ethylene oligomerisation,[6] and that of the Pd(II) complexes **3a,b** (Scheme 2) in ethylene–CO copolymerisation.[7] Starting from **3a,b**, we have now isolated the initial intermediates in CO–ethylene or CO–methyl acrylate copolymerisation reactions, without the need to use excess methyl acrylate. The structures of the new insertion products **4b**, **6b** and **7a,b** have been determined by X-ray diffraction as well as those of the known **2a,b** and **3a,b** for comparative purposes.‡



Scheme 1

Reactions of **2a,b** and **3a,b** with CO in CH_2Cl_2 at room temperature were monitored by $^{31}P\{^1H\}$ and ^1H NMR. CO insertion into their Pd–Me bond produced within a few minutes the acyl complexes **4a,b** and **5a,b**, respectively (Scheme 2), as evidenced by the large high-field shift of the $^{31}P\{^1H\}$ NMR resonance ($\Delta\delta = -14.7$ **4a**, $\Delta\delta = -14.8$ **4b**, $\Delta\delta = -15.4$ **5a**, $\Delta\delta = -15.1$ **5b**, Table 1).

In order to detect the usually elusive palladium acyl, carbonyl complexes of the type [Pd{C(O)Me}(CO)(P,N)]OTf, a CD_2Cl_2 solution of **3b** was exposed to an atmosphere of ^{13}CO, and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded at different temperatures. At room temperature, the $^{31}P\{^1H\}$ NMR resonance for **5b** is a doublet centred at δ 21.6 ($^2J_{PC} = 9.7$ Hz). Its acyl carbon appears in the $^{13}C\{^1H\}$ spectrum as an intense doublet at δ 222.7 ($^2J_{PC} = 9.7$ Hz), and the weak signal observed at δ 179.8 corresponds to the coordinated CO of the acyl, carbonyl derivative. Upon decreasing the temperature to −60 °C, the $^{31}P\{^1H\}$ resonance significantly broadened and shifted to δ 19.1 while the $^{13}C\{^1H\}$ resonances for the acyl carbon and the coordinated CO also became broader and shifted to δ 222.6 and 175.5, respectively. This is indicative of an equilibrium between CO and OTf coordination which, at −100 °C, is completely shifted towards the acyl, carbonyl species and the $^{31}P\{^1H\}$ resonance becomes a doublet of doublets centred at δ 18.3 ($^2J_{PC(cis)} = 4.1$, $^2J_{PC(trans)} = 83.8$ Hz) while the acyl carbon and coordinated CO $^{13}C\{^1H\}$ resonances appear as doublets at δ 223.1 and 175.3, respectively (see ESI for details).† These results are in agreement with those for related complexes stabilized by P,P ligands,[8] but at variance with those with a P,N ligand in which no significant amount of palladium acyl, carbonyl species was detected at −70 °C.[3d]

Complexes **2a,b**, **3a,b** and **4b** have slightly distorted square planar coordination geometries with the methyl (**2a,b** and **3a,b**) and acyl (**4b**) ligands *cis* to the phosphorus atom (ESI),† in agreement with the donor groups with the largest *trans* influence avoiding a mutually *trans* position, as observed in other complexes of the type [Pd(Me)Cl(P,N)].[3e,9] The Pd–N bond distance in **2a** (Table 2) is longer than that reported for the analogous $PdCl_2$ complex [2.058(2) Å],[7] which reflects the larger *trans* influence of the methyl group compared with chloride. The Pd–C distance of

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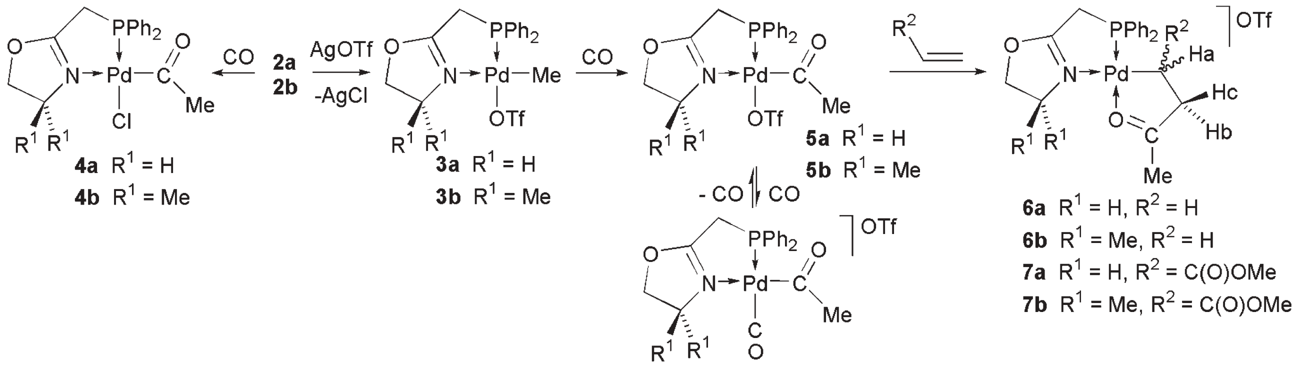
† Electronic supplementary information (ESI) available: Complete sets of crystallographic parameters for **2a,b**, **3a,b**, **4b**, **6b**, **7a,b**; experimental procedures and spectroscopic characterizations. See DOI: 10.1039/b613865a



Scheme 2 All reactions were performed at room temperature in CH_2Cl_2.

Table 1 Selected IR and NMR data of the ligands and complexes

	IR		NMR^d	
	ν_{CN}	ν_{CO}	^{1}H	^{31}P
1a	1660^a (s)			−15.8
1b	1660^a (s)			−15.8
2a	1647^a (s)		0.55 Pd–CH_3 (d, $^3J_{PH}$ = 2.7)	33.1
2b	1628^a (s)		0.65 Pd–CH_3 (d, $^3J_{PH}$ = 3.3)	32.8
3a	1633^b (s)		0.60 Pd–CH_3 (s)	37.4
3b	1632^b (s)		0.70 Pd–CH_3 (s)	37.4
4a	1642^b (s)	1684^b (s)	2.20 PdC(O)CH_3 (d, $^4J_{PH}$ = 1.1)	18.4
4b	1632^b (s)	1685^b (s)	2.17 PdC(O)CH_3 (d, $^4J_{PH}$ = 1.6)	18.0
5a	1644^a (s)	1704^a (s)		22.0
5b	1655^a (s)	1707^a (s)		22.3
	$\nu_{CN/CO}$	$\nu_{C(O)OMe}$		
6a	1634^b (s)		2.45 C(O)CH_3 (s)	34.4
6b	1629^b (s)		2.49 C(O)CH_3 (s)	34.7
7a	1633^b (s)	1683^b (s)	2.52 C(O)CH_3 (s)	32.8
7b	1629^b (s)	1684^b (s)	2.55 C(O)CH_3 (s)	34.3

^{a} In CH_2Cl_2. ^{b} In KBr, cm^{-1}. ^{d} In $CDCl_3$, ppm, J in Hz.

1.9701(13) Å in **4b**, although slightly shorter than in the analogous Pd–Me complex (**2b**), is normal for an acetyl–palladium bond. The acyl group adopts an orientation approximately perpendicular to the metal coordination plane, as observed in other complexes of the type [Pd{C(O)Me}Cl(P,N)].[3e,10]

Ethylene or methyl acrylate insertion into the Pd–acyl bond of **5a** and **5b** was completed in less than 1 h at room temperature under atmospheric pressure (^{31}P NMR monitoring) and afforded **6a,b** or **7a,b**, respectively (Scheme 2). In all four complexes, coordination of the ketonic oxygen atom to Pd (see ν_{CO}, Table 1) results in a stabilizing chelate which makes β-hydrogen elimination less likely.[11] These complexes are stable at room temperature for several hours in solution and weeks in the solid state, which illustrates the beneficial role of the P–N chelates. The ^{31}P{^{1}H} NMR signals of **6a,b** and **7a,b** are shifted to low field relative to those of **5a,b** (Table 1). In the ^{1}H NMR spectrum of **6a,b** the Pd–CH_2 protons give rise to a triplet of doublets (δ 1.65, **6a** and δ 1.67, **6b**) whereas the CH_2C=O protons appear as a broad triplet (δ 3.08, **6a** and δ 3.12, **6b**), indicating a smaller $^{4+5}J_{HP}$ coupling.† The CH and CH_2 protons Ha, Hb and Hc of **7a,b** were unambiguously identified and resonate at δ 2.46, 2.90 and 3.26 (**7a**) and δ 2.46, 2.87 and 3.27 (**7b**) respectively (vicinal and geminal J_{HH} and J_{HP} coupling constants are given in the ESI).†

The crystal structures of **6b** and **7a,b** (see Fig. 1) were determined by X-ray diffraction and the latter two established the regioselective 2,1 insertion of methyl acrylate, which leads to an α-methoxycarbonyl complex. Deviations from idealized square planar geometries are small (Table 2). The similar Pd–C distances in **6b**, **7a** and **7b** are in agreement with that in the only other

Table 2 Selected bond lengths [Å] and angles [°] in complexes **2a,b**, **3a,b**, **4b**, **6b** and **7a,b**

	2a	2b	3a	3b	4b	6b	7a	7b
Pd1–N1	2.103 (12)	2.171 (3)	2.131 (4)	2.1550 (18)	2.1896 (11)	2.104 (4)	2.082 (3)	2.114 (3)
Pd1–P1	2.212 (4)	2.1879 (10)	2.1699 (12)	2.1771 (12)	2.2549 (13)	2.1878 (14)	2.2051 (10)	2.2091 (14)
Pd1–C17	2.057 (13)	2.049 (4)	2.026 (5)	2.031 (2)	1.9701 (13)	2.030 (5)	2.046 (4)	2.052 (4)
Pd1–O2			2.156 (3)	2.1631 (17)		2.125 (4)	2.112 (2)	2.138 (3)
Pd1–Cl1	2.383 (4)	2.378 (1)			2.3734 (13)			
N1–C3	1.291 (18)	1.279 (5)	1.281 (6)	1.275 (2)	1.2757 (15)	1.270 (6)	1.285 (5)	1.273 (6)
C3–C4	1.468 (19)	1.485 (5)	1.476 (6)	1.493 (3)	1.4897 (15)	1.480 (7)	1.496 (5)	1.498 (6)
C4–P1	1.847 (13)	1.835 (4)	1.839 (5)	1.837 (2)	1.8468 (12)	1.841 (5)	1.837 (4)	1.835 (4)
C17–C18					1.506 (2)	1.527 (8)	1.545 (6)	1.528 (7)
C18–C19						1.485 (8)	1.472 (6)	1.486 (7)
C19–O2						1.248 (6)	1.220(5)	1.239 (6)
N1–Pd1–P1	82.2 (3)	82.29 (9)	84.85 (11)	83.03 (6)	80.66 (3)	83.91 (12)	82.13 (9)	81.99 (10)
N1–Pd1–C17	176.4 (5)	171.94 (14)	174.97 (17)	174.30 (8)	173.83 (4)	177.1 (2)	174.17 (15)	175.94 (15)
N1–Pd1–O2			95.14 (14)	94.79 (7)		100.03 (14)	96.10 (12)	100.26 (13)
N1–Pd1–Cl1	93.2 (3)	97.94 (9)			97.09 (3)			
P1–Pd1–O2			172.64 (9)	177.32 (4)		174.72 (10)	175.29 (8)	177.54 (9)
P1–Pd1–C17	94.5 (4)	89.70 (13)	90.68 (15)	91.69 (8)	96.35 (4)	93.30 (16)	99.24 (11)	97.25 (14)
P1–Pd1–Cl1	174.66 (15)	179.21 (4)			173.211 (11)			
C17–Pd1–O2			89.00 (18)	90.42 (8)		82.80 (18)	82.10 (14)	80.57 (16)
C17–Pd1–Cl1	90.1 (5)	90.09 (13)			86.48 (4)			

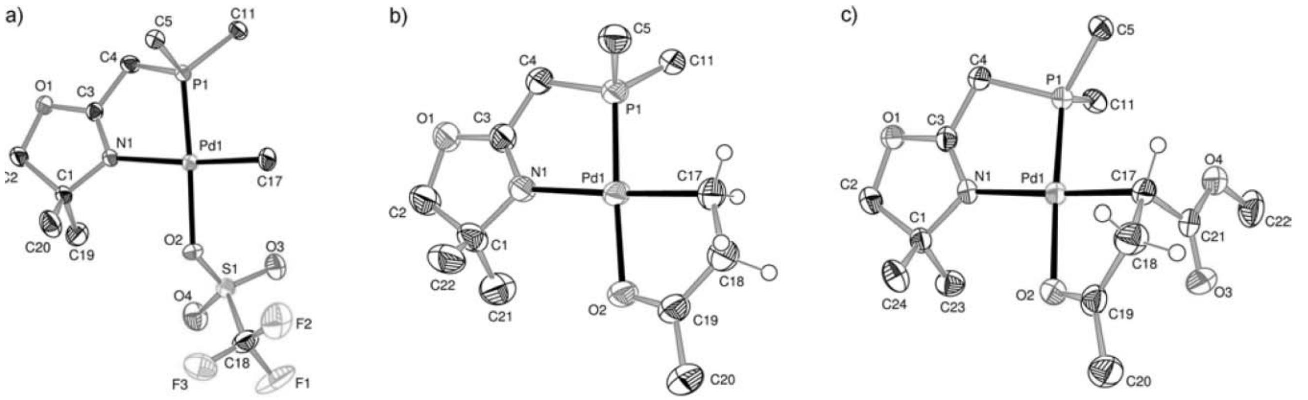


Fig. 1 Molecular structure of: a) complex **3b**, b) the cation in **6b**, c) the cation in **7b** (CH groups of phenyl rings and H atoms omitted, except inserted olefin). Displacement ellipsoids are drawn at the 50% probability level.

reported structure of a CO–methyl acrylate complex.[3e] The Pd–O bond distances in **6b**, **7a** and **7b** are similar and compare with those in related complexes stabilized by P,N ligands.[3d,e,12] At least in the solid state, there is no interaction between the CO_2Me group of **7a,b** and the metal centre, which would have reduced its electrophilicity and increased its steric shielding. It is also interesting to note that related Pd(II) complexes with the P,O chelating ligand $Ph_2PNHC(O)Me$ were generally found to be less reactive than **3a,b** or **5a,b**, longer reaction times being required.[3b]

In addition to the structural characterization of CO–ethylene and CO–methyl acrylate insertion products, we have spectroscopically observed a temperature-dependent equilibrium between a triflate, acyl complex, **5b**, and a cationic carbonyl, acyl Pd(II) complex. Previous studies have shown that **3a,b** catalyse the CO–ethylene copolymerisation at 60–90 °C.[6] Further investigations are in progress to determine the influence of the ligand bite angle on the reactivity of the chelate ring in **7a,b** towards further insertion of small molecules.

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‡ CCDC 622170–622177. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613865a

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