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Cationic methylpalladium(II) complexes containing bidentate N–O ligands as catalysts for the copolymerisation of CO and ethylene. Identification and isolation of intermediates from the stepwise insertion reactions, and subsequent detailed mechanistic interpretation ‡

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A series of cationic methylpalladium(II) complexes containing bidentate N–O ligands, of the general formula $[PdMe(N–O)L]BF_4$ (N–O = methyl picolinate, methyl 6-methylpicolinate, *N*,*N*-diisopropylpicolinamide, 6-methyl-*N*,*N*-diisopropylpicolinamide; L = PPh_3 or PCy_3) have been prepared and characterised. The solid-state structure of $[PdMe(N–O)(PPh_3)]BF_4$ (N–O = *N*,*N*-diisopropylpicolinamide), in comparison with that for the complex with N–O = methyl picolinate, indicates a significant lengthening of the Pd–P bond [Δ(Pd–P) = 0.018(3) Å] possibly due to the presence of the more strongly co-ordinating N–O ligand. Complexes with L = PPh_3 were found to be active for the copolymerisation of CO and ethylene to give polyketone. The complexes $[PdMe(N–O)(PPh_3)]BF_4$ (N–O = methyl 6-methylpicolinate or diisopropylpicolinamide) have the highest catalytic activities (80 g polymer per g Pd per hour and 58 g polymer per g Pd per hour respectively, at 20 °C). Examples of the complexes form simple acyl complexes when treated with CO at room temperature and pressure and the spectroscopic data of the resulting acetyl complexes are reported. The stepwise migratory insertion of CO and ethylene into the complex $[PdMe(N–O)(PPh_3)]BF_4$ (N–O = methyl picolinate) has been carefully monitored and the individual insertion products have been characterised. Insertion of ethylene into the Pd–acyl bond of $[Pd(COMe)(N–O)(PPh_3)]BF_4$ (N–O = methyl picolinate) affords one of the first examples of an isolable product from insertion of an unstrained alkene into a Pd–acyl bond. A detailed mechanism for the co-reaction of CO and ethylene catalysed by complexes containing chelate ligands with distinct donor groups is discussed and an explanation of the observed reaction behaviour provided. The proposed mechanism represents one of the most comprehensive interpretations of this important reaction.

With the introduction of Shell's Carilon® thermoplastic polymers in 1995 the production of polyketone became an economic reality. This initial success is likely to stimulate other groups into looking for commercial opportunities with this class of polymer.[1] For example, new developments in this area that have been recently reported include: the synthesis of catalysts for the formation of alternating copolymers of functionalised alkenes with CO,[2] synthesis of stereoblock polyketones,[3] the use of alumoxanes as cocatalysts in polyketone formation,[4,5] and the application of bis(chelate)palladium complexes in the copolymerisation of CO with alkenes.[6]

The stepwise migratory insertion of CO and alkenes into Pd–alkyl and Pd–acyl bonds are key steps in catalytic polyketone formation. These insertion reactions have been examined in some detail and the studies have provided valuable information on mechanistic aspects of polyketone formation.[7–13] Very recently Vrieze and co-workers have also investigated the stepwise insertion of CO with allenes.[14] However, despite the range of studies undertaken the direct observation of carbonyl alkyl and alkene acyl complexes and their subsequent migratory insertion reactions is rare. Tóth and Elsevier have investigated the reaction of CO with the palladium complex $[Pd(Me)\{(S,S)\text{-BDPP}\}(solv)]BF_4$ [where (*S*,*S*)-BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane].[15] They identified spectroscopically the square-planar *cis*-alkyl(carbonyl) complex $[Pd(Me)(CO)\{(S,S)\text{-BDPP}\}]BF_4$ which they propose is an intermediate in the formation of the acyl complex $[Pd(COMe)\{(S,S)\text{-BDPP}\}(CO)]BF_4$. By working at very low temperatures Brookhart and co-workers[10,11] have been able to prepare the unstable cationic 1,10-phenanthroline palladium complexes containing *cis* carbonyl alkyl, carbonyl acyl, ethylene alkyl and ethylene acyl groups. The migratory insertion reactions of these intermediates were monitored by low-temperature NMR spectroscopy and energy barriers for insertion were calculated.

The majority of the studies into stepwise insertion reactions have been concerned with stoichiometric reactions of CO with strained or bulky olefins; intermediates from the insertion of alkenes into Pd–acyl complexes were generally only observable if strained or bulky olefins were used. Furthermore, the systems investigated were not reported as being catalytically active for polyketone formation. In all studies it was found that migratory insertion of alkenes into metal–acyl species results in the formation of chelated alkyl/carbonyl species of the type $[\overline{PdCRHCR'HC(O)R''}]^+$ containing five-membered ring structures and in several cases six-membered chelates are formed upon migratory insertion of a further CO unit.[7–13,16,17] In a preliminary communication we reported an active catalytic system for CO/ethene copolymerisation, $[PdMe(N–O)(PPh_3)]BF_4$ **1a** (Fig. 1) (N–O = $NC_5H_4CO_2Me$, methyl picolinate), for which we were able to spectroscopically monitor the formation of intermediates resulting from stepwise CO and ethene insertion.[12] We were also able to isolate and record a crystal structure

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‡ *Non-SI units employed*: 1 atm = 101.325 kPa, 1 bar = 10^2 kPa. Picolinate = 2-pyridinecarboxylate, picolinamide = 2-pyridinecarboxamide.

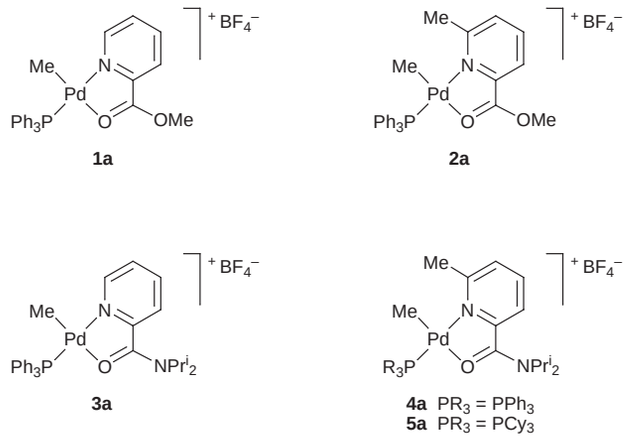
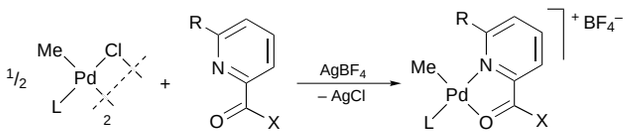


Fig. 1 Cationic organopalladium complexes with bidentate N–O ligands



Scheme 1 Preparation of complexes **1a**–**5a**

for the intermediate, **1c** in Scheme 3, formed from the migratory insertion of ethene into the metal–acyl bond. The complex has a square-pyramidal structure with a chelating alkyl/carbonyl ligand and a long Pd–O (ester carbonyl) bond [2.78(1) Å] in the apical position.[12] The only other example of an isolable compound from the insertion of ethene into a Pd–acyl bond was reported by Brookhart and co-workers.[10,11]

Herein we report details of the preparation and characterisation of a series of cationic methylpalladium complexes, **1a**–**5a** (Fig. 1), containing the chelating N–O ligands methyl picolinate ($NC_5H_4CO_2Me$-2), *N*,*N*-diisopropylpicolinamide [$NC_5H_4C(O)NPr^i_2$-2] and their 6-methyl derivatives. We also report their reactions with CO and their application in the copolymerisation of CO and ethene. The significance of the intermediates identified during the copolymerisation reaction is discussed with reference to the overall reaction mechanism. The detailed mechanism proposed includes a discussion of possible isomerisation processes occurring during the copolymerisation and provides an explanation of the observed reaction behaviour. The solid-state structure of the complex $[PdMe\{C_5H_4NC(O)NPr^i_2\}(PPh_3)]BF_4$, **3a**, has been determined and is compared to that of the related complex **1a**.

Results and Discussion

Preparation and characterisation of the complexes $[PdMe(N–O)L]BF_4$ and $[Pd(COMe)(N–O)L]BF_4$

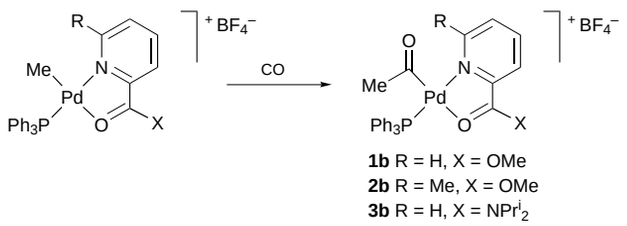
Complexes **1a**–**5a** were prepared by adding 2 equivalents of the methyl picolinate or diisopropylpicolinamide ligand to a suspension of $[PdMe(PPh_3)(\mu\text{-}Cl)]_2$, with subsequent addition of $AgBF_4$ (Scheme 1). The reaction proceeds smoothly with high yields, provided that the exact stoichiometric amount of $AgBF_4$ is used.

It was anticipated that an amide N–O ligand may strengthen the N–O chelate and thus provide a more stable complex. However, complexes **1a**–**5a** are all unstable in solution, decomposing to Pd^0 and unidentified products within 1 d at room temperature and the complexes **4a** and **5a** which both have the 6-methyl-*N*,*N*-diisopropylpicolinamide ligand are significantly more unstable. It is evident that the presence of the methyl group in the 6 position on the pyridine ring has a destabilising influence probably due to steric interaction with the Pd–methyl ligand.

Table 1 Selected IR data [ν(C=O)] for complexes **1a**–**5a** and **1b**–**3b**[a]

	ν(C=O)/cm^{-1}		
Complex	Free ligand	Complex	Δν(C=O)/cm^{-1}
1a	1739, 1726	1671	68, 55
2a	1735, 1724	1672	63, 52
3a	1634	1569	65
4a	1630	1572	58
5a	1630	1595	35
1b[b]	1739, 1726	1673	66, 53
2b[c]	1735, 1724	1673	62, 51
3b[d]	1634	1569	65

[a] In CH_2Cl_2 solution. [b] ν(C=O) PdCOMe 1721 cm^{-1}. [c] ν(C=O) PdCOMe 1720 cm^{-1}. [d] ν(C=O) PdCOMe 1707 cm^{-1}.



Scheme 2 Carbonylation of complexes **1a**–**3a**

The carbonylation of complexes **1a**–**3a** to yield the acyl complexes **1b**–**3b** is complete and quantitative after 10–15 min treatment with CO at room temperature and pressure (Scheme 2). The acyl complexes decompose in solution at room temperature to Pd^0 and unidentified organic products. Complex **1b** has been isolated in the solid state and stored overnight at 5 °C without significant decomposition. The stability of the other complexes was not investigated.

Selected spectroscopic data for the complexes **1a**–**3b** are presented in Tables 1 and 2. From the IR spectra, a decrease in the carbonyl stretching frequency [ν(C=O)] of the N–O ligands by 50–70 cm^{-1} is observed upon co-ordination of the carbonyl oxygen. The changes in the carbonyl peaks may be used to monitor the extent and rate of reaction of **1b**⟶**1c** (see below). The IR spectra of the two ester ligands (*i.e.* methyl picolinate and methyl 6-methylpicolinate) exhibit two equally intense peaks in the carbonyl stretching region (13 and 11 cm^{-1} apart respectively) whether performed neat or in a CH_2Cl_2 solution. A consideration of the carbonyl stretching region for similar compounds indicates that this result is also observed for other pyridine-based esters having a 2-substituted CO_2R group (*e.g.* ethyl picolinate).[18] The reason for the existence of two carbonyl stretching peaks is uncertain, but the effect disappears upon co-ordination of the picolinate ligand (Table 1).

A comparison of the NMR data for the methyl complexes **1a**–**5a** and related acyl complexes **1b**–**3b** is provided in Table 2. The Pd–methyl peaks moves downfield by approximately 1 ppm in the ^{1}H NMR and 30 ppm in the ^{13}C NMR spectrum on insertion of CO into the Pd–methyl bond. This is accompanied by a small downfield shift in the ^{13}C NMR carbonyl resonance of the N–O ligand, and ≈10 ppm upfield shift of the ^{31}P NMR signal.

For the series of complexes **1a**–**1d**, formed from the stepwise insertion of CO and ethylene, regular changes in the IR carbonyl stretch [Δν(C=O) = 55–83 cm^{-1}] and ^{13}C NMR carbonyl signal [Δδ(C=O) = 6–12 ppm] are observed, corresponding to the co-ordination/dissociation of the carbonyl groups of the N–O ligand and the growing polymer chain (Table 3). From this data it is clearly evident that the N–O ligand in **1d** has reco-ordinated after the reaction of **1c** with further CO and that the carbonyl group of the growing polyketone chain of **1d** does not co-ordinate to the palladium to form a six-membered chelate (such chelates are known to be weak[11]). The ^{31}P NMR reson-

Table 2 Selected ^{1}H, ^{13}C and ^{31}P NMR data for complexes **1a**–**5a** and **1b**–**3b**[a]

Complex	^{1}H NMR δ($PdCH_3$ or $PdCOCH_3$) [J_{HP} in Hz]	^{13}C NMR δ($PdCH_3$ or $PdCOCH_3$) [J_{CP} in Hz]	^{13}C NMR δ(C=O) N–O ligand	^{13}C NMR δ(C=O) $PdCOCH_3$	^{31}P NMR δ
1a	1.09 [d, 1.4]	5.74	171.3		35.8
2a	0.97	3.25	171.0		37.7
3a	0.98	6.33	171.2		35.5
4a	0.90	3.31	170.2		35.4
5a	0.71	−7.59	168.7		39.2
1b	2.25 [d, 1.7]	35.6 [d, 25.0]	170.3	221.0	24.2
2b	2.17	37.0 [d, 28.2]	169.4	221.5	25.4
3b	1.97 (s), 2.29 [d, 1.8][b]	36.9 [d, 24.0]	170.2	224.5	24.1, 24.9[b]

[a] In $CDCl_3$ solution. [b] Two isomers observed in 6:1 ratio.

Table 3 Comparison of spectral data for products from the stepwise insertion reactions

Compound	IR data,[a] ν(C=O)/cm^{-1} N–O Ligand	IR data,[a] ν(C=O)/cm^{-1} Acyl/alkyl	^{13}C NMR,[b] δ(C=O) N–O Ligand	^{13}C NMR,[b] δ(C=O) Acyl/alkyl	^{31}P NMR[b] δ PPh_3
Methyl picolinate	1726		165.3		
1a	1671		171.3		35.8
1b	1672	1720	170.3	221.0	24.2
1c	1733	1637	164.2	232.4	36.2
1d	1670	1715	171.2	221.0	24.7
		1715		206.8	

[a] In CH_2Cl_2 solution. [b] In $CDCl_3$ solution.

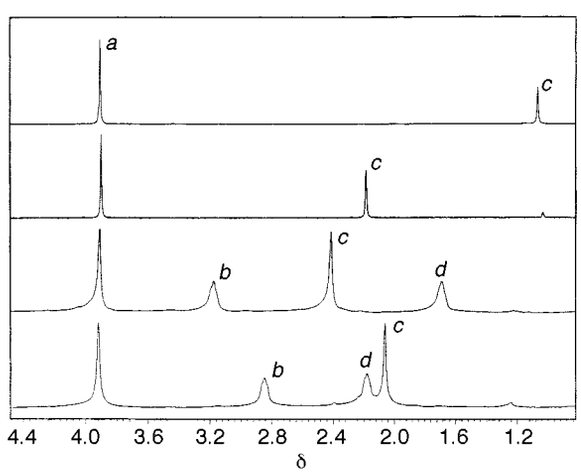


Fig. 2 Proton NMR spectra of the CO/ethylene insertion products **1a**–**1d** [where *a* is the methoxy signal for the N–O ligand; *b* and *d* are the methylene signals for the ethylene inserted products; *c* is the methyl group initially co-ordinated to the palladium (which becomes the acyl methyl then keto methyl)]

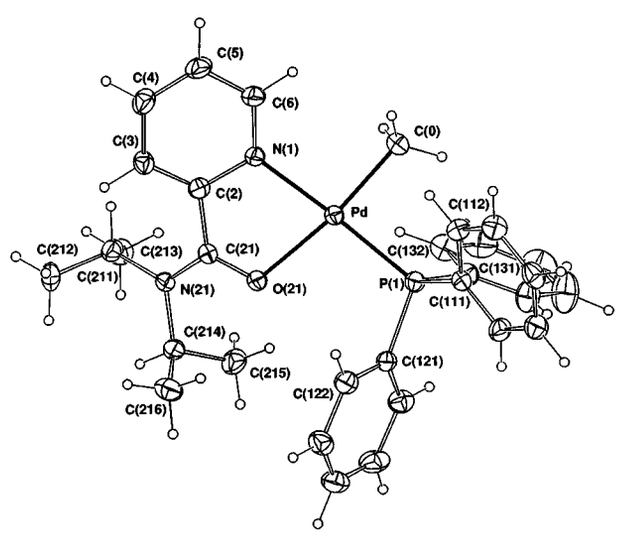


Fig. 3 View normal to the co-ordination plane for the complex **3a**; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å

ance of PPh_3 shifts by ±10 ppm on alternating insertions of CO and ethylene. Fig. 2 shows the characteristic variation of the methyl (*c*) and methylene signals (*b* and *d*) in the ^{1}H NMR spectra of the insertion products, while the methoxy signal (*a*) of the N–O ligand remains virtually unchanged at δ ≈ 4 throughout.

Only one isomer of each of the methyl complexes **1a**–**5a** is observed in the NMR spectra. This is believed to be the P *trans* N isomer for all complexes (see below). The NMR spectra of the acyl complexes **1b** and **2b** also indicate that only one isomer is present in each case. A similar neutral acyl complex, [Pd(COMe)($NC_5H_4CO_2$-2){$P(CH_2Ph)_3$}], was found to exhibit P *trans* N geometry,[19] thus it is to be expected that complexes **1b** and **2b** will have the same arrangement of ligands. Complex **3b** exists as both the P *trans* N and the P *trans* O isomers in a 6:1 ratio. Two peaks due to the methyl protons are observed in the ^{1}H NMR spectrum of **3b**, one at δ 2.29 and one at δ 1.97 which together integrate for three protons (assigned to the acyl group) and have integral ratios of 6:1. This is supported by the ^{31}P NMR spectrum of **3b** which shows two peaks (at δ 24.1 and 24.9), also in a 6:1 ratio. It is likely that the major isomer is the P *trans* N isomer.

Solid-state structures of 3a and 1c

Crystal structure determinations of complexes **1a**[20] and **3a** (Fig. 3) confirm that these complexes exist as the isomer with P *trans* N in the solid state. This geometry is also preferred for analogous neutral complexes [PdMe(PR_3)($NC_5H_4CO_2$-2)].[21] A comparison of important bond lengths is shown in Table 4. The only notable difference in the palladium co-ordination sphere for the two complexes is the longer Pd–P bond for complex **3a** [2.226(2) Å] compared to complex **1a** [2.208(3) Å]. A small decrease in the size of the chelate angle (O–Pd–N) is observed

Table 4 Comparison of selected bond lengths (Å) and angles (°) for complexes **1a**, **3a** and **1c**

	Complex **1a**[20]	Complex **3a**	Complex **1c**
Pd–P	2.208(3)	2.226(2)	2.215(6)
Pd–N	2.141(9)	2.122(4)	2.19(1)
Pd–C	2.02(1)	2.032(5)	2.00(1)
Pd–O	2.180(7)	2.173(4)	2.78(1)[a] 2.16(2)[b]
P–Pd–N	174.7(3)	175.5(1)	97.3(5)
P–Pd–O	99.9(2)	100.1(1)	169.5(3)
P–Pd–C	88.3(3)	88.3(2)	89.5(6)
N–Pd–O	74.8(4)	76.6(1)	91.6(6)
N–Pd–C	96.9(4)	95.3(2)	172.9(8)
O–Pd–C	170.3(2)	170.3(2)	81.4(7)

[a] Distance of axial contact between Pd and the oxygen of the N–O ligand. [b] Bond distance for oxygen of the butanonyl ligand to palladium.

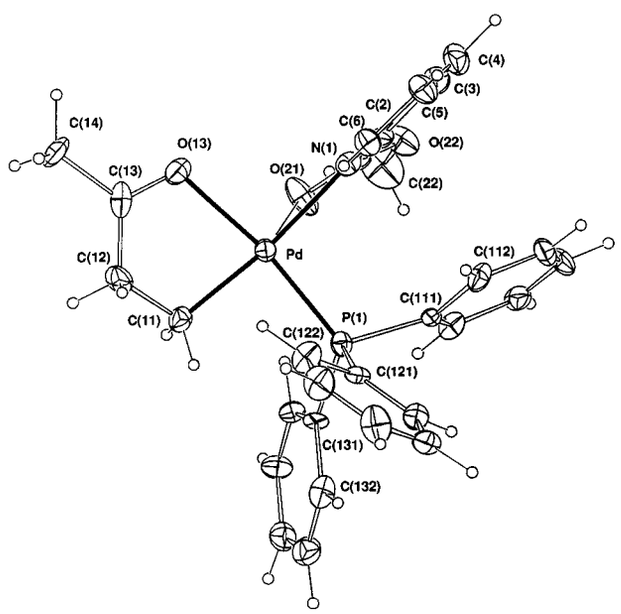


Fig. 4 View of the complex **1c** normal to the co-ordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å

for complex **1a** [74.8(4)°] compared with the picolinamide ligand of complex **3a** [76.6(1)°]. This seems to be compensated for by a smaller N–Pd–C angle for complex **3a** [95.3(2) *cf.* 96.9(4)° for complex **1a**].

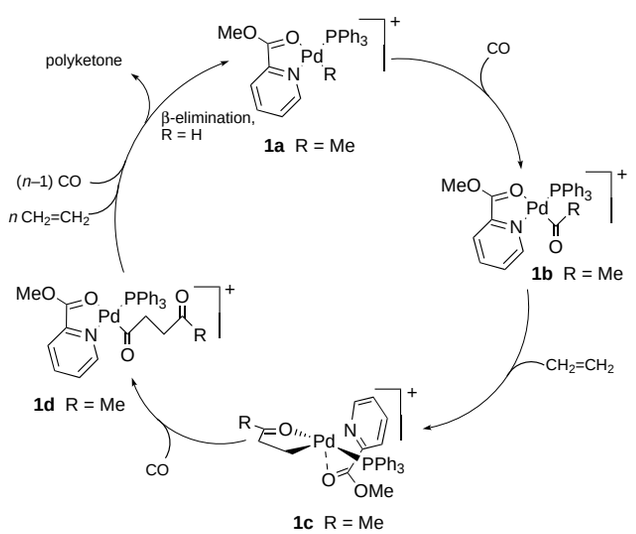
The methyl complex **1a** and the CO and ethylene inserted complex **1c** (Fig. 4) have quite different arrangements of ligands (with N *trans* P for **1a** and N *trans* C for **1c**) (Scheme 3). The Pd–P bond distances are similar for the two complexes [2.208(3) and 2.215(6) Å]. However, there is an increase in the Pd–N bond length for complex **1c** [2.19(1) Å] compared to **1a** [2.141(9) Å] consistent with the stronger *trans* influence of the alkyl group relative to PPh_3.

Complex **1c** has a Pd–C bond length of 2.00(1) Å, which is typical of those found in other alkene inserted complexes.[9,16] However, the Pd–O bond distance [2.16(2) Å] of the chelating alkylketo group reflects the relative *trans* influence of the PPh_3 ligand, being significantly longer than those reported by Markies *et al.*[9] for complexes with bidentate nitrogen ligands [≤2.033(5) Å], but similar to the complex reported by Brumbaugh *et al.* having two PPh_3 ligands [2.114(6) Å].[16] Bond lengths of the carbon–oxygen double bond in analogous complexes in the literature range from 1.236(8) to 1.249(6) Å[9,16] which are close to the value found for complex **1c** [1.23(2) Å].

Table 5 Catalytic results for complexes **1a**–**5a**[a]

Run	Catalyst complex	*n*/mmol	Reaction conditions *T*/°C	*t*/h	Results TON	g(PK) per g(Pd)
1	**1a**	0.097	20	1	41	21
2	**1a**	0.093	20	20	115	60
3	**2a**	0.104	20	1	103	54
4	**2a**	0.090	20	0.5	75	40
5	**2a**	0.092	20	20	146	77
6	**3a**	0.103	20	1	0	0
7	**3a**	0.098	40	22.5	272	143
8	**4a**[b]	0.102	65	2	88	46
9	**4a**	0.103	20	1	111	58
10	**4a**[c]	0.093	20	20	179	94
11	**4a**	0.103	40	1	196	103
12	**4a**	0.103	20	20	411	216
13	**5a**	0.103	20	1	0	0
14	**5a**	0.097	40	1	0	0

[a] Catalytic conditions: 40 mL CH_2Cl_2; initial $p(CO) = 20$ bar; initial $p(CH_2{=}CH_2) = 20$ bar. [b] 50 mL $CHCl_3$. [c] Initial $p(CO) = 5$ bar; initial $p(CH_2{=}CH_2) = 25$ bar.

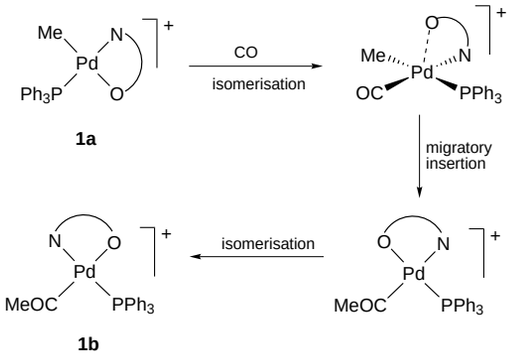


Scheme 3 Proposed catalytic cycle for complex **1a** showing the first three isolated intermediates (**1b**–**1d**)

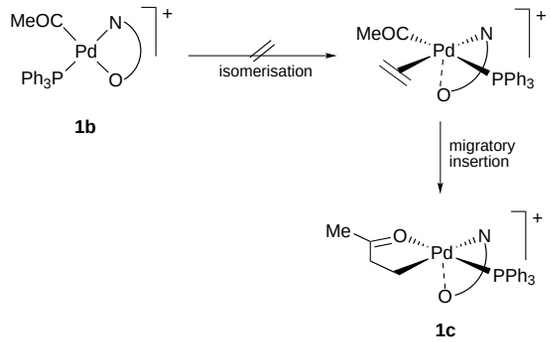
Copolymerisation of CO and ethylene

The results of the copolymerisation experiments are given in Table 5, with activities expressed both as TON (*i.e.* moles of substrate converted per moles of Pd) and also in g of polyketone per g of palladium. Complexes **1a**–**4a** are all active catalysts for the copolymerisation of CO and ethylene, but the activity is low in comparison with some reported catalysts.[4,5,22–28] Analysis of the solvent by GC after the removal of all solid product showed the presence of only trace amounts of oligomeric products when complexes **3a**–**5a** were used. The co-oligomers were identified by GC–MS and are identical to those reported by Keim *et al.*,[29] obtained using cationic palladium catalysts with P–O ligands.

Under the conditions used, the activity of the complexes towards polyketone formation decreases in the order: **4a** > **2a** > **1a** > **3a** ≫ (**5a** = 0). The 6-methyl substituent on the pyridyl ring of the N–O ligand has an activating effect and both complexes **2a** and **4a** are substantially more active than the respective complexes with unsubstituted N–O ligands (**1a** and **3a**). The higher activity of complexes **2a** and **4a** can be explained by sterically induced weakening of the Pd–N bond by the 6-methyl substituent, facilitating isomerisation of the complex during catalysis (see later discussion under Mechanism). The 6-methyl substituent also leads to decreased stability in



Scheme 4 Pathway for CO insertion



Scheme 5 Mechanism for ethylene insertion

complexes **2a** and **4a** compared to complexes **1a** and **3a**. Increasing the reaction temperature results in an increase in the activity of complexes **3a** (runs 6 and 7) and **4a** (runs 8, 9 and 11), but the higher temperature also has a detrimental effect on catalyst stability.

In contrast to complex **4a**, which contains triphenylphosphine, the complex **5a** containing the highly basic tricyclohexylphosphine as a ligand has no observable catalytic activity. The inhibitory effect of PCy_3 in carbonylation reactions of related neutral complexes has previously been noted.[21] The possible reason for this effect is described below in the discussion of the mechanism.

Mechanism

Recently, we presented a preliminary report on the stepwise migratory insertion of CO and ethylene into the catalytically active complex **1a** (Scheme 3).[12] Reaction of CO with **1a** yields the acyl complex $[Pd(COMe)(NC_5H_4CO_2Me\text{-}2)(PPh_3)]BF_4$ **1b**, which has been identified spectroscopically. Subsequent reaction of **1b** with ethylene yields an isolable intermediate, $[Pd(CH_2CH_2COMe)(NC_5H_4CO_2Me\text{-}2)(PPh_3)]BF_4$ **1c**, for which the crystal structure was determined. This five-co-ordinate, square pyramidal intermediate has the weakly interacting methyl picolinate carbonyl oxygen in an apical position. The methyl picolinate oxygen has apparently been displaced from the square plane by the more strongly co-ordinating alkyl carbonyl oxygen of the growing polyketone chain. In the solid state, complex **1c** exists only as the isomer having P *cis* N, in contrast to complexes **1a** and **1b** (both P *trans* N). This result shows clearly that isomerisation has also occurred during the migratory insertion process, thus converting **1b** into **1c**. Addition of further CO to intermediate **1c** leads to formation of a new acyl complex **1d**. Spectroscopic evidence supports a P *trans* N geometry for **1d** (an analogue of **1b**), which indicates that isomerisation has again occurred during the migratory insertion of CO into the Pd–alkyl bond.

This study of the stepwise insertion of CO and ethylene demonstrates that isomerisation is a general step in the copolymerisation reaction with complex **1a** as the catalyst. Such a pathway is likely to be pertinent to other systems containing chelate ligands with different donor groups. Supporting evidence for the detailed mechanism comes from a recent theoretical study in which the model cationic complex, $[Pd(CH_3)(HN{=}CHCHO)(PH_3)]^+$ was investigated.[30,31] *Ab initio* calculations indicate that the lowest energy pathway for the carbonylation of the model complex occurs *via* a five-co-ordinate, square pyramidal intermediate (akin to the isolated complex **1c**) with *trans-cis* isomerisation (of P and N) preceding the insertion step (Scheme 4).[30,31] A similar low energy pathway involving *trans* ⟶ *cis* isomerisation of the P and N ligands was also noted for the insertion of ethylene into the resulting Pd–acyl bond (Scheme 5).[31] Importantly, the predicted structure of the intermediate formed following ethylene insertion is a square pyramidal complex directly analogous to **1c**. The calculated value for the long apical Pd–O bond is 2.76 Å, compared with 2.78(1) Å obtained in the experimental work.

The only products observed from the carbonylation of complexes **1a** and **2a** were the P *trans* N acyl complexes **1b** and **2b** respectively, while ^1H NMR and ^{31}P NMR data suggest that **3b** is a 6:1 mixture of the *trans* and *cis* isomers. It is difficult to account for the existence of the P *cis* N isomer of **3b** when complexes **1b** and **2b** only have a *trans* geometry, given the small differences in ligand environment of these complexes. Calculations indicate that although the P *cis* N isomer is the initial product of the CO migratory insertion step, the P *trans* N acyl isomer is thermodynamically preferred (Scheme 4).[31] A similar isomerisation process has been observed previously by Markies *et al.* in the neutral Pd^{II} acyl complexes [Pd(COMe)(bipy)X] (X = Cl or Br).[9] They found that irradiation of either of the inequivalent H^6 protons of bipy resulted in the disappearance of the ^1H NMR signal of the other. Such isomerisation processes are common for square-planar complexes.[4,32]

It was noted above that more strongly co-ordinating phosphines such as tricyclophosphine deactivate complexes of type **1a**. From experimental data alone this behaviour is hard to explain. It may be expected that a stronger donor phosphine would further weaken the *trans* ligand and in fact promote the catalytic reaction. That this does not happen may be understood by further reference to the *ab initio* modelling studies. Calculations show that more strongly co-ordinating phosphines such as PCy_3 deactivate complexes of this type by preventing the necessary isomerisation of the complex during reaction with CO and ethylene.[30] A low energy pathway for isomerisation which proceeds *via* a weakening or elongation of the Pd–P bond was identified. If this elongation is impeded, *i.e.* by strong co-ordination of the phosphine (as in the case of a more basic phosphine) the barrier to isomerisation becomes too great. If isomerisation cannot take place then migratory insertion cannot proceed.

The proposed mechanism for the copolymerisation of CO and ethylene catalysed by complexes of type **1a**–**4a** is presented in Scheme 3. The first step, the carbonylation of the methylpalladium complex to give an acyl complex, occurs readily for all complexes and is therefore not the rate-determining step in the cycle. The second CO insertion reaction is much slower than the first (2 h *versus* 10 min for completion at room temperature and 1 atm pressure). The slower reaction is probably due to the energy required to break the stronger butanonyl chelate in complex **1c** which occurs during insertion of the second CO. However, the slowest step in the overall reaction is ethylene insertion into the palladium–acyl bond (*ca.* 3 h), which is generally believed to be the rate-determining stage in polyketone formation.[33] It is interesting to consider the stepwise insertion process as a competitive switching of one carbonyl donor for another in which firstly one chelate co-ordinates strongly and then the other.

Experimental

Reagents

All reagents were used as received unless otherwise stated. High purity nitrogen was further dried and deoxygenated over 4 Å molecular sieves and BASF R 3-11 catalyst at 135 °C. Manipulations of all complexes were carried out using carefully dried glassware employing standard vacuum line and Schlenk techniques under a dry nitrogen atmosphere. All solvents were dried and purified by standard methods and freshly distilled under nitrogen before use. Methyl 6-methylpicolinate was prepared by the method given by Mathes *et al.*[34] The compound [PdMeCl(COD)] was prepared by the method described by Rülke *et al.*[35] The dimeric complex $[PdMe(\mu\text{-}Cl)PPh_3]_2$ was prepared according to the method of Ladipo and Anderson,[36] with the exception that CH_2Cl_2 was used as the solvent instead of benzene. The complex $[PdMe(\mu\text{-}Cl)(PCy_3)]_2$ was prepared by a similar method to that employed for $[PdMe(\mu\text{-}Cl)(PPh_3)]_2$. However, the reaction was much slower, needing 20 h to reach completion. The precipitate was too fine to collect by filtration, therefore it was washed with 5 × 5 mL hexane and dried under vacuum. The product was a very pale yellow powder insoluble in all common solvents (yield: 93%) (Found: C, 52.51; H, 8.35. Calc. for $C_{19}H_{36}ClPPd$: C, 52.28; H, 8.32%).

Nuclear magnetic resonance spectra were recorded at 22 °C (unless otherwise indicated) on a Bruker AM-300 spectrometer at 300.13 (^{1}H), 75.48 (^{13}C) and 121.50 MHz (^{31}P) or a Varian Gemini-200 spectrometer at 199.98 MHz (^{1}H). Chemical shifts (δ) are reported in ppm relative to internal $SiMe_4$ (^{1}H, ^{13}C), or to external 85% H_3PO_4 (^{31}P). Infrared (IR) spectra were recorded in absorbance units on a Bruker IFS-66 FTIR spectrometer; KBr disks and CH_2Cl_2 or $CDCl_3$ solutions were used in the mid IR range (400–4000 cm^{-1}). Microanalyses were performed by the Central Science Laboratory, University of Tasmania, using a Carlo Erba EA1108 Elemental Analyser.

Crystallography

Structure determination. 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; graphite 'single crystal' monochromator; Mo-Kα radiation, λ = 0.710 73 Å); 5859 independent reflections were obtained without significant crystal decomposition, 3325 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement ($n_v = 397$) after Gaussian absorption correction, and solution of the structure by the heavy-atom method. 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. Difference map residues were modelled on dichloromethane of solvation, site occupancy set at 0.5 after trial refinement (final $|\Delta\rho_{max}|$ 0.4 e $Å^{-3}$). Conventional residuals R ($\Sigma\Delta|F|/\Sigma|F_o|$), R' $(\Sigma w\Delta^2/\Sigma|F_o|^2)^{\frac{1}{2}}$ on $|F|$ were 0.039, 0.038 $[S = \Sigma w\Delta^2/(n-p)^{\frac{1}{2}} = 1.6]$ at convergence ($\Delta/\sigma_{max,mean} = 0.1$, 0.004), 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,[37] neutral-atom complex scattering factors being employed.

Crystal data. $C_{31}H_{36}BF_4N_2OPPd\cdot0.5CH_2Cl_2$, $M = 719.29$, orthorhombic, space group *Pbca*, $a = 18.788(7)$, $b = 18.993(4)$, $c = 18.700(7)$ Å, $U = 6673(4)$ $Å^3$ ('calibrated' on {9 9 9}), D_c ($Z = 8$) = 1.43$_2$ g cm^{-3}, $F(000) = 2936$, $\mu_{Mo} = 7.3$ cm^{-1}, (yellow) specimen, 0.32 × 0.45 × 0.21 mm, $A^*_{min,max} = 1.16$, 1.22.

CCDC reference number 186/879.

See http//www.rsc.org/suppdata/dt/1998/1137/ for crystallographic files in .cif format.

Synthesis and characterisation of ligands and complexes

***N*,*N*-Diisopropylpicolinamide.** This compound was prepared by an adaption of the synthesis given for *N*,*N*-diisopropylnicotinamide by Swain and Naegele.[38] Picolinic acid (6.16 g, 50 mmol) and freshly distilled thionyl chloride (18 mL, 250 mmol) was refluxed for 1 h. Excess $SOCl_2$ was removed by vacuum distillation to leave a burgundy solid. To this was added dry benzene (30 mL), pyridine (8 mL, 100 mmol) and diisopropylamine (21 mL, 150 mmol). The reaction mixture was refluxed for 15 min and left to stir overnight. This mixture was filtered and the residue washed with benzene. The filtrate was made basic with aqueous NaOH and the aqueous layer extracted with three portions of diethyl ether. The combined extracts were washed with water and dried over $MgSO_4$. After removal of the solvent the remaining brown liquid was fractionally distilled under vacuum. The first fraction (a pale yellow solid) was collected at 72–78 °C (10^{-2} atm) and recrystallised from heptane to give a white solid. IR (CH_2Cl_2): ν(C=O) 1634 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.58 (ddd, 1 H, $J = 4.9$, $J = 1.7$, $J = 1.1$, C_5H_4N), 7.77 (dt, 1 H, $J = 7.7$, $J = 1.7$, C_5H_4N), 7.44 (td, 1 H, $J = 7.7$, $J = 1.1$, C_5H_4N), 7.30 (ddd, 1 H, $J = 7.6$, $J = 4.9$, $J = 1.1$, C_5H_4N), 3.83 (spt, $J = 6.6$, 1 H, NCH), 3.56 (spt, 1 H, $J = 6.6$, NCH), 1.57 [d, 6 H, $J = 6.6$ Hz, $CH(CH_3)_2$], 1.18 [d, 6 H, $J = 6.6$ Hz, $CH(CH_3)_2$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.6 (C=O), 156.5, 148.6, 136.9, 123.6, 121.8 (C_5H_4N), 50.7 (NCH), 46.0 (NCH), 20.7 [$CH(CH_3)_2$], 20.5 [$CH(CH_3)_2$].

6-Methyl-*N*,*N*-diisopropylpicolinamide. The method of Swain and Naegele for the synthesis of *N*,*N*-diethylpicolinamide hydrochloride was used.[38] Thus 6-methylpicolinic acid (5.46 g, 40 mmol) in 30 mL toluene was heated to 80 °C in the presence of diisopropylamine (14.44 g, 140 mmol). At this temperature P_2O_5 (9.3 g, 65 mmol) was added in three portions, each 10 min apart. After refluxing overnight, the dark brown reaction mixture was treated with base (10% by weight NaOH solution), and extracted with a 1:1 solution of diethyl ether and toluene. The dark brown solid isolated from these extracts was recrystallised several times with hexane to give a white solid. IR (CH_2Cl_2): ν(C=O) 1630 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.64 (t, 1 H, $J = 7.7$, C_5H_3N), 7.20 (d, 1 H, $J = 7.7$, C_5H_3N), 7.12 (d, 1 H, $J = 7.7$, C_5H_3N), 3.78 (spt, $J = 6.6$, 1 H, NCH), 3.55 (spt, 1 H, $J = 6.6$, NCH), 2.56 (s, 3 H, $C_5H_3NCH_3$), 1.56 [d, 6 H, $J = 6.6$, $CH(CH_3)_2$], 1.18 [d, 6 H, $J = 6.6$ Hz, $CH(CH_3)_2$]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6 (C=O), 157.2, 155.5, 136.6, 122.7, 118.2 (C_5H_3N), 50.2 (NCH), 45.5 (NCH), 24.0 ($C_5H_3NCH_3$), 20.2 {$N[CH(CH_3)_2]_2$}.

Preparation of complexes 1a–5a. The preparation of complex **1a** was reported earlier.[20] Complexes **2a**–**5a** were prepared similarly by reacting 2 equivalents of the N–O ligand and $AgBF_4$ with 1 equivalent of $[PdMeL(\mu\text{-}Cl)]_2$ (L = PPh_3 or PCy_3) in CH_2Cl_2 at room temperature. Crystals suitable for an X-ray structure determination of **3a** were obtained by layering diethyl ether onto a CH_2Cl_2 solution of **3a** at room temperature.

$[Pd(Me)(PPh_3)(NC_5H_3CO_2Me\text{-}2\text{-}Me\text{-}6)]BF_4$ **2a**. Yellow solid (Found: C, 51.13; H, 4.50; N, 2.37. Calc. for $C_{27}H_{27}BF_4NO_2PPd\cdot0.2CH_2Cl_2$: C, 51.15; H, 4.32; N, 2.19%). IR (CH_2Cl_2): ν(C=O) 1672 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.09–8.02 (m, 3 H, C_5H_3N), 7.67–7.27 (m, 15 H, C_6H_5), 3.81 (s, 3 H, OCH_3), 2.80 (s, 3 H, $C_5H_3NCH_3$), 0.97 (s, 3 H, $PdCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0 (C=O), 163.0, 146.7, 140.7, 134.7–129.4, 126.0 (C_6H_5 and C_5H_3N), 55.7 (OCH_3), 26.5 ($C_5H_3NCH_3$), 3.25 ($PdCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 37.7.

$[Pd(Me)(PPh_3)(NC_5H_4CONPr^i_2\text{-}2)]BF_4$ **3a**. Yellow solid (yield: 87%) (Found: C, 55.22; H, 5.20; N, 4.17. Calc. for $C_{31}H_{36}BF_4NOPPd\cdot0.5CH_2Cl_2$: C, 55.01; H, 5.36; N, 4.14%). IR (CH_2Cl_2): ν(C=O) 1569 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (br m, 1 H, C_5H_4N), 8.44 (br m, 1 H, C_5H_4N), 8.01 (br m, 1 H, C_5H_4N), 7.88 (br m, 1 H, C_5H_4N), 7.7–7.4 (m, 15 H,

C_6H_5), 4.58 (br m, 1 H, NCH), 3.55 (br m, 1 H, NCH), 1.39 [br s, 6 H, $CH(CH_3)_2$], 0.98 [br s, 9 H, $CH(CH_3)_2$ and $PdCH_3$]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2 (C=O), 151.5, 149.0, 141.9, 135.5–128.8, 127.4 (C_6H_5 and C_5H_4N), 54.2, 49.1 (NCH), 21.5, 19.9 [$NCH(CH_3)_2$], 6.33 ($PdCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 35.5.

[Pd(Me)(PPh_3)($NC_5H_3CONPr^i_2$-2-6-Me)]BF_4 **4a**. Yellow solid (yield: 90%). IR (CH_2Cl_2): ν(C=O) 1572 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.10 (t, 1 H, J = 7.8, C_5H_3N), 7.7–7.4 (m, 17 H, C_6H_5 and C_5H_3N), 4.38 (br m, 1 H, NCH), 3.57 (br m, 1 H, NCH), 2.82 (s, 3 H, $C_5H_3NCH_3$), 1.4–1.1 {m, 12 H, $[CH(CH_3)_2]_2$}, 0.90 (d, 3 H, J = 2.3 Hz, $PdCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2 (C=O); 161.9, 151.9, 140.1, 134.2–128.6, 122.3 (C_6H_5 and C_5H_3N), 53.4, 47.7 (NCH), 26.3 ($C_5H_3NCH_3$), 20.7, 19.7 [$NCH(CH_3)_2$], 3.31 ($PdCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 35.4.

[Pd(Me)(PCy_3)($NC_5H_4CONPr^i_2$-2-6-Me)]BF_4 **5a**. Yellow solid (yield: 95%) (Found: C, 49.00; H, 7.70; N, 3.44. Calc. for $C_{32}H_{56}BF_4NOPPd\cdot1.25CH_2Cl_2$: C, 48.99; H, 7.23; N, 3.44%), IR (CH_2Cl_2): ν(C=O) 1595 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.02 (t, 1 H, J = 7.3, C_5H_4N), 7.57 (t, 2 H, J = 7.6 Hz), 3.87 [br m, 2 H, $N(CH)_2$], 2.79 (s, 3 H, $C_5H_4NCH_3$), 2.1–1.1 {br m, 45 H, C_6H_{11} and $[CH(CH_3)_2]_2$}, 0.71 (s, 3 H, $PdCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7 (C=O), 161.1, 153.4, 140.1, 127.3, 120.1 (C), 52.1, 46.7 (NCH), 32.5–25.6 (C_6H_{11} and $C_5H_4NCH_3$), 20.7 {$N[CH(CH_3)_2]_2$}, −7.59 ($PdCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 39.2.

Carbonylation of complexes 1b–3b. The acyl complexes **1b**–**3b** were prepared by bubbling CO for 10–15 min through a CH_2Cl_2 or $CDCl_3$ solution of complexes **1a**–**3a**. The yields appear to be quantitative on the basis of NMR spectroscopy. The preparation of complex **1b** has been previously reported.[20]

[Pd(COMe)(PPh_3)($NC_5H_3CO_2Me$-2)]BF_4 **1b**. IR (CH_2Cl_2): ν(C=O) 1721 cm^{-1} (PdCOMe), 1673 cm^{-1} (CO_2Me). ^1H NMR (300 MHz, $CDCl_3$): δ 8.16 (br s, 1 H, C_5H_3N), 7.70–7.43 (m, 15 H, C_6H_5), 3.99 (br s, 3 H, OCH_3), 2.25 (d, 3 H, J = 1.7 Hz, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.0 (PdCO), 170.3 (CO_2Me), 150.2, 145.3, 141.3, 134.1–127.7 (C_6H_5 and C_5H_3N), 55.5 (OCH_3), 35.6 (d, J = 25 Hz, $COCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.2.

[Pd(COMe)(PPh_3)(6-Me-$NC_5H_3CO_2Me$-2)]BF_4 **2b**. IR (CH_2Cl_2): ν(C=O) 1720 cm^{-1} (PdCOMe), 1673 cm^{-1} (CO_2Me). ^1H NMR (300 MHz, $CDCl_3$): δ 8.13–7.28 (m, 18 H, C_6H_5 and C_5H_3N), 3.83 (s, 3 H, OCH_3), 2.70 (s, 3 H, $C_5H_3NCH_3$), 2.17 (s, 3 H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.5 (PdCO), 169.4 (CO_2Me), 161.7, 146.1, 141.3, 139.4–125.8 (C_6H_5 and C_5H_3N), 55.4 (OCH_3), 37.0 (d, J = 28.2 Hz, $COCH_3$), 26.7 ($C_5H_3NCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 25.4.

[Pd(COMe)(PPh_3)($NC_5H_4CONPr^i_2$-2)]BF_4 **3b**. IR (CH_2Cl_2): ν(C=O) 1707 cm^{-1} (PdCOMe), 1569 cm^{-1} (CON). ^1H NMR (300 MHz, $CDCl_3$): δ 8.31 (t, 2 H, J = 7.8, C_5H_4N), 7.93 (s, 1 H, C_5H_4N), 7.74–7.43 (m, 17 H, C_6H_5 and C_5H_4N), 4.62 (br m, 1 H, NCH), 3.55 (br m, 1 H, NCH), 2.29 (d, J = 1.8 Hz), 1.97 (s) (peak integral 6:1, 3 H, $COCH_3$), 1.7–0.9 {br m, 12 H, $[CH(CH_3)_2]_2$}. ^{13}C NMR (75 MHz, $CDCl_3$): δ 224.5 (PdCO), 170.2 (CO_2Me), 150.3, 140.9, 134.1–126.0 (C_6H_5 and C_5H_4N), 53.4, 48.3 (NCH), 36.9 (d, J = 24 Hz, $PdCOCH_3$), 20.8, 19.6 [$NCH(CH_3)_2$]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.9, 24.1 (peak integrals 1:6).

Carbon monoxide and ethylene insertion products. The preparation and selected spectroscopic data of complexes **1b**–**1d** has been reported earlier.[12,20] The spectroscopic data are reported here in full for complexes **1c** and **1d**.

[Pd(CH_2CH_2COMe)($NC_5H_4CO_2Me$-2)(PPh_3)]BF_4 **1c**. Yellow solid (Found: C, 52.71; H, 4.18; N, 2.14. Calc. for $C_{29}H_{29}BF_4NO_3PPd$: C, 52.48; H, 4.40; N, 2.11%). IR (CH_2Cl_2): ν(C=O) 1733 cm^{-1} (CO_2Me), 1637 cm^{-1} ($PdCH_2CH_2COMe$). ^1H NMR (300 MHz, $CDCl_3$): δ 9.1–8.1 (br m, 1 H, C_5H_4N), 7.88 (s, 1 H, C_5H_4N), 7.7–7.3 (m, 17 H, C_6H_5 and C_5H_4N), 3.93 (s, 3 H, OCH_3), 3.17 (t, 2 H, J = 6.0, $PdCH_2CH_2$), 2.41 (s, 3 H, $COCH_3$), 1.72 (dt, 2 H, J = 6.0, J = 2.7 Hz, $PdCH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 232.4 (COMe), 164.2 (CO_2Me), 152.2, 145.8, 138.9, 134.1–128.7, 127.7 (C_6H_5 and C_5H_4N), 53.3 (OCH_3), 51.0 ($PdCH_2CH_2$), 27.8 ($COCH_3$), 23.0 ($PdCH_2$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 36.2.

[Pd($COCH_2CH_2COMe$)($NC_5H_4CO_2Me$-2)(PPh_3)]BF_4 **1d**. Yellow $CDCl_3$ solution. IR (CH_2Cl_2): ν(C=O) 1715 cm^{-1} (PdCO and COMe), 1670 cm^{-1} (CO_2Me). ^1H NMR (300 MHz, $CDCl_3$): δ 8.71 (s, 1 H, C_5H_4N), 8.3 (m, 2 H, C_5H_4N), 7.96 (m, 1 H, C_5H_4N), 7.8–7.3 (m, 15 H, C_6H_5), 3.93 (s, 3 H, OCH_3), 2.86 (t, 2 H, J = 4.8, CH_2CH_2COMe), 2.18 (t, 2 H, J = 4.8 Hz, $PdCOCH_2CH_2$), 2.07 (s, 3 H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.0 (PdCO), 206.8 (COMe), 171.2 (CO_2Me), 145.2, 141.6, 134.2–127.9, 127.7 (C_6H_5 and C_5H_4N), 55.8 (OCH_3), 44.0 (d, J = 24 Hz, $PdCOCH_2$), 37.9 (CH_2COMe), 29.6 ($PdCOCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.7.

Copolymerisation of CO and ethylene

A solution of the appropriate complex (0.01 mmol) in CH_2Cl_2 (40 mL) was transferred to a 350 mL V4A steel autoclave, which was equipped with a glass inlet and a magnetic stirring bar. For experiments at higher temperatures, the autoclave was heated in an oil bath and the temperature allowed to equilibrate before pressurising the vessel. With continuous stirring, the autoclave was pressurised with 20 bar CO and then ethylene until a total pressure of 40 bar was reached. After allowing the reaction to proceed for the appropriate time the excess gases were vented, and the product mixture filtered to remove polyketone which was washed with CH_2Cl_2, dried and weighed. The filtrate was analysed by GC. The polyketone has a strictly alternating structure as confirmed by ^{13}C NMR (CF_3CO_2H–C_6D_6) and microanalysis.

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