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Synthesis and structure of Pd(II) complexes containing chelating (phosphinomethyl)oxazoline *P*,*N*-type ligands; copolymerisation of ethylene/CO †

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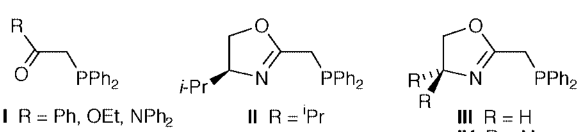
The ligands (2-oxazoline-2-ylmethyl)diphenylphosphine (**III** or PCH_2ox) and (2-oxazoline-2-ylmethyl-4,4-dimethyl)diphenylphosphine (**IV** or PCH_2ox^{Me2}) have been used as chelates towards Pd(II) methyl complexes. The complexes [PdMe(Cl)(PCH_2ox)] **2a** and [PdMe(Cl)(PCH_2ox^{Me2})] **2b** were obtained from [PdMe(Cl)(cod)] (cod = cycloocta-1,5-diene) in 83% and 94% yield, respectively, and compared to [$PdCl_2$(PCH_2ox^{Me2})] **1** which was characterised by X-ray diffraction. A series of cationic methyl complexes obtained by chloride abstraction in the presence of MeCN, SMe_2, $P(OPh)_3$ or no added donor except the counter ion were prepared in order to evaluate their catalytic performances in ethylene/CO copolymerisation.

Introduction

In coordination and organometallic chemistry the use of heteroditopic type ligands provides several advantages. When they behave as hemilabile ligands by reversible dissociation of one arm of the ligand, they can selectively liberate a coordination site at the metal and thus favor the formation and stabilization of intermediate species.[1–3] As static chelates, such ligands can give rise to selective metal–ligand interactions that may control the reactivity at the metal site owing to the different (stereo)electronic properties of the donor groups. In many reactions catalysed by late transition metals, the precatalyst is stabilized by ligands having phosphorus donor atoms which are compatible with a wide variety of metal oxidation states and therefore with redox changes that may occur.[4] In the past 15 years, several groups including our laboratory have investigated the stoichiometric and catalytic properties of complexes containing *P*,*O* ligands of type **I**.[1,2,5–8]



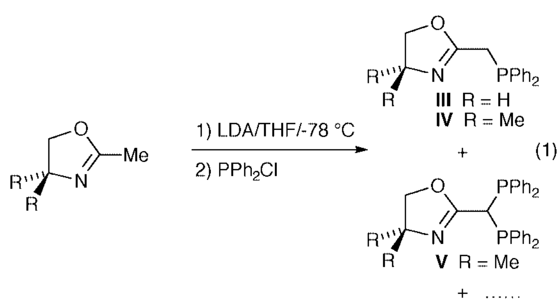
I R = Ph, OEt, NPh_2 **II** R = ^iPr **III** R = H **IV** R = Me

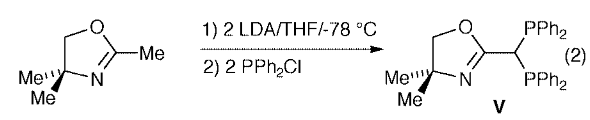
Even if nitrogen donor ligands have been less extensively developed for synthetic organic catalytic applications compared to phosphorus, they perform equally well or better in some reactions than their phosphine analogues.[9] Unfortunately, they have the disadvantage of being often less stabilising under catalytic conditions when coordinated to late transition metals. Designing heteroditopic ligands which bear both phosphorus and nitrogen donors should thus lead to a rich chemistry. In fact such hybrid *P*,*N* type ligands have been reported to confer high reactivity and selectivity in some catalytic reactions.[10–16] Recently the groups of Helmchen and Pfaltz have synthesized and used the *P*,*N* ligand **II** that can form five-membered ring chelates, in allylic alkylation with Pd[17] and W.[18] This prompted our synthesis and study of related phosphine oxazoline type ligands such as **III** and **IV** and the investigation of another C–C coupling reaction of current interest, the copolymerisation of ethylene and CO.

Results

Ligands

We first attempted the synthesis of the ligands (2-oxazoline-2-ylmethyl)diphenylphosphine (**III** or PCH_2ox) and (2-oxazoline-2-ylmethyl-4,4-dimethyl)diphenylphosphine (**IV** or PCH_2ox^{Me2}) following the methodology previously developed for the *P*,*O* ligands **I**.[19] However, the reaction was not selective and the desired product was formed in only *ca.* 10% yield [eqn. (1)]. The major by-product is a bisphosphino-oxazoline, **V** (see Discussion), which we have synthesized independently by reaction of the 2,4,4-trimethyl-2-oxazoline with two equiv. LDA and subsequent reaction with two equiv. PPh_2Cl [eqn. (2)]. The ^1H





† Part of the Doctoral thesis of F. N. Dedicated to Professor Y. Jeannin on the occasion of his retirement, with our best wishes.
‡ Deceased, October 27, 1998.

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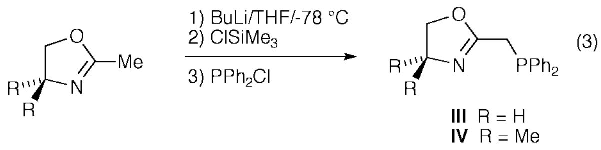
NMR spectrum of compound **V** shows three singlets at δ 0.75, 3.20 and 4.30 for the $NCMe_2$, OCH_2 and P_2CH protons, respectively. The presence of the two phosphorus atoms on the same carbon was confirmed by $^{13}C\{^1H\}$ NMR spectroscopy where the P_2CH carbon appears as a triplet ($^1J_{PC}$ = 27.7 Hz). This ligand was not further used in this work.

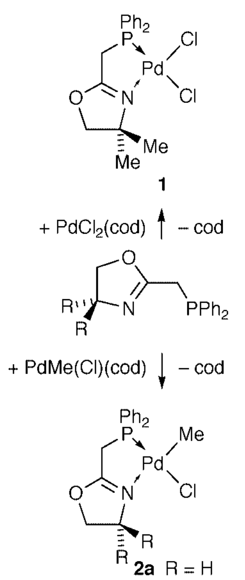
We then adapted a one-pot procedure recently described by Sprinz and Helmchen for **II** which consists first of the deprotonation of the corresponding 2-methyl-2-oxazoline in THF at −78 °C, followed by the addition at this temperature of $ClSiMe_3$ to form the *N*-silyl derivative and finally reaction with PPh_2Cl [eqn. (3)].[17] To the best of our knowledge this is the first



time the procedure has been described in full detail. The ^1H NMR spectra of **III** and **IV** show no unusual pattern and their PCH_2 protons appear as a broad singlet rather than a doublet and their $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ −17.3 and −17.5, respectively. The IR spectra contain the characteristic $\nu_{C=N}$ band for the oxazoline at 1660 cm^{-1}. Ligand **III** is a fairly air-stable white powder which is best kept under inert atmosphere and **IV** is a pale yellow oil that can be exposed to air for short periods of time.

Neutral complexes

Reaction of one equiv. of **IV** with $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) afforded $[PdCl_2(PCH_2ox^{Me2})]$ **1** in almost quantitative yield (Scheme 1). Upon coordination of the ligand,



Scheme 1

the PCH_2 protons give rise to a doublet in the ^1H NMR spectrum (δ 3.40, $^2J_{PH}$ = 10 Hz) and the $\nu_{C=N}$ absorption shifts to 1622 cm^{-1}. Other characterizing data are given in the Experimental section. For comparative purposes, the crystal structure of $[PdCl_2(PCH_2ox^{Me2})]$ was determined in $\mathbf{1}\cdot 2CDCl_3$ since $[W(\eta^3\text{-}C_3H_5)Cl(CO)(\mathbf{II})]$ is the only other structurally characterized complex with a five-membered phosphine-oxazoline-type ligand (search on the Cambridge Structural Data Base). A view of the structure is shown in Fig. 1 and selected distances and angles are given in Table 1.

Table 1 Selected bond distances (Å) and angles (°) for complex $[PdCl_2(PCH_2ox^{Me2})]$ in $\mathbf{1}\cdot 2CDCl_3$

Pd(1)–Cl(1)	2.3836(8)	P(1)–C(4)	1.840(3)
Pd(1)–Cl(2)	2.2894(9)	C(4)–C(1)	1.480(4)
Pd(1)–P(1)	2.2128(8)	C(1)–N(1)	1.276(4)
Pd(1)–N(1)	2.058(2)	C(1)–O(1)	1.326(3)
Cl(1)–Pd(1)–Cl(2)	90.75(3)	Pd(1)–N(1)–C(1)	118.8(2)
Cl(1)–Pd(1)–N(1)	97.22(7)	N(1)–C(1)–C(4)	125.0(3)
Cl(1)–Pd(1)–P(1)	177.78(4)	C(1)–C(4)–P(1)	106.9(2)
Cl(2)–Pd(1)–N(1)	171.90(7)	C(4)–P(1)–Pd(1)	102.6(1)
Cl(2)–Pd(1)–P(1)	88.29(3)	O(1)–C(1)–N(1)	118.3(3)
P(1)–Pd(1)–N(1)	83.69(7)	O(1)–C(1)–C(4)	116.7(3)

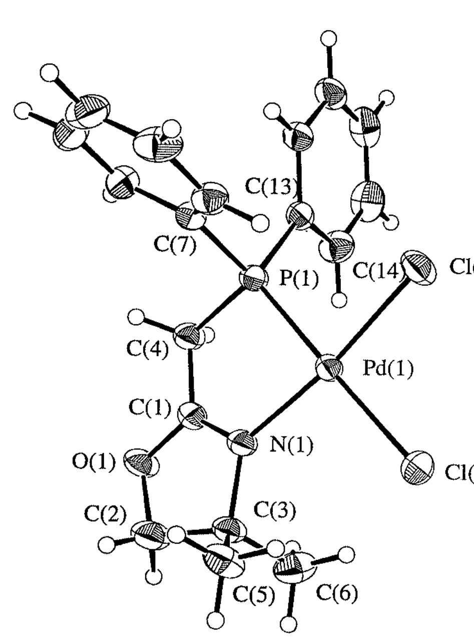


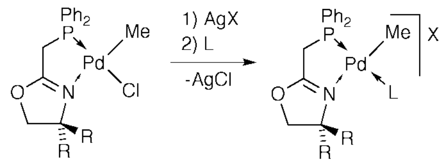
Fig. 1 ORTEP view of the molecular structure of $[PdCl_2(PCH_2ox^{Me2})]$ in $\mathbf{1}\cdot 2CDCl_3$.

The Pd–Cl bond distances are in the expected range and that *trans* to the P atom is longer than that *trans* to N, consistent with the respective *trans* influences of the P and N donor atoms.[20–22] The P,N chelate bite angle is equal to 83.69(7)° and is in accordance with other five-membered phosphorus, nitrogen chelates [82.5(2)°].[22] As expected on going from this five-membered ring chelate to a six-membered ring as in $[Pd(\eta^3\text{-}C_3H_5)L](PF_6)$ (L = phosphinoaryloxazoline) or $[PdCl_2L']$ derivatives [L′ = diphosphinobis(oxazolinyl)ferrocene], the chelate bite angle increases by about 5°.[21,23]

The complexes $[PdMe(Cl)(PCH_2ox)]$ **2a** and $[PdMe(Cl)(PCH_2ox^{Me2})]$ **2b** were similarly obtained from [PdMe(Cl)(cod)] in 83 and 94% yield, respectively (Scheme 1). In the ^1H NMR spectrum of **2a** the NCH_2 protons appear as a triplet of triplets owing to a $^5J_{HH}$ coupling between the PCH_2 and NCH_2 protons ($^5J_{HH}$ = 1.9 Hz). This was confirmed by selective ^1H homonuclear decoupling experiments. Of course this feature is not observed for **2b**. Note that a similar $^5J_{HH}$ coupling has been recently observed in a related *N*,*P*,*N* phosphine-oxazoline based ligand.[24] The Pd–Me resonances of **2a** and **2b** appear as doublets at δ 0.55 and 0.65 with $^3J_{PH}$ = 2.7 and 3.3 Hz, respectively. The magnitudes of these coupling constants indicate a *cis* relationship between the two groups which have the largest *trans* influence, namely the phosphorus atom and the methyl group.

Cationic complexes

The synthesis of the cationic complexes $[PdMe(L)(PCH_2ox)]^+$ **3**–**9** was achieved in two steps: first by displacement of the cod ligand leading to pure $[PdMe(Cl)(PCH_2ox)]$, followed by chloride abstraction and coordination of a labile ligand L, except



(4)

3a R = H, L = nothing, X = $CF_3SO_3^-$
3b R = Me, L = nothing, X = $CF_3SO_3^-$
4a R = H, L = NCMe, X = BF_4^-
4b R = Me, L = NCMe, X = BF_4^-
5a R = H, L = NCMe, X = PF_6^-
6a R = H, L = SMe_2, X = $CF_3SO_3^-$
6b R = Me, L = SMe_2, X = $CF_3SO_3^-$
7a R = H, L = SMe_2, X = BF_4^-
7b R = Me, L = SMe_2, X = BF_4^-
8a R = H, L = SMe_2, X = PF_6^-
9a R = H, L = $P(OPh)_3$, X = $CF_3SO_3^-$

for **3a**,**b** which were prepared in CH_2Cl_2 [eqn. (4)]. Even when prepared in acetonitrile, complexes **3a**,**b**, did not contain this ligand after precipitation and drying under vacuum for two days. This was established by elemental analysis and ^{1}H NMR spectroscopy. The counter ion, $CF_3SO_3^-$, is therefore expected to occupy in the solid state the coordination site liberated by the removal of L. This is obviously not the case of the anions BF_4^- and PF_6^- in the acetonitrile complexes **4a**,**b** and **5a**. However, addition of 1 equiv. of acetonitrile to a $CDCl_3$ solution of $[PdMe(O_3SCF_3)(PCH_2ox)]$ **3a** leads to the coordination of acetonitrile as observed by the appearance of a singlet peak at δ 2.30 in the ^{1}H NMR spectrum and a singlet at δ 2.60 in the $^{13}C\{^1H\}$ NMR spectrum, which are assigned to the protons and carbon atom of the methyl group of coordinated acetonitrile. Similarly, addition of 1 equiv. of dimethyl sulfide to a $CDCl_3$ solution of **3a** yielded compound **6a**.

As for the neutral complexes, the Pd–Me protons appear in the ^{1}H NMR spectrum as doublets with $^3J_{PH}$ values in agreement with a *cis* arrangement of the phosphorus atom and the methyl group. From the $^{13}C\{^1H\}$ NMR spectrum one can also conclude that the phosphorus atom is *cis* to the methyl group since no $^2J_{PC}$ coupling constant was detected. The ^{1}H NMR chemical shift of the Pd–Me protons is moderately sensitive to the nature of the *P*,*N* ligand but is affected by the nature of the solvent, although not as much as the PCH_2 protons (*cf.* **6a**: δ 0.45 and 0.40 for Pd–Me and δ 3.90 and 3.55 for PCH_2 in acetone-d_6 and $CDCl_3$, respectively; for **7a**: δ 0.50 and 0.35 for Pd–Me and δ 3.90 and 3.55 for PCH_2 in acetone-d_6 and $CDCl_3$, respectively). As for **2a**, complexes **3a**, **6a** and **7a** show a $^5J_{HH}$ coupling between the PCH_2 and NCH_2 protons. All cationic compounds were characterized in the $^{31}P\{^1H\}$ NMR spectra by a singlet in the range δ 31–36 which is only slightly downfield shifted compared to the neutral $[PdMe(Cl)(PCH_2ox)]$ complexes. For complex **9a** where L = $P(OPh)_3$ two AX spin systems are observed. Each of them corresponds to the isomers with mutually *cis* and *trans* phosphorus atoms, with the *cis* isomer being always the major species in solution. Changing the NMR solvent from $CDCl_3$ to benzene-d_6 did not affect this ratio.

Catalytic studies

In recent years several groups have reported on the Pd(II)-catalyzed alternating copolymerisation of olefins with carbon monoxide to yield copolymers with very attractive physical properties.[25] In 1996, Shell started up a plant with an annual capacity of 20 000 tonnes, and marketed its polymer under the trade name of Carilon®. Other chemical companies (Akzo Nobel, BASF, BP, Enichem) filed patents and several research groups are very active in this field in order to develop new classes of catalysts and to understand the different steps involved in the overall catalytic process.[26–31] Catalysts are usually of the type $[Pd(solvent)_2(L_2)]^{2+}$ or $[PdMe(solvent)(L_2)]^+$ where L_2 is a diphosphine or diimine ligand. With complexes **1**–**9a** in hand we decided to test them in ethylene/CO copolymerisation reactions.

Table 2 Catalytic results for ethylene/CO copolymerisation with complexes **3a**–**9a**[a]

Run	Catalyst complex	*T*/°C	*t*/h	TON	g(PK)/g(Pd)
1	**3a**	90	1	15	8
2	**3a**	90	4	141	77
3	**3a**	60	4	100	55
4	**3a**	90	24	190	104
5	**3b**	60	4	83	45
6	**3b**	90	4	64	35
7	**4a**	90	4	38	21
8	**5a**	90	4	31	17
9	**6a**	60	4	250	137
10	**6a**	90	4	86	47
11	**6b**	60	4	82	45
12	**6b**	90	4	91	50
13	**7a**	90	4	33	18
14[b]	**8a**	90	4	29	16
15[c]	**8a**	90	4	33	18
16	**9a**	60	4	120	66

[a] Catalytic conditions: 40 mL CH_2Cl_2, initial p(CO) = 25 bar, initial p(ethylene) = 25 bar, n(catalyst) = 0.05 mmol. [b] p(CO) = 5 bar, p(ethylene) = 20 bar. [c] p(CO) = 12.5 bar, p(ethylene) = 12.5 bar.

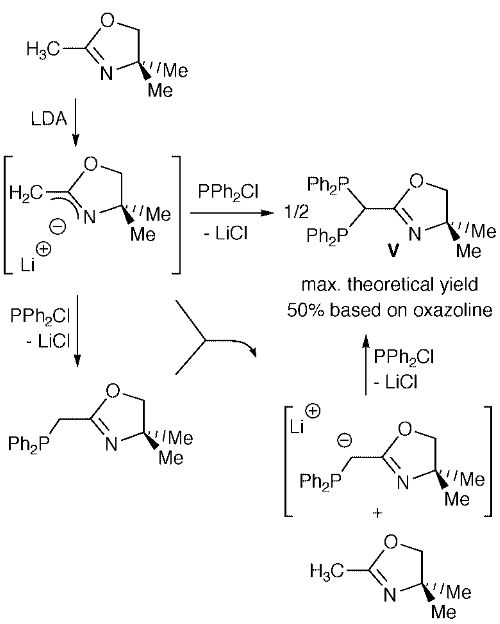
Before testing the reactivity of the new Pd cationic complexes, we first checked the feasability of the carbonylation which is the first necessary step in the catalytic formation of the polyketones. Treating a CD_2Cl_2 solution of $[PdMe(O_3SCF_3)(PCH_2ox)]$ **3a**, in an NMR tube with 1 atm of CO at room temperature, yielded the corresponding acyl complex within 5 min. Use of $CDCl_3$ led to rapid precipitation of palladium metal (5 min). The ^{1}H NMR spectrum of the acyl complex shows a characteristic downfield shift of the methyl protons from δ 0.50 to 2.10 indicative of the insertion of CO into the Pd–Me bond.[29,32] The carbonylation reaction induces in the $^{31}P\{^1H\}$ NMR spectrum an upfield shift of the singlet resonance from δ 34 to 20. This feature appears general for diphenylphosphino derivatives and the magnitude of the NMR shift is in accord with other literature reports.[33–35] The IR spectrum contains a new band at 1695 cm^{-1} which is assigned to the Pd–acyl C=O stretch.[33,36] The instability of this complex is not due to decarbonylation (^{1}H and ^{13}C NMR monitoring did not indicate the presence of **3a**) but prevented satisfactory elemental analyses from being obtained. Note that the neutral complex $[PdMe(Cl)(PCH_2ox)]$ also reacted with CO under similar conditions but formation of the acyl complex was much slower (16 h) than for the cationic analog.

Ethylene/CO copolymerisation experiments have shown that all complexes **3**–**9a** are active but only the most significant runs are reported in Table 2. Activities are expressed both in turnover numbers (TON) (moles of substrate converted per mole of Pd) and in grams of polyketone per gram of palladium and are based on the mass of the insoluble polymer collected after reaction (details in the Experimental section). The $^{13}C\{^1H\}$ NMR spectra of the polyketones formed show the characteristic singlets at δ 35.0 ($-CH_2-$) and 212.0 (C=O) and no resonances for end groups could be detected. This is indicative of long polymer chains with more than 400 monomeric units.[37] The best activities were obtained with **6a** at 60 °C (run 9). Lowering the CO : ethylene ratio from 1 : 1 to 1 : 4 did not affect the production of polymers (see runs 14 and 15 with **8a**). Even though the catalyst remains active after 4 h as shown by run 4, its efficiency decreases, most likely owing to the combined effects of increasing difficulty of the monomers to access the polymer-bound or -entrapped catalytic sites and of some decomposition of the active species. Catalytic experiments were therefore run for 4 h for all the complexes tested. Although after 1 h reaction, a significant amount of insoluble copolymer was produced, the TOF measured was lower than that obtained after 4 h. Two temperatures, 60 and 90 °C, were considered for the catalytic experiments and the effect of temperature on the amount of insoluble copolymer formed was strongly dependent on the catalyst used. The counter ion has a clear effect on the activity of the catalyst. Runs 2, 7, 8 show $CF_3SO_3^-$ to be better than BF_4^- or PF_6^-.

Owing to the poor solubility of the ethylene/CO copolymers in usual organic solvents it is difficult to know their exact mass distribution. However, when we used nbd (nbd = norbornadiene), a strained olefin expected to be more reactive than ethylene,[38] the NBD/CO copolymers could be investigated by gel permeation chromatography (see Experimental section for details). The analysis shows that the copolymers formed are oligomers ($M_p = 1801$, $M_w/M_n = 2.06$) of average degree of polymerisation ($\tilde{n}$) equal to 11.

Discussion

The synthesis of ligands **III** and **IV** according to eqn. (3) is straightforward and allows their gram-scale preparation from cheap and readily available reagents. Although the general synthetic strategy is the same as that described for the *P*,*O* ligands **I**, namely deprotonation of a functionalized methyl group followed by quenching of the Li salt with PPh_2Cl, modifications had to be introduced because of side reactions hampering the isolation of the desired product in high yield. Formation of the diphosphorylated compound **V** as the major by-product when using the ratio oxazoline : LDA : PPh_2Cl = 1 : 1 : 1 under the conditions of eqn. (1) seems to indicate that once the monophosphorylated oxazoline is formed, immediate deprotonation of the acidic PCH_2 proton by the carbanion present occurs. This accounts for the double functionalization of the initial methyl group and subsequent treatment with PPh_2Cl leads to formation of **V** (Scheme 2).



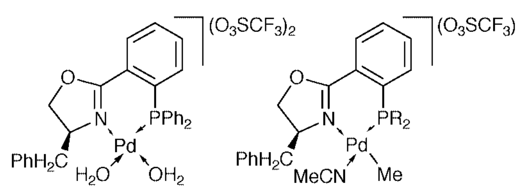
Scheme 2

The new ligand **V** is of the functional dppm-type and it was prepared in a rational manner according to eqn. (2), thus allowing future investigations. Changing either the order of introduction of the reagents or their speed of addition did not have a significant effect on the yield of **IV**. The important benefit in the use of $ClSiMe_3$ in eqn. (3) is that the *N*-silyl derivative, which upon reaction with PPh_2Cl gives the desired product **IV**, cannot deprotonate **IV** in the course of its synthesis owing to its bulkiness ($SiMe_3$ substituent) and low basicity. Protection by $ClSiMe_3$ has also been used to improve the synthesis of imidazolyl-phosphine ligands.[39]

Ligands **III** and **IV** easily form chelate complexes of the type $[PdCl_2(P,N)]$ or $[PdMe(Cl)(P,N)]$. The fact that in the case of the cationic complexes **3b**, **4b**, **6b**, **7b** the chemical shifts of the Pd–Me protons are downfield shifted, although slightly, compared to their analogues **3a**, **4a**, **6a**, **7a** appears surprising since one would expect the Me substituents on the oxazoline of ligand **IV** to donate more electron density to the metal centre. In terms of catalytic activity, it is generally observed that electrophilic Pd centres give rise to more active systems. Thus, based on our ^{1}H NMR data, complexes with ligand **IV** should be more active than those with **III**. However, the superior results of the catalytic tests with complexes containing ligand **III** are consistent with its being a weaker electron donor ligand than **IV** (compare runs 3 with 5 and 9 with 11 in Table 1). One should not forget that the methyl substituents may also contribute to the steric bulk around the metal centre. In an ethylene/CO copolymerisation study by Cavell and co-workers, a pyridine-based *N*,*O* ligand was used and the 6-methyl substituent was found to have an activating effect compared to the unsubstituted ligand.[29] This was explained by a sterically induced weakening of the Pd–N bond by the 6-methyl substituent, thus facilitating isomerization of the complex during catalysis. From the crystal structure of **1** it seems however that if a steric effect had to be invoked in the catalytic process, it should be related to the phenyl groups of the phosphorus rather than to the methyl groups on the oxazoline since the former appear to be in closer proximity to the catalytic site [P(1)–Pd(1)–Cl(2) 88.29(3)°, N(1)–Pd(1)–Cl(1) 97.22(7)°].

The catalytic activity of complex **9a** in which the phosphite ligand is more strongly bound to the metal than L in the other complexes could be either due to the existence in solution of the isomer with the methyl group *trans* to the phosphorus of the *P*,*N* chelate—which is perhaps more active than the other isomer—or to a hemilabile behaviour of the latter. We have, however, no direct evidence for this behaviour throughout this work, although other workers have observed high lability of bidentate nitrogen ligands on palladium.[40]

The lower activity of complexes **3**–**9** compared to cationic palladium catalysts with bidentate *P*,*P* or *N*,*N* ligands may be attributed to necessary pre- or post-insertion isomerization steps of the different intermediate species with the Pd–C bond *cis* or *trans* to P.[36] However, our $[PdMe(L)(PCH_2ox)]^+$ systems exhibit higher activity for ethylene/CO copolymerisation than the related complex $[Pd(OH_2)_2L](O_3SCF_3)_2$ **10** (L = phosphino-



10 **11**

aryloxazoline) described by Consiglio and co-workers which contains a six-membered ring chelate.[41–43]

Our experiments were run under milder conditions (40 *vs.* 290 bar 1 : 1 ethylene/CO). Very recently the same group has described the synthesis and reactivity of $[PdMe(NCMe)L](O_3SCF_3)$ **11** (L = phosphinoaryloxazoline) where the catalytic activity towards ethylene/CO copolymerisation is lower compared to its dicationic analog.[43–45] Their carbonylation study of compound **11** reports the slow formation of the corresponding acyl complex which reaches completion after 17 h at room temperature under 1 bar of CO. Under similar conditions, complex **3a** is fully converted to the acyl compound within 5 min. Considering the very close similarity of our cationic complexes with complex **11**, this difference in reactivity may be due, at least in part, to the size of the chelating ligand. In fact, careful studies on the carbonylation of $[PdMe(L)\{Ph_2P(CH_2)_nPPh_2\}]^+$ (n = 2–4) have shown that the rate of migration in methyl–palladium complexes is strongly influenced by the bite angle and backbone flexibility of the ligand.[34] This ligand effect has also been observed with diphosphine $Ph_2P(CH_2)_nPPh_2$ ligands where the highest productivity is obtained for $n = 3$.[37]

Concerning the choice of the counter ion, it is usually observed that better reactivity is associated with non-coordinating and inert anions.[28] Thus we would have expected the following order of decreasing reactivity $PF_6^- \geqslant BF_4^- > CF_3SO_3^-$. However, this is not consistent with the experimental results since $[PdMe(NCMe)(PCH_2ox)](O_3SCF_3)$ is more than twice as reactive as $[PdMe(NCMe)(PCH_2ox)](BF_4)$ or $[PdMe(NCMe)(PCH_2ox)](PF_6)$ (runs 3, 7 and 8, Table 1). In another study a cationic Pd complex with triflate as the counter ion was found to be more active than its PF_6^- or SbF_6^- analogs.[41]

Having in hand a general route for the synthesis of active catalyst precursors for copolymerisation of ethylene and CO, we plan to prepare a complex analogous to **6a** containing the chiral ligand **II** and study its properties towards formation of isotactic co- and ter-polymers from prochiral functional olefins, a subject of current interest which has generated so far only a limited number of reports.[42,46–54] We recently found in a preliminary study that a prochiral olefin such as methylacrylate inserts in the Pd–Me bond of compound **4a**, as shown by ^1H, ^{13}C, $^{31}P\{^1H\}$ NMR and mass spectroscopy data.[55]

Experimental

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC300 instrument, $^{13}C\{^1H\}$ NMR spectra at 50.32 MHz on a FT Bruker AC200 instrument, $^1H\{^{31}P\}$ NMR spectra at 500.13 MHz on a FT Bruker ARX500 instrument, IR spectra in the range 4000–400 cm^{-1} on a Bruker IFS66 FT spectrometer and FIR spectra in the range 500–90 cm^{-1} on a Bruker ATS 83 spectrometer. The complexes $[PdCl_2(cod)]$ and $[PdMe(Cl)(cod)]$ were prepared according to literature procedures.[56]

Synthesis of the ligands

(2-Oxazoline-2-ylmethyl)diphenylphosphine (PCH_2ox) III. A THF solution (5 mL) of 2-methyl-2-oxazoline (5.230 g, 61.5 mmol) was added over a period of 10 min with a cannula to a solution of butyllithium in hexane (38.45 mL, 1.6 mol L^{-1}, 61.5 mmol) in a 250 mL flask containing THF (150 mL) at −78 °C. The mixture was stirred for 1 h and degased $ClSiMe_3$ (7.75 mL, 61.5 mol) was added. The mixture was stirred for 1 h at −78 °C and PPh_2Cl (11.0 mL, 61.5 mmol) was added. The solution was stirred until it reached room temperature. After evaporation of the solvent under reduced pressure, the yellow residue was successively triturated with hexane (2 × 10 mL) and Et_2O (2 × 20 mL) to eliminate residual THF and $ClSiMe_3$ and obtain a yellow powder which was then extracted with toluene (60 mL). The solution was filtered over Celite and a pale yellow solid was obtained after evaporation of the toluene *in vacuo*. The product was recrystallized from ethanol at −28 °C. Yield: 10.35 g (61% based on methyl oxazoline) (mp 59 °C) (Calc. for $C_{16}H_{16}NOP$: C, 71.37; H, 5.99; N, 5.20. Found: C, 71.74; H, 5.95; N, 4.98%). $IR(CH_2Cl_2)$: $\nu_{C=N}$ 1660s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 3.05 (s, 2 H, PCH_2), 3.75 (t, 2 H, $^3J_{HH}$ = 9.4 Hz, NCH_2), 4.15 (t, 2 H, $^3J_{HH}$ = 9.4 Hz, OCH_2), 7.20–7.50 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 28.3 (d, $^1J_{PC}$ = 19.2 Hz, PCH_2), 54.7 (s, NCH_2), 67.6 (s, OCH_2), 128.5 (d, $^2J_{PC}$ = 7.0 Hz, *o*-aryl), 128.9 (s, *p*-aryl), 132.7 (d, $^3J_{PC}$ = 19.7 Hz), 137.7 (d, $^1J_{PC}$ = 14.1 Hz, *ipso*-aryl), 165.4 (d, $^3J_{PC}$ = 7.0 Hz, C=N). $^{31}P\{^1H\}$ (121.5 MHz, $CDCl_3$): δ −17.3 (s).

(4,4-Dimethyl-2-oxazoline-2-ylmethyl)diphenylphosphine (PCH_2ox^{Me2}) IV. This ligand was obtained following the procedure described for **III**, starting from 80 mmol of 2,4,4-trimethyl-2-oxazoline. This oily compound was purified by washing with hexane (2 × 15 mL). Yield: 16.12 g (75%) (Calc. for $C_{18}H_{20}NOP$: C, 72.71; H, 6.78; N, 4.71. Found: C, 72.54; H, 6.71; N, 4.97%). $IR(CH_2Cl_2)$: $\nu_{C=N}$ 1660s cm^{-1}. ^1H NMR (500.13 MHz, C_6D_6): δ 1.05 [s, 6 H, $NC(CH_3)_2$], 3.15 (br s, 2 H, PCH_2), 3.45 (s, 2 H, OCH_2), 7.00–7.10 (m, 6 H, aryl), 7.50–7.60 (m, 4 H, aryl). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 28.0 [s, $NC(\mathit{C}H_3)_2$], 28.2 (d, $^1J_{PC}$ = 19.5 Hz, PCH_2), 66.9 [s, $N\mathit{C}(CH_3)_2$], 79.0 (s, OCH_2), 127.0–137.5 (aryl), 162.3 (d, $^3J_{PC}$ = 7.0 Hz, C=N). $^{31}P\{^1H\}$ (121.5 MHz, $CDCl_3$): δ −17.5 (s).

(4,4-Dimethyl-2-oxazoline-2-ylmethyl)bis(diphenylphosphine) V. A THF solution (5 mL) of 2,4,4-trimethyl-2-oxazoline (0.880 g, 7.7 mmol) was added over a period of 10 min with a cannula to a solution of lithium diisopropylamide (15.4 mmol in hexane) (from equimolar amounts of butyllithium and diisopropylamine) in a 250 mL flask containing THF (100 mL) at −78 °C. The colorless cloudy solution was stirred for 1 h and PPh_2Cl (2.76 mL, 15.4 mmol) was added. The solution was allowed to slowly reach room temperature and stirred overnight. After evaporation of the solvent under reduced pressure, the yellow residue was treated with hexane (2 × 10 mL) and Et_2O (2 × 20 mL) to obtain a yellow powder which was then extracted with toluene (60 mL). The solution was filtered over Celite and a pale yellow solid was obtained after evaporation of the toluene *in vacuo*. The product was recrystallized from Et_2O–hexane (1 : 3). Yield: 0.890 g (24%) (mp 63 °C) (Calc. for $C_{30}H_{22}NOP_2$: C, 74.83; H, 6.07; N, 2.91. Found: C, 75.01; H, 5.96; N, 3.06%). IR(KBr): $\nu_{C=N}$ 1652s cm^{-1}. ^1H NMR (300.16 MHz, $CDCl_3$): δ 0.75 [s, 6 H, $NC(CH_3)_2$], 3.20 (s, 2 H, OCH_2), 4.30 (s, 1 H, P_2CH), 7.20–7.70 (m, 20 H, aryl). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 27.6 [s, $NC(\mathit{C}H_3)_2$], 37.3 (t, $^1J_{PC}$ = 27.7 Hz, PCH), 66.5 [s, $N\mathit{C}(CH_3)_2$], 78.5 (s, OCH_2), 127.0–136.5 (aryl), 162.3 (d, $^3J_{PC}$ = 3.8 Hz, C=N). $^{31}P\{^1H\}$ (300.13 MHz, $CDCl_3$): δ −11.6 (s).

Synthesis of the palladium complexes

$[PdCl_2(PCH_2ox^{Me2})]$ 1. Solid $[PdCl_2(cod)]$ (0.245 g, 0.90 mmol) was added to a solution of ligand **IV** (0.269 g, 0.90 mmol) in CH_2Cl_2 (15 mL). The yellow solution was stirred overnight, and the solvent evaporated under reduced pressure. The yellow powder was washed with Et_2O (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo*. X-Ray quality crystals were obtained in an NMR tube by slow diffusion of the $CDCl_3$ solvent. Yield: 0.392 g (92%) (Calc. for $C_{18}H_{20}Cl_2NOPPd\cdot 2CDCl_3$: C, 33.58; H, 2.82. Found: C, 33.45; H, 3.02%). $IR(CH_2Cl_2)$: $\nu_{C=N}$ 1622s cm^{-1}. ^1H NMR (200.13 MHz, CD_2Cl_2): δ 1.60 [s, 6 H, $NC(CH_3)_2$], 3.40 (d, 2 H, $^2J_{PH}$ = 10 Hz, PCH_2), 4.15 (s, 2 H, OCH_2), 7.40–7.60 (m, 6 H, aryl H), 7.75–7.90 (m, 4 H, aryl H). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 25.1 (s).

$[PdMe(Cl)(PCH_2ox)]$ 2a. Ligand **III** (2.295 g, 8.53 mmol) was added to a solution of $[PdMe(Cl)(cod)]$ (2.260 g, 8.53 mmol) in CH_2Cl_2 (10 mL). The pale yellow solution was stirred for 2 h. After evaporation of the solvent, the white solid was washed with Et_2O and dried *in vacuo*. Yield: 3.775 g (83%) (Calc. for $C_{17}H_{19}ClNOPPd$: C, 47.91; H, 4.49; N, 3.29. Found: C, 48.29; H, 4.58; N, 3.36%). $IR(CH_2Cl_2)$: $\nu_{C=N}$ 1647s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.55 (d, 3 H, $^3J_{PH}$ = 2.7 Hz, Pd–Me), 3.30 (dt, 2 H, $^2J_{PH}$ = 10.1 Hz, $^5J_{HH}$ = 1.9 Hz, PCH_2), 4.00 (tt, 2 H, $^3J_{HH}$ = 9.9 Hz, $^5J_{HH}$ = 1.9 Hz, NCH_2), 4.55 (t, 2 H, $^3J_{HH}$ = 9.9 Hz, OCH_2), 7.35–7.75 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2): δ −5.2 (s, Pd–Me), 32.0 (d, $^1J_{PC}$ = 30.4 Hz, PCH_2), 52.1 (s, NCH_2), 72.1 (s, OCH_2), 129.1 (d, $^3J_{PC}$ = 11.4 Hz, *m*-aryl), 129.5 (overlapped d, $^1J_{PC}$ = 44 Hz, *ipso*-aryl), 131.6 (s, *p*-aryl), 133.1 (d, $^2J_{PC}$ = 13.1 Hz, *o*-aryl), 171.7 (d,

$^3J_{PC}$ = 18.1 Hz, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 31.8 (s).

[PdMe(Cl)(PCH$_2$ox^{Me2})] 2b. Ligand **IV** (0.215 g, 0.72 mmol) was added to a solution of [PdMe(Cl)(cod)] (0.191 g, 0.72 mmol) in CH_2Cl_2 (10 mL). The pale yellow solution was stirred for 2 h. After evaporation of the solvent, the yellow solid was washed with hexane (2 × 10 mL). Yield: 0.309 g (94%) (Calc. for $C_{19}H_{23}ClNOPPd$: C, 50.24; H, 5.10; N, 3.08. Found: C, 49.95; H, 4.96; N, 2.80%). IR(CH_2Cl_2): $\nu_{C=N}$ 1628s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.65 (d, 3 H, $^3J_{PH}$ = 3.3 Hz, Pd–Me), 1.60 [s, 6 H, $NC(CH_3)_2$], 3.35 (d, 2 H, $^2J_{PH}$ = 10.5 Hz, PCH_2), 4.15 (s, 2 H, OCH_2), 7.25–7.70 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ −2.3 (s, Pd–Me), 27.8 [s, $NC(CH_3)_2$], 32.5 (d, $^1J_{PC}$ = 29.9 Hz, PCH_2), 68.4 [s, $NC(CH_3)_2$], 83.4 (s, OCH_2), 127.0–134.0 (aryl), 169.1 (d, $^3J_{PC}$ = 12.8 Hz, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 31.5 (s).

[PdMe(O$_3$SCF$_3$)(PCH$_2$ox)] 3a. Solid $AgCF_3SO_3$ (0.060 g, 0.236 mmol) was added to a solution of [PdMe(Cl)(PCH$_2$ox)] (0.100 g, 0.235 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred for 2 h. The suspension was filtered through a cannula fitted with glass fiber paper and the solution was evaporated to dryness *in vacuo*. The pale yellow solid was washed with pentane (2 × 5 mL) and hexane (2 × 5 mL) and dried *in vacuo* (0.113 g, 83%) (Calc. for $C_{18}H_{19}F_3NO_4PSPd$: C, 40.05; H, 3.55; N, 2.70. Found: C, 39.68; H, 3.94; N, 2.70%). IR(KBr): $\nu_{C=N}$ 1633s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.50 (d, 3 H, $^3J_{PH}$ = 1.5 Hz, Pd–Me), 3.40 (dt, 2 H, $^2J_{PH}$ = 10.5 Hz, $^5J_{HH}$ = 1.9 Hz, PCH_2), 4.00 (tt, 2 H, $^3J_{HH}$ = 9.5 Hz, $^5J_{HH}$ = 1.9 Hz, NCH_2), 4.60 (t, 2 H, $^3J_{HH}$ = 9.5 Hz, OCH_2), 7.50–7.80 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ −1.1 (s, Pd–Me), 33.0 (d, $^1J_{PC}$ = 34.2 Hz, PCH_2), 52.8 (s, NCH_2), 72.8 (s, OCH_2), 128.0–133.6 (m, aryl), 172.7 (d, $^2J_{PC}$ = 13.4 Hz, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 35.5 (s).

[PdMe(O$_3$SCF$_3$)(PCH$_2$ox^{Me2})] 3b. Following the procedure described for **3a**, but starting from [PdMe(Cl)(PCH$_2$ox^{Me2})] (0.170 g, 0.374 mmol) and $AgCF_3SO_3$ (0.096 g, 0.374 mmol), **3b** was obtained as a yellow solid (0.200 g, 88%) (Calc. for $C_{20}H_{23}F_3NO_4PSPd$: C, 42.30; H, 4.08; N, 2.47. Found: C, 42.63; H, 4.06; N, 2.35%). IR(CH_2Cl_2): $\nu_{C=N}$ 1635s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.65 (s, 3 H, Pd–Me), 1.45 [s, 6 H, $NC(CH_3)_2$], 3.45 (d, 2 H, $^2J_{PH}$ = 10.9 Hz, PCH_2), 4.25 (s, 2 H, OCH_2), 7.25–7.70 (m, 10 H, aryl). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 34.8 (s, br).

[PdMe(NCMe)(PCH$_2$ox)](BF$_4$) 4a. Following the procedure described for **3a**, but starting from [PdMe(Cl)(PCH$_2$ox)] (0.100 g, 0.235 mmol) and $AgBF_4$ (0.046 g, 0.235 mmol), **4a** was obtained as a pale brown solid, yield: 0.110 g (91%) (Calc. for $C_{19}H_{22}BF_4N_2OPPd$: C, 44.01; H, 4.28. Found: C, 44.23; H, 4.54%). IR(CH_2Cl_2): $\nu_{C=N}$ 1643 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.40 (d, 3 H, $^3J_{PH}$ = 1.3 Hz, Pd–Me), 2.40 (s, 3 H, CH_3CN), 3.40 (d, 2 H, $^2J_{PH}$ = 10.6 Hz, PCH_2), 4.05 (t, 2 H, $^3J_{HH}$ = 9.6 Hz, NCH_2), 4.65 (t, 2 H, $^3J_{HH}$ = 9.6 Hz, OCH_2), 7.50–7.65 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ −4.2 (s, Pd–Me), 2.6 (s, CH_3-CN), 32.3 (d, $^1J_{PC}$ = 34.4 Hz, PCH_2), 52.5 (s, NCH_2), 72.8 (s, OCH_2), 126.9–133.3 (m, aryl), 172.7 (d, $^2J_{PC}$ = 16.6 Hz, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 33.2 (s).

[PdMe(NCMe)(PCH$_2$ox^{Me2})](BF$_4$) 4b. Following the procedure described for **3a**, but starting from [PdMe(Cl)-(PCH$_2$ox^{Me2})] (0.100 g, 0.220 mmol) and $AgBF_4$ (0.043 g, 0.220 mmol), **4b** was obtained as a white solid, yield: 0.112 g (93%) (Calc. for $C_{21}H_{26}BF_4N_2OPPd$: C, 46.14; H, 4.79. Found: C, 45.88; H, 4.53%). IR(CH_2Cl_2): $\nu_{C=N}$ 1638 cm^{-1}. ^1H NMR (300.13 MHz, acetone-d_6): δ 0.50 (d, 3 H, $^3J_{PH}$ = 1.6 Hz, Pd–Me), 1.45 [s, 6 H, $NC(CH_3)_2$], 2.40 (s, 3 H, CH_3CN), 3.90 (d, 2 H, $^2J_{PH}$ = 11.4 Hz, PCH_2), 4.40 (s, 2 H, OCH_2), 7.60–7.80 (m, 10 H, aryl). $^{31}P\{^1H\}$ (121.5 MHz, $CDCl_3$): δ 34.7 (s).

[PdMe(NCMe)(PCH$_2$ox)](PF$_6$) 5a. Following the procedure described for **3a**, but starting from [PdMe(Cl)(PCH$_2$ox)] (0.100 g, 0.235 mmol) and $TlPF_6$ (0.132 g, 0.235 mmol), **5a** was obtained as a white solid, yield: 0.122 g (90%) (Calc. for $C_{19}H_{23}F_6N_2OP_2Pd$: C, 39.57; H, 3.84. Found: C, 39.49; H, 3.66%). IR(CH_2Cl_2): $\nu_{C=N}$ 1641s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.40 (s, 3 H, Pd–Me), 2.05 (s, 3 H, CH_3CN), 3.35 (d, 2 H, $^2J_{PH}$ = 10.5 Hz, PCH_2), 4.05 (t, 2 H, $^3J_{HH}$ = 9.7 Hz, NCH_2), 4.70 (t, 2 H, $^3J_{HH}$ = 9.7 Hz, OCH_2), 7.55–7.85 (m, 10 H, aryl). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 34.4 (s).

[PdMe(SMe$_2$)(PCH$_2$ox)](O$_3$SCF$_3$) 6a. Following the procedure described for **3a**, but starting from [PdMe(Cl)(PCH$_2$ox)] (0.100 g, 0.235 mmol), $AgCF_3SO_3$ (0.060 g, 0.236 mmol) and SMe_2 (17 µL, 0.235 mmol) in CH_2Cl_2 (10 mL), **6a** was obtained as a pale yellow powder, yield: 0.065 g (42%) (Calc. for $C_{20}H_{35}F_3NO_4PS_2Pd$: C, 39.91; H, 4.19; N, 2.33. Found: C, 39.89; H, 4.05; N, 2.37%). IR(CH_2Cl_2): $\nu_{C=N}$ 1638 cm^{-1}. ^1H NMR (300.13 MHz, acetone-d_6): δ 0.45 (d, 3 H, $^3J_{PH}$ = 2.2 Hz, Pd–Me), 2.50 [s, 3 H, $S(CH_3)_2$], 3.90 (dt, 2 H, $^2J_{PH}$ = 11.1 Hz, $^5J_{HH}$ = 1.9 Hz, PCH_2), 4.00 (tt, 2 H, $^3J_{HH}$ = 9.5 Hz, $^5J_{HH}$ = 1.9 Hz, NCH_2), 4.75 (t, 2 H, $^3J_{HH}$ = 9.5 Hz, OCH_2), 7.60–7.90 (m, 10 H, aryl). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 32.5 (s).

[PdMe(SMe$_2$)(PCH$_2$ox^{Me2})](O$_3$SCF$_3$) 6b. Following the procedure described for **3a**, but starting from [PdMe(Cl)-(PCH$_2$ox^{Me2})] (0.100 g, 0.220 mmol), $AgCF_3SO_3$ (0.056 g, 0.220 mmol) and SMe_2 (0.5 mL) in CH_2Cl_2 (10 mL), **6b** was obtained as a pale yellow powder, yield: 0.082 g (62%) (Calc. for $C_{22}H_{29}F_3NO_4PS_2Pd$: C, 41.95; H, 4.64. Found: C, 41.59; H, 4.49%). IR(CH_2Cl_2): $\nu_{C=N}$ 1640s cm^{-1}. ^1H NMR (300.13 MHz, acetone-d_6): δ 0.45 (d, 3 H, $^3J_{PH}$ = 1.7 Hz, Pd–Me), 1.40 [s, 6 H, $NC(CH_3)_2$], 2.40 [s, 6 H, $S(CH_3)_2$], 3.95 (d, 2 H, $^2J_{PH}$ = 11.6 Hz, PCH_2), 4.40 (s, 2 H, OCH_2), 7.55–8.00 (m, 10 H, aryl). $^{31}P\{^1H\}$ (121.5 MHz, $CDCl_3$): δ 34.9 (s).

[PdMe(SMe$_2$)(PCH$_2$ox)](BF$_4$) 7a. Following the procedure described for **3a**, but starting from [PdMe(Cl)(PCH$_2$ox)] (0.100 g, 0.235 mmol), $AgBF_4$ (0.060 g, 0.235 mmol) and SMe_2 (0.5 mL) in CH_2Cl_2 (10 mL), **7a** was obtained as a yellow powder, yield: 0.091 g (72%) (Calc. for $C_{19}H_{25}BF_4NOPSPd$: C, 42.29; H, 4.67; N, 2.60. Found: C, 41.89 H, 4.87; N, 2.48%). IR(CH_2Cl_2): $\nu_{C=N}$ 1642s cm^{-1}. ^1H NMR (300.13 MHz, acetone-d_6): δ 0.50 (d, 3 H, $^3J_{PH}$ = 2.2 Hz, Pd–Me), 2.50 [s, 6 H, $S(CH_3)_2$], 3.90 (dt, 2 H, $^2J_{PH}$ = 11.0 Hz, $^5J_{HH}$ = 1.8 Hz, PCH_2), 4.05 (tt, 2 H, $^3J_{HH}$ = 9.6 Hz, $^5J_{HH}$ = 1.8 Hz, NCH_2), 4.75 (t, 2 H, $^3J_{HH}$ = 9.6 Hz, OCH_2), 7.60–7.85 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ −1.8 (s, Pd–Me), 19.8 [s, $S(CH_3)_2$], 31.6 (d, J_{PC} = 31.6 Hz, PCH_2), 52.3 (s, NCH_2), 72.2 (s, OCH_2), 126.9–133.3 (m, aryl), 173.9 (d, $^2J_{PC}$ = 18.4 Hz, C=N) $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 36.8 (s).

[PdMe(SMe$_2$)(PCH$_2$ox^{Me2})](BF$_4$) 7b. Following the procedure described for **3a**, but starting from [PdMe(Cl)-(PCH$_2$ox^{Me2})] (0.100 g, 0.220 mmol), $AgBF_4$ (0.043 g, 0.220 mmol) and SMe_2 (0.5 mL) in CH_2Cl_2 (10 mL), **7b** was obtained as a yellow powder, yield: 0.106 g (85%) (Calc. for $C_{21}H_{29}$-$BF_4NOPSPd$: C, 44.43; H, 5.15. Found: C, 44.13 H, 4.97%). IR(CH_2Cl_2): $\nu_{C=N}$ 1639s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.55 (d, 3 H, $^3J_{PH}$ = 2.2 Hz, Pd–Me), 1.45 [s, 6 H, $NC(CH_3)_2$], 2.50 [s, 6 H, $S(CH_3)_2$], 3.90 (d, 2 H, $^2J_{PH}$ = 11.4 Hz, PCH_2), 4.35 (s, 2 H, OCH_2), 7.60–7.90 (m, 10 H, aryl). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 31.4 (s, br).

[PdMe(SMe$_2$)(PCH$_2$ox)](PF$_6$) 8a. Following the procedure described for **3a**, but starting from [PdMe(Cl)(PCH$_2$ox)] (0.150

g, 0.350 mmol), $TlPF_6$ (0.198 g, 0.350 mmol) and SMe_2 (0.5 mL) in CH_2Cl_2 (10 mL), **8a** was obtained as a white powder, yield: 0.150 g (71%) (Calc. for $C_{19}H_{25}BF_4NOPSPd$: C, 38.17; H, 4.22. Found: C, 38.37; H, 4.29%). IR(CH_2Cl_2): $\nu_{C=N}$ 1648s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.35 (d, 3 H, $^3J_{PH}$ = 2.4 Hz, Pd–Me), 2.40 [s, 6 H, $S(CH_3)_2$], 3.50 (d, 2 H, $^2J_{PH}$ = 10.8 Hz, PCH_2), 3.95 (t, 2 H, $^3J_{HH}$ = 9.7 Hz, NCH_2), 4.70 (t, 2 H, $^3J_{HH}$ = 9.7 Hz, OCH_2), 7.25–7.70 (m, 10 H, aryl). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 30.6 (s).

[PdMe{P(OPh)$_3$}(PCH$_2$ox)](O$_3$SCF$_3$) 9a. Solid $AgCF_3SO_3$ (0.060 g, 0.236 mmol) was added to a solution of [PdMe(Cl)-(PCH_2ox)] (0.100 g, 0.235 mmol) in CH_2Cl_2 (10 mL), and then $P(OPh)_3$ (30.7 µL, 0.235 mmol) was added to the mixture with a syringe. After 2 h of continuous stirring the suspension was filtered through a cannula fitted with a glass fiber paper and the slightly brown solution was evaporated to dryness *in vacuo*. The yellow–brown oil was washed with pentane (2 × 10 mL), then triturated with hexane (2 × 10 mL) and dried *in vacuo* to afford a yellow–brown powder, yield: 0.135 g (60%). This complex was isolated as the mixture of the *cis* (85%) and *trans* (15%) isomers. The following data refer to the *cis* isomer, unless otherwise specified (Calc. for $C_{36}H_{34}F_3NO_7P_2SPd$: C, 50.87; H, 4.03; N, 1.65. Found: C, 50.11; H, 4.02; N, 1.59%). IR(CH_2Cl_2): $\nu_{C=N}$ 1629s cm^{-1}. ^1H NMR (300.13 MHz, acetone-d_6): δ 0.70 (dd, 3 H, $^3J_{PH}$ = 7.3, 1.6 Hz, Pd–Me), 3.80 (d, 2 H, $^2J_{PH}$ = 10.0 Hz, $^5J_{HH}$ = 1.0 Hz, PCH_2), 3.95 (t, 2 H, $^3J_{HH}$ = 9.0 Hz, NCH_2), 4.80 (t, 2 H, $^3J_{HH}$ = 9.0 Hz, OCH_2), 7.05–7.70 (m, 25 H, aryl). $^{31}P\{^1H\}$ (121.5 MHz, acetone-d_6): AX spin systems: δ_A 20.9 (d, 1 P, $^2J_{PP}$ = 42.3 Hz, PPh_2), δ_X 113.8 [d, 1 P, $^2J_{PP}$ = 42.3 Hz, $P(OPh)_3$] for the *cis* isomer; δ_A 26.3 (d, 1 P, $^2J_{PP}$ = 580 Hz), δ_X 112.4 (d, 1 P, $^2J_{PP}$ = 580 Hz) for the *trans* isomer.

Catalysis

Ethylene/CO copolymerisation reactions. The copolymerisation reactions were carried out in a 80 mL Pyrex glass beaker placed into a stainless-steel autoclave of *ca.* 100 mL in order to prevent metal contamination by metallic species. The catalyst was introduced in solution and the autoclave was then pressurized with the mixture of monomers to the required pressure. The vessel was heated to the desired temperature and the polymerisation was carried out isothermally maintaining a constant pressure level by a continuous feed of monomers. After 4 h, the autoclave was cooled to room temperature, the residual pressure discharged, and the polymer removed by filtration, washed with methanol, and vacuum dried.

Norbornadiene/CO copolymerisation reactions. The copolymerisation reactions were carried out in a 500 mL Büchi miniclave. The catalyst **4a** (0.136 g, 0.2 mmol) in THF (100 mL) was introduced into the autoclave and 5 mL of nbd (nbd = norbornadiene). The autoclave was then pressurized to 5 bar of CO. The colorless reaction mixture was stirred for 18 h at room temperature after which the solution turned yellow with no precipitation of polymers and significant deposition of palladium black. The solvent was removed under reduced pressure and the off-white solid thus obtained was washed with MeOH. Gel permeation chromatography analysis was performed with THF as the solvent and polystyrene standards were used to calibrate the instrument. The ^1H and $^{13}C\{^1H\}$ NMR and IR data of the oligomers are in agreement with previously described nbd/CO copolymers.[57]

X-Ray crystallographic analysis of [PdCl$_2$(PCH$_2$ox^{Me2})]·2CDCl$_3$

Crystal data. $C_{18}H_{20}Cl_2NOPPd\cdot 2CDCl_3$, M = 713.4, triclinic, space group $P\bar{1}$ (no. 2), a = 9.585(2), b = 17.536(3), c = 8.940(2) Å, α = 104.04(1), β = 104.62(1), γ = 78.32(1)°, U = 1394.5(5) Å^3, λ = 0.71069 Å, T = 294 K, Z = 2, μ(Mo-Kα) = 15.04 cm^{-1}, 8135 unique reflections measured (R_{int} = 0.023), 4991 having $I > 3\sigma(I)$. There are two molecules of $CDCl_3$ in the asymmetric unit. One of the solvent molecules was disordered and was modeled by refining all of the major peaks in the region as partially occupied Cl sites. Population parameters were refined from all of the disordered Cl atoms, some of which overlap with the carbon atoms. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed in calculated positions [C–H 0.98 Å, B_{iso} = 1.2B(parent atom)]. Final R = 0.033, R' = 0.032.

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