Synthesis and characterisation of palladium(II) complexes with new diphosphine ligands. Application in the alternating copolymerisation of carbon monoxide and ethene.

Abstract

The diphosphine *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac*-*o*-MeO-bdpp) has been synthesised. The last ligand has been employed to synthesised new neutral palladium(II) complexes. Ligand and complexes have been fully characterised in solution by multinuclear NMR spectroscopy.

This C_2-briged ligand is compared with the C_3-briged and more rigid ligand bis-cationic diphosphonium-diphosphine 6,7-bis(di(2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphoniumbicyclo[3.1.1]heptane-bis(PF_6) (*o*-MeO-PCP)($(PF_6)_2$) in the copolymerisation of CO with ethene in different reaction media in order to compare the effect of the backbone rigidity.

Irrespective of the reaction media, perfectly alternating polyketones were obtained in excellent yields and with number-average molecular weights ranging from 7.1 to 13.9 kg mol^{-1} with the diphosphonium-diphosphine catalysts and from 37.2 to 48.2 kg mol^{-1} with the diphosphine catalysts.

3.1. Introduction

As previous mentioned in *chapter 1*, the design of conformationally rigid polyphosphine ligands for the coordination of late transition metals is a subject of much interest in organometallic chemistry and homogeneous catalysis.[1] Indeed, decreasing the flexibility of the supporting ligand decreases the number of the possible conformations of the metal-ligand assembly, thus leading to improved selectivity. Unlike selectivity, the effect of the skeletal rigidity on the activity is unpredictable as it mainly depends on the reaction under investigation rather than on the structural and conformational properties of the metal-diphosphine precursor. In the particular case of the copolymerisation of CO with ethene by palladium(II) catalysis[2], a direct correlation between catalytic productivity and structural rigidity of the chelating diphosphine has been unambiguously observed for a number of ligands, including C_2-bridged[3] and C_3-bridged[4] diphosphines, 1,1'-bis(diorganylphosphino)ferrocenes,[5] and bis(phosphino)ferrocenophanes.[6] **Figure 1** shows the molecular sketches of two 1,3-diphosphine ligands bearing backbone substituents that decrease the ligand flexibility (*rac*-bdpp and *meso*-bdpp; bdpp = 2,4-bis(diphenylphosphino)pentane). Below each sketch is reported the productivity as kg(polyketone) (g(Pd) × h)$^{-1}$ exhibited by the corresponding palladium(II) catalysts under comparable reaction conditions. For comparative purposes, it is also reported the palladium(II) catalyst with the commonly used 1,3-bis(diphenylphosphino)propane (dppp) ligand.

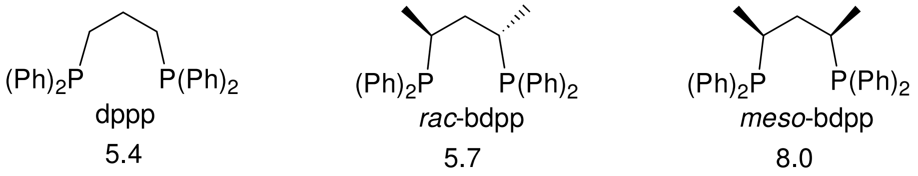
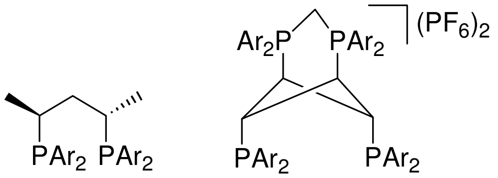


Figure 1

In this work is reported the synthesis of the new diphosphine *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac*-*o*-MeO-bdpp) (**a**) (**Figure**)as well as its $PdCl_2$ and $Pd(OAc)_2$ complexes $PdCl_2$(*rac*-*o*-MeO-bdpp) (**1a**) and $Pd(OAc)_2$(*rac*-*o*-MeO-bdpp) (**2a**). All these palladium(II) complexes have been tested as catalyst precursors for the copolymerisation of CO and ethene in different solvents and compared with $PdCl_2$((*o*-MeO-PCP)$(PF_6)_2$) (**1b**) and $Pd(OAc)_2$((*o*-MeO-PCP)$(PF_6)_2$) (**2b**) containing the ligand bis-cationic diphosphonium-diphosphine 6,7-bis(di(2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphoniumbicyclo[3.1.1]heptane-bis(PF_6) ((*o*-MeO-PCP)$(PF_6)_2$) (**b**) (**Figure 2**) respectively in order to study the effect of the backbone rigidity. All complexes have shown high activity and a remarkable control on the molecular weight of the alternating polyketone products.



rac-*o*-MeO-bdpp (*o*-MeO-PCP)$(PF_6)_2$

a **b**

Ar = 2-methoxyphenyl

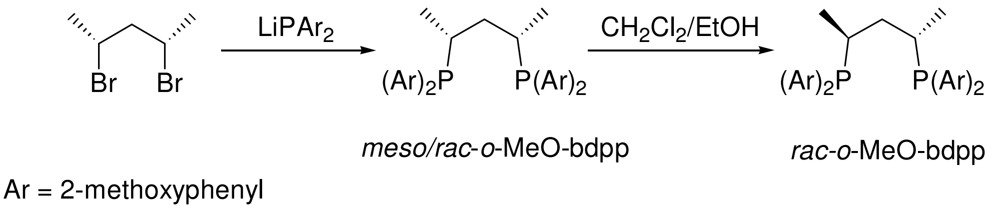
Figure 2

3.2. Results and discussion

Syntheses

Synthesis of the ligand

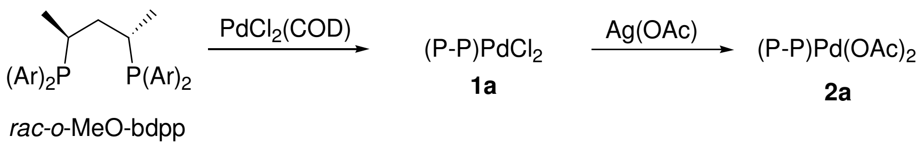
The diphosphine *rac*-*o*-MeO-bdpp was synthesised by the reaction of $LiPAr_2$ (Ar = 2-methoxyphenyl)[7] with a 26/74 *meso/rac* mixture of 2,4-dibromopentane in THF (**Scheme 1**). Only the *rac* isomer of *o*-MeO-bdpp could be isolated in a pure form (36% yield) as an white off solid by recrystallisation of the stereoisomeric mixture from CH_2Cl_2/ethanol.



Scheme 1

Synthesis and characterisation of the catalytic precursors

The reaction of *rac*-*o*-MeO-bdpp with $PdCl_2$(COD) in CH_2Cl_2 gave $PdCl_2$(*rac*-*o*-MeO-bdpp) (**1a**), while the analogous reaction with $Pd(OAc)_2$ yielded $Pd(OAc)_2$(*rac*-*o*-MeO-bdpp) (**2a**) as an impure product. However, the reaction of **1a** with Ag(OAc) in CH_2Cl_2 gave **2a** in a pure form. **1a** and **2a** were obtained in 70% and 60% yield, respectively (**Scheme 2**). The diphosphine *rac*-*o*-MeO-bdpp is just the *o*-methoxy derivative of the well-known ligand *skew*phos ligand.[8]



Scheme 2. Synthesis of the neutral palladium(II) complexes **1a** and **2a**

The crystal structure of **1a** shows the *S,S* stereoisomer (*S,S*-**1a**), which crystallises in the chiral space group *P*2$_1$. A selected ORTEP plot of *S,S*-**1a** is reported in **Figure 3**. Crystallographic data and selected bond distances and angles for (*S,S*)-**1a** are reported in **Table 1** and **Table 2**, respectively.

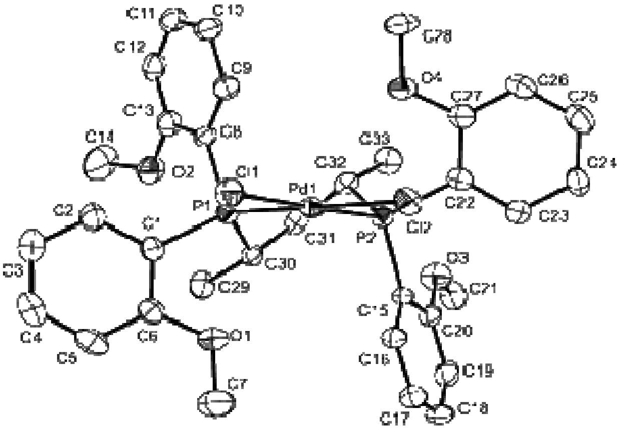


Figure 3. ORTEP plot of **1a**. Thermal ellipsoids are shown at the 30% probability level

Table 1. Crystalographic data for (*S*,*S*) **1a**

Empirical formula	$C_{33}H_{38}Cl_2O_4P_2Pd$
Formula weight	737.87
T/K	293(2)
λ/Å	0.71073
Crystal system, space group	Monoclinic, $P2_1$
a/Å	10.6259(7)
b/Å	13.6492(11)
c/Å	11.9265(9)
α/°	90.0
β/°	107.937(7)
γ/°	90.0
V/ Å^3, Z	1645.7(2), 2
D_c/Mgm^{-3}	1.489
μ/mm^{-1}	0.859
F(000)	756
Crystal size/mm	0.40 × 0.20 × 0.10
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameter	10051/1/391
Goodness-of-fit on F^2	0.855
Final R indices	$[I > 2\sigma(I)]$ $R1 = 0.0451$, w$R2 = 0.0808$
R indices (all data)	$R1 = 0.1015$, w$R2 = 0.0949$
Largest diff. Peak, hole/e Å^3	1.122, -0.375

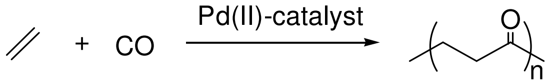
Table 2. Selected bond distances (Å) and angles (^{o}) for and (*S,S*)-**1a**

Pd(1)-P(1)	2.2671(11)
Pd(1)-P(2)	2.2757(11)
Pd(1)-Cl(1)	2.3620(11)
Pd(1)-Cl(2)	2.3608(10)
P(1)-Pd(1)-P(2)	90.11(4)
Cl(1)-Pd(1)-Cl(2)	91.53(4)
Cl(1)-Pd(1)-P(2)	177.98(4)
Cl(2)-Pd(1)-P(1)	179.62(5)
Intramolecular distances in (Å)	
Pd(1)-O(1)	3.5077(36)
Pd(1)-O(2)	5.1814(31)
Pd(1)-O(3)	5.1989(31)
Pd(1)-O(4)	3.4846(35)

The palladium centre is square-planar coordinated by two phosphorus and two chloride atoms. The deviation of the metal centre from the coordination plane, defined by the atoms P(1), P(2), Cl(1) and Cl(2), is 0.0192(7) Å in direction of C(1). (*S,S*)-**1a** exhibits a typical P(1)-Pd(1)-P(2) bite angle of 90.11(4)^{o}, which is comparable to that of many other six-membered palladium diphosphine complexes.[9] The Pd(1)-P(1) and Pd(1)-P(2) bond lengths in (*S,S*)-**1a** are of 2.2671(11) and 2.2757(11) Å, respectively. Like in other *S,S-skew*phos metal complexes, the carbon backbone of the ligand in (*S*,*S*)-**1a** exhibits a diagonal disposition with respect to the coordination plane, which is the most common conformation for skewphos metal complexes.[8] Strictly related to the diagonal disposition of the C5 carbon backbone, the four 2-methoxyphenyl groups are disposed diagonally with respect to the palladium coordination plane, which is shown by the deviation of the four *ipso* carbon atoms from the coordination plane (C(1) 0.9327(51) Å, C(8) -1,7077(45) Å, C(15) 1.6957(43) Å and C(22) -0.8764 Å). Furthermore, two *o*-methoxy oxygen atoms, namely O(1) and O(4) show shorter intramolecular distances to Pd(1) (3.5077(36) Å and 3.4846(35) Å, respectively), while O(2) and O(3) show by far a higher intramolecular distance to Pd(1) of 5.1814(31) and 5.1989(31) Å, respectively.

Catalytic copolymerisation of CO and ethene

The solvent of choice of most CO/C_2H_4 copolymerisation reactions by PdX_2(diphosphine) catalysis (**Scheme 3**) is either MeOH or water.



Scheme 3

This implies the use of weakly coordinating co-ligands (X = TsO^-, $CF_3CO_2^-$) to allow for the activation of either solvent to give Pd-H, Pd-OMe or Pd-OH initiators.[2] Recently, however, Toniolo et al. have shown that the bis-chloride and bis-acetate complexes PdX_2(diphosphine) (diphosphine = dppe, dppp, dppb) (X = Cl^-, OAc^-) can generate very active catalysts in water/AcOH mixtures.[10] Therefore, the bis-chloride complexes **1a** and **1b** were tested in different mixtures of water/AcOH under standard experimental conditions (40 bar 1/1 CO/ethene, 85°C). The results obtained are reported in **Table 3**. Irrespective of catalyst and solvent composition, perfectly alternating polyketone products were obtained with exclusively ketone end-groups.

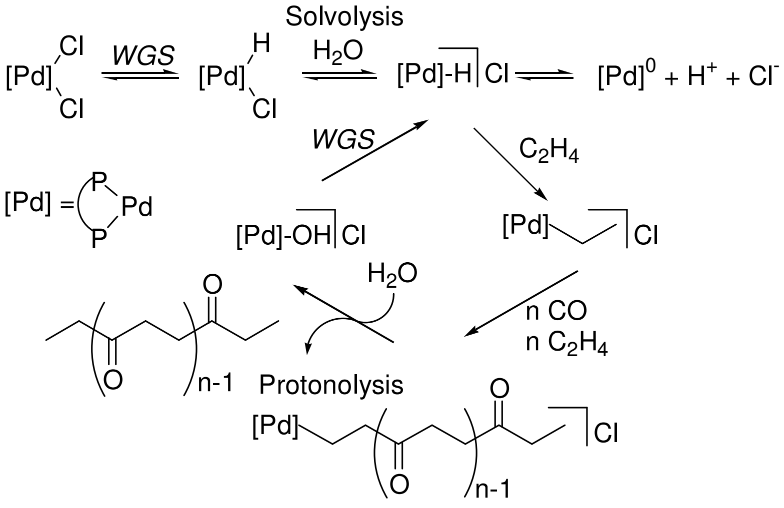
A maximum catalytic activity for **1a** was observed with the use of a 75/25 mol% mixture of water/AcOH (entry 3), while a mixture containing 65 mol% water was the optimum value for **1b** (entry 7). In reactions lasting 1 and 2 h, **1a** was slightly more active than **1b** but appreciably less stable with time (entries 3 and 4 vs. 7 and 8). However, the most striking catalytic difference between **1a** and **1b** was the M_n of the polyketone products: around 37 kg mol^{-1} with **1a** and 7 kg mol^{-1} with **1b** (**Table 3**). These results indicate that the chain-transfer rate is significantly faster in the reactions catalysed by **1b** than for the reactions catalysed by **1a**.

Table 3. Alternating copolymerisation of CO with ethene catalysed by $PdCl_2$(**a**), (**1a**) and $PdCl_2$(**b**), (**1b**) in water/AcOH[a]

Entry	Precatalyst	Water (mol%)	Time (h)	Polymer (g)	Productivity[b]	M_n (kg mol^{-1})
1	**1a**	55	1	4.12	7.74	
2	**1a**	65	1	4.75	8.93	37.4
3	**1a**	75	1	5.28	9.92	37.2
4	**1a**	75	2	7.84	7.37	
5	**1a**	85	1	3.91	7.35	
6	**1b**	55	1	3.10	5.83	
7	**1b**	65	1	3.70	6.95	7.3
8	**1b**	65	2	6.46	6.07	
9	**1b**	75	1	3.18	5.98	7.1
10	**1b**	85	1	2.19	4.11	

[a] Catalytic conditions: catalyst precursor, 0.005 mmol; p(CO)/p(C_2H_4), 20/20 bar; water/AcOH, 100 ml; temperature, 85 °C; stirring rate, 1100 rpm. [b] Expressed as kg(polyketone) (g(Pd) x $h)^{-1}$.

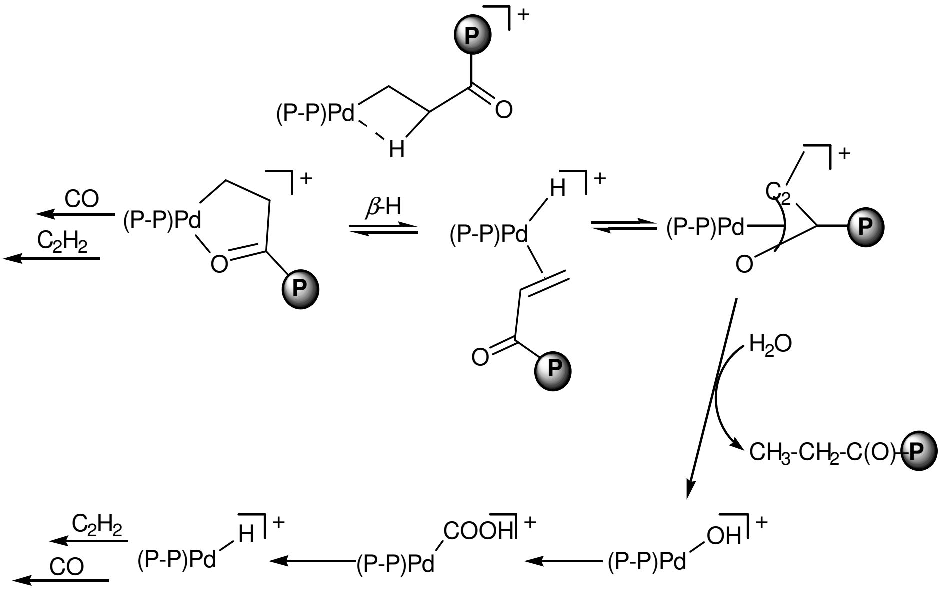
The mechanism of the CO/C_2H_4 copolymerisation by palladium(II)-diphosphine catalysis has been intensely studied over the last years and most of the elementary steps involved, especially chain-transfer and propagation, have been clarified.[2] **Scheme 4** provides a brief summary of the mechanism proposed for CO/ethene copolymerisation catalysed by $PdCl_2$(diphosphine) complexes in acidic aqueous media.[11]



Scheme 4

It is agreed that the neutral palladium(II)-H complexes are generated from the bis-chloride precursors by a water gas shift reaction (WGS),[11] and then converted into the catalytically active cationic palladium(II) hydride species by a water-controlled solvolysis process.[11a] Toniolo[10] and Zudin[11] have also demonstrated that increasing the water proportion in the water/AcOH mixture increases the concentration of the cationic palladium(II)-H species by speeding up the solvolysis process. On the other hand, a too large proportion of water has been found to have a detrimental effect on the solubility of CO and C_2H_4.[10] This may account for the significant decrease in productivity (from 6.95 to 4.11 kg (g (Pd) x h)$^{-1}$) by increasing the water proportion from 65 to 85 mol% (Table 3, entries 7,9,10).

The chain-transfer reaction of CO/ethene copolymerisation performed in acidic aqueous media has been demonstrated to occur exclusively *via* protonolysis by water with formation of a Pd-OH unit that re-generates a Pd-H initiator by WGS.[12] In these conditions, the intimate mechanism of chain transfer involves β-hydride elimination in a β-keto alkyl chelate, followed by hydride migration to give an enolate whose regioselective protonation terminates the chain growth (**Scheme 5**).[13] The rate of the *β*-H elimination determines the overall chain transfer rate, hence it controls the molecular weight of the polyketone produced.[2] *β*-H elimination reactions in organometallics are steered by both electronic and steric factors.[14] In particular, it is agreed that the agostic interaction between the metal and *β*-hydrogens (precursor to hydrogentransfer to the metal) is favoured by a low electron density at the metal centre.



Scheme 5

In complexes of the same metal ion, the electron density at the metal depends on the electronic and steric characteristics of the supporting ligands as well as on the overall charge of the complex. In the present case, a lower electron-donating ability of (*o*-MeO-PCP)(PF_6)$_2$ (**b**) as compared to *rac*-*o*-MeO-bdpp (**a**) is indicated by the significantly shorter Pd-P bond distances in **1b**[15] as compared to **1a** (2.2546(13) and 2.2403(13) Å *vs*. 2.2671(11) and 2.2757(11)

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Å). As a further, indirect proof of the lower metal basicity of complexes with (*o*-MeO-PCP)(PF_6)$_2$ vs. complexes with *rac*-*o*-MeO-bdpp, we have found that the IR spectrum of the bis-carbonyl complex *cis*-[Rh(CO)$_2$(*o*-MeO-PCP)](PF_6)$_3$ shows, in CH_2Cl_2, ν(CO) bands at 2097 and 2052 cm^{-1},[15] while *cis*-[Rh(CO)$_2$(*rac*-*o*-MeO-bdpp)](PF_6) exhibits red-shifted bands at 2086 and 2036 cm^{-1}.

Besides metal basicity, the *β*-H elimination rate in the propagating palladium-alkyl (**Scheme 5**) might be influenced by the interaction of the metal centre with the oxygen atoms from the *o*-methoxy substituents. Indeed, evidence has been reported in the literature for the coordinative interaction of this oxygen to metal centres.[16] In the eventuality of an analogous interaction in the propagating alkyls generated by **1a** and **1b**, the oxygen atoms would compete with the *β*-hydrogens for coordination, with a retarding effect on the *β*-H elimination rate. In this mechanistic picture, the stereochemical rigidity of (*o*-MeO-PCP)(PF_6)$_2$ (**b**) would disfavour the interaction of the *o*-methoxy units with the palladium centre, whereas a simple twisting of the C_5 backbone of *rac*-*o*-MeO-bdpp would allow for an axial interaction between the *o*-methoxy groups and the metal centre.

In an attempt of gaining further information on the present copolymerisation reactions in water/AcOH, a catalytic run was performed in a HP-NMR tube containing D_2O/AcOH (45 mol% D_2O) and catalyst precursor $PdCl_2$(**a**) (**1a**). A selected sequence of $^{31}P\{^1H\}$ HP-NMR spectra is presented in **Figure 4**.

A 10 mm sapphire tube was charged with $PdCl_2$(**a**) (**1a**) (14.8 mg, 0.02 mmol) in a solvent mixture D_2O/AcOH (45 mol% D_2O) (2 ml). A $^{31}P\{^1H\}$ NMR spectrum acquired at 20 °C showed a broad resonance centred at 28.00 ppm (trace **a**).[17] The HP-NMR tube was then pressurised with a 1/1 mixture of CO/C_2H_4 to a total pressure of 40 bar and a $^{31}P\{^1H\}$ NMR spectrum was acquired at 20 °C (trace **b**), which showed no substantial change. The probe-head was heated to

85 °C for 1 h during which time $^{31}P\{^{1}H\}$ NMR spectra were acquired every 20 min. Since the first spectrum, a quite sharp singlet appeared at 25.5 ppm. The $^{31}P\{^{1}H\}$ spectrum acquired after 1 h at 85 °C is reported in **Figure 4** as trace **c**. When the probe-head was cooled to 20 °C, the $^{31}P\{^{1}H\}$ NMR spectrum showed the same broad hump (trace **d**) as in the initial spectrum (trace **a**). The tube was removed from the NMR probe showing formation of the copolymer as a white off powder.

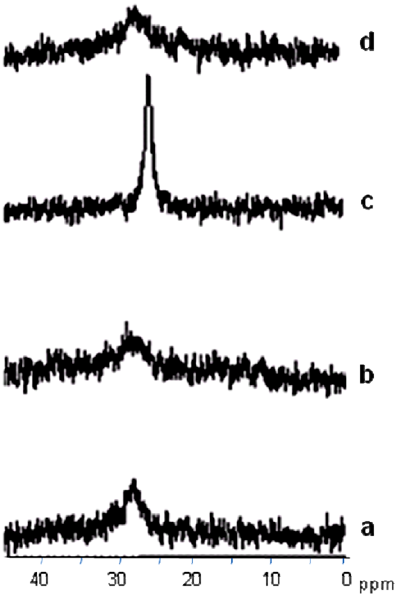

Figure 4. Selected $^{31}P\{^{1}H\}$ HPNMR spectra (sapphire tube, D_2O/AcOH, 20-85 °C, 81.01 MHz) recorded during a CO/C_2H_4 copolymerisation reaction catalysed by 1a: (**a**) **1a** suspended in D_2O/AcOH (45 mol% D_2O) at 20 °C; (**b**) after pressurisation of the tube with a 1/1 mixture of CO/C_2H_4 (40 bar total pressure) at 20 °C; (**c**) spectrum taken after 1 h at 85 °C); (**d**) after cooling to 20 °C

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A very similar sequence of $^{31}P\{^{1}H\}$ HPNMR spectra has been observed for the CO/ethene copolymerisation catalysed by $Pd(CF_3CO_2)_2$(NaDPPPDS) in water.[12b] It was suggested, and the same can be said for the present case, that most of the palladium remains incorporated into the precursor from which a small and undetectable aliquot is delivered into the catalysis cycle.

The catalytic activity of the neutral bis-acetate complexes **2a** and **2b** was tested in MeOH in the presence of 2 or 20 equiv. of TsOH, which serves both as scavenger of the acetate ion and oxidising agent for Pd(0) species eventually formed by palladium(II) reduction (**Scheme 4**).[2] The results of this study are reported in **Table 4**.

Table 4. Alternating copolymerisation of CO with ethene catalysed by $Pd(OAc)_2$(**a**), (**2a**) and $Pd(OAc)_2$(**b**), (**2b**) in MeOH in the presence of TsOH[a]

Entry	Precatalyst	TsOH (equiv.)	Time (h)	Polymer (g)	Productivity[b]	M_n (kg mol^{1})
1	**2a**	2	1	3.94	7.41	47.0
2	**2a**	2	3	11.54	7.23	
3	**2a**	20	1	2.90	5.45	48.2
4	**2a**	20	3	6.45	4.04	
5	**2b**	2	1	4.00	7.52	7.7
6	**2b**	2	3	4.50	2.82	
7	**2b**	20	1	5.21	9.79	13.9
8	**2b**	20	3	13.48	8.45	

[a]Catalytic conditions: catalyst precursor, 0.005 mmol; $p(CO)/p(C_2H_4)$, 20/20 bar; MeOH, 100 ml, temperature, 85 °C; stirring rate, 1100 rpm. [b]Expressed as kg(polyketone) $(g(Pd) \times h)^{-1}$.

With either catalyst precursor, the copolymer contained keto and ester end-groups in a 1/1 ratio. As observed in water/AcOH as solvent, the *rac*-*o*-MeO-bdpp precursor, **2a**, gave higher-molecular-weight products (47.0-48.2 kg mol^{-1}) as compared to the (*o*-MeO-PCP)$(PF_6)_2$ one, **2b** (7.7-13.9 kg mol^{-1}). However,

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with either catalyst the copolymers exhibited larger M_n values as compared to the products obtained in water/AcOH, which is consistent with a slower chain transfer rate in MeOH than in water/AcOH. Increasing the concentration of TsOH had a detrimental effect on that of **2a** (entries 1 *vs* 3 and 2 *vs* 4) and a beneficial effect on the productivity of **2b** (entries 5 *vs* 7 and 6 *vs* 8). The lower activity in the presence of 2 equiv. of TsOH and the much higher M_n of the polyketones obtained with 20 equiv. of acid in the reactions with **2b** suggest that the acid concentration is important not only for decreasing the extent of palladium(II) reduction but also for stabilising the overall metal-ligand assembly, likely by inhibiting the deprotonation of the diphosphonium-diphosphine ligand with formation of ylide species.

The reverse dependence of the productivity on the acid concentration for the reactions catalysed by the *rac*-*o*-MeO-bdpp precursor **2a** (**Table 4**, entries 1-4) is quite surprising as the opposite trend is generally observed for CO/ethene copolymerization in MeOH by palladium(II)-diphosphine catalysis.[2] This effect could be a direct consequence of the presence of the *o*-methoxy substituents on the phenyl rings. Indeed, a large excess of TsOH, containing one water molecule of crystallisation, would promote the creation of a web of hydrogen-bonding interactions around the metal centre, involving not only the coordinated solvent molecules but also the four oxygen atoms of the *o*-methoxyphenyl groups. As a result, the palladium(II) centre would become less accessible to the incoming monomers,[18,19] and contemporaneously the beneficial effect of the *o*-methoxy groups on the propagation rate would be diminished and even lost.[2d,16,20]

Support to the hydrogen-bonding interactions around the palladium centre in *rac*-*o*-MeO-bdpp catalysis intermediates is provided by several molecular structures of palladium(II)-aquo complexes with tosylate anions, which show the presence of hydrogen bonds between the coordinated water molecules and the

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oxygen atoms of both tosylate ligands and counter-anions.[5c,18] Moreover, DFT calculations performed on cationic $[L_3Pd(H_2O)]^+$ compounds have confirmed that the stability of such compounds is due to an efficient interaction of the counter-anions with the coordinated water molecule.[21]

3.3. Conclusions

The pool of available chelating diphosphine ligands has been enriched by a new member. A standard procedure has been employed to prepare the *rac*-*o*-MeO-bdpp. The ligand has been used to coordinate $PdCl_2$ and $Pd(OAc)_2$ yielding square-planar complexes that generate active catalysts for the copolymerisation of CO and ethene in either water/AcOH mixtures or MeOH/TsOH. The synthesised complexes have been compared with $PdCl_2$ and $Pd(OAc)_2$ complexes with (*o*-MeO-PCP)$(PF_6)_2$ ligand in the CO ethene copolymerisation reaction using both, water/AcOH mixture in the case of neutral palladium dichloride complexes or MeOH in the case of palladium diacetate complexes, as solvent media. The perfectly alternating polyketones bear either exclusively ketone or 1:1 ketone:ester end groups depending on the reaction solvent. The polyketone products produced with the phosphine catalysts show number-average molecular weights up to five times bigger than those obtained with the diphosphonium-diphosphine catalysts. These results have been interpreted in terms of faster chain-transfer rate due to the electronic and steric properties of the diphosphonium diphosphine ligand.

3.4. Experimental Section

General procedures

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deoxygenated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. $PdCl_2$(COD) (COD = 1,5-cyclooctadiene)[22], bis(*o*-methoxyphenyl)phosphine[23] and *meso*/*rac*-2,4-pentanediol dimesylate[7] were prepared according to literature methods. $PdCl_2$((*o*-MeO-PCP)(PF_6)$_2$) and Pd(OAc)$_2$((*o*-MeO-PCP)(PF_6)$_2$) complexes were synthesised by Peter Brüeggeller et al..[15] All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerisation reactions were performed with a 250 ml stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25µm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz), respectively. Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (^1H and ^{13}C NMR) or 85% H_3PO_4 as an external standard (^{31}P NMR). High-pressure NMR (HP-NMR) experiments were carried out on the Bruker ACP 200 spectrometer, using a 10 mm HPNMR tube (Saphikon sapphire tube; titanium high-pressure charging head constructed at the ICCOM-CNR).[24] Elemental analyses were performed

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using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer). The conductivity of ionic compounds was measured with an Orion model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data were obtained at a sample concentration of *ca.* 10^{-3} M in nitroethane solutions.[25] Polyketone products were analysed by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR measurements were performed in a solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2/C_6H_6-d_6 (5/1, v/v) showing a perfectly alternating structure with ketone or ketone/ester end groups. The number-average molecular weight (M_n) of the copolymers was determined by ^1H NMR spectroscopy.

Syntheses

Synthesis of the meso/rac-2,4-dibromopentane

This mixture of stereoisomers was synthesised using a modified version of the synthetic protocol reported by Wiberg et al.[26] LiBr (7.33 g, 84.4 mmol) was added to an acetone solution of *meso*/*rac*-2,4-pentanediol dimesylate (5.50 g, 21.1 mmol). The mixture was refluxed for 20 h, then it was cooled to room temperature. The solvent was removed by distillation and the crude residue was suspended in a solvent mixture of water/Et_2O/*n*-pentane (60 ml) (30/15/15, v/v/v). The organic layer was separated and the solvent was removed under reduced pressure to give a yellow liquid residue.

(*meso*/*rac*)-2,4-dibromopentane (26/74): 3.19 g (65.7%). $C_5H_{10}Br_2$ (229.85 g/mol): calc. C 26.13, H 4.35; found C 26.40, H 4.55%. ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 °C) 1.73 (d, $^3J_{HH}$ = 6.72 Hz, 6H, CH_3), 1.77 (d, $^3J_{HH}$ = 6.60 Hz 6H, CH_3), 2.15 (m, 3H, *meso*-CHH, *rac*-CH_2), 2.47 (dt, $^2J_{HH}$ 14.2 Hz, $^3J_{HH}$ 8.0 Hz, 1H, *meso*-CHH), 4.21 (m, 1H, Br-CH), 4.38 (m, 1H, Br-CH)

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Synthesis of the ligand (*rac*-*o*-MeO-bdpp) (a)

n-BuLi (6.80 ml, 10.8 mmol) was slowly added to bis(*o*-methoxyphenyl)phosphine (2.00 g, 8.13 mmol) dissolved in anhydrous and degassed THF (150 ml) at 0 °C. After the yellow Li salt precipitated, the suspension was stirred for 1 h at room temperature. A 26/74 mixture of *meso*/*rac*-2,4-dibromopentane (0.92 g, 4.02 mmol) was added dropwise to this suspension at room temperature, then the yellow solution was stirred overnight. Afterwards, the reaction was quenched with water (3 ml), concentrated to dryness, and washed with water and ethanol. Yield of *meso*/*rac*-*o*-MeO-bdpp 71.0% (1.60 g, 2.86 mmol). Recrystallisation of the mixture from CH_2Cl_2/EtOH led to the precipitation of a pure sample of *rac*-*o*-MeO-bdpp as a off white powder.

***rac*-*o*-MeO-bdpp**: 817.9 mg (36.0%). $C_{33}H_{38}O_4P_2$ (560.26 g/mol): calc. C 70.70, H 6.83; found C 70.65, H 6.85%. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, $CDCl_3$, 21 °C) -23.8 (s); ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 °C) δ 1.06 (dd, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 1.53 (m, 2H, CH_2), 2.75 (m, 2H, P-CH), 3.63 (s, 6H, OCH_3), 3.69 (s, 6H, OCH_3), 6.72-7.83 (m, 16H, Ar-H). All attempts to isolate the *meso* ligand in a pure form were unsuccessful

Syntheses of the neutral complexes

Synthesis of $PdCl_2$(*rac*-*o*-MeO-bdpp) (1a)

Rac-*o*-MeO-bdpp (112.1 mg, 0.20 mmol) was dissolved in degassed CH_2Cl_2 (20 ml) under nitrogen. To this colourless solution was added $PdCl_2$(COD) (57.1 mg, 0.20 mmol). The resultant suspension was stirred for 1 h, and then it was concentrated to half volume. The addition of a 1/1 (v/v) mixture of *n*-pentane and diethyl ether (20 ml) completed the precipitation of **1a** as a white off

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microcrystalline solid, which was filtered off and dried in a stream of nitrogen. Crystals of **1a** suitable for X-ray analysis were obtained by slow diffusion of toluene into a saturated CH_2Cl_2 solution at room temperature.

Complex 1a: 102.9 mg (69.8%). $C_{33}H_{38}Cl_2O_4P_2Pd$ (737.58 g/mol): calc. C 53.71, H 5.19; found C 53.69, H 5.20%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 °C) 34.50 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 0.86 (dd, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3), 1.82 (m, 2H, CH_2), 3.24 (m, 2H, P-C*H*), 3.72 (s, 6H, OCH_3), 3.90 (s, 6H, OCH_3), 6.80-7.70 (m, 16H, Ar-*H*)

Synthesis of $Pd(OAc)_2$(*rac*-*o*-MeO-bdpp) (2a)

Compound **1a** (258.2 mg, 0.35 mmol) was dissolved in degassed CH_2Cl_2 (30 ml) under nitrogen. To this solution was added Ag(OAc) (128.5 mg, 0.77 mmol) and the resultant suspension was stirred for 30 min. The precipitated AgCl was removed by filtration through a column of Celite and the clear solution was concentrated to *ca.* 5 ml. The addition of a 1/1 (v/v) mixture of *n*-hexane and diethyl ether (20 ml) completed the precipitation of **2a** as yellow microcrystals which were filtered off, and dried in a stream of nitrogen.

Complex 2a: 164.8 mg (60%). $C_{37}H_{44}O_8P_2Pd$ (784.69 g/mol): calc. C 56.60, H 5.65; found C 56.63, H 5.66%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 °C) 31.78 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 1.01 (dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, CH_3), 1.10 (s, 6H, OAc-CH_3), 1.88 (m, 2H, CH_2), 3.12 (m, 2H, P-C*H*), 3.68 (s, 6H, OCH_3), 3.93 (s, 6H, OCH_3), 6.95-7.68 (m, 16H, Ar-*H*)

Catalytic copolymerisation of CO and ethane

HP-NMR experiment in water/AcOH with 1a as catalyst precursor

A 10 mm sapphire HP-NMR tube was charged with a suspension of **1a** (14.8 mg, 0.02 mmol) in a mixture of D_2O and AcOH (0.4 ml/1.6 ml) under nitrogen and then placed into the NMR probe maintained at 20 ^{o}C. After a $^{31}P\{^1H\}$ NMR spectrum was acquired, the sapphire tube was removed from the NMR probe and pressurised with a 1/1 mixture of CO/C_2H_4 to a total pressure of 40 bar at room temperature. A $^{31}P\{^1H\}$ NMR spectrum was recorded at 20 ^{o}C and then the probe-head was heated to 80 ^{o}C. This temperature was maintained for 1 h, during which time $^{31}P\{^1H\}$ NMR spectra were acquired every 20 min. The tube was then allowed to cool to 20 ^{o}C and a final $^{31}P\{^1H\}$ NMR spectrum was acquired. The formation of copolymer was observed.

Autoclave experiments in water/AcOH with 1a and 1b as catalyst precursors

A deoxygenated mixture of distilled water and AcOH (100 ml) was introduced by suction into an autoclave (250 ml), previously evacuated by a vacuum pump, containing the catalyst precursor **1a** or **1b** (0.005 mmol). The autoclave was charged with a 1/1 CO/C_2H_4 mixture to 30 bar at room temperature. The temperature was increased to 85 ^{o}C while the pressure inside the autoclave was maintained at 40 bar. The autoclave was stirred (1100 rpm) for the desired time. Then it was cooled with an ice-water bath. The unreacted gases were released and the insoluble copolymer was filtered off, washed with water, and dried under vacuum at 60 ^{o}C to constant weight.

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Autoclave experiments in MeOH with 2a and 2b as catalyst precursors

MeOH (reagent grade from Aldrich, 100 ml) was introduced under a nitrogen into an autoclave (250 ml) containing the catalytic precursor **2a** or **2b** (0.005 mmol) and the desired amount of *p*-toluenesulphonic acid monohydrate (TsOH). The autoclave was pressurised with a 1/1 CO/C_2H_4 mixture to 30 bar at room temperature. The temperature was increased to 85 °C while the pressure inside the autoclave was maintained at 40 bar. The autoclave was stirred (1100 rpm) for the desired time. Then it was cooled with an ice-water bath. The unreacted gases were released and the insoluble copolymer was filtered off, washed with water, and dried under vacuum at 60 °C to constant weight. The filtered solutions were analysed by GC/MS.

X-ray crystallographic data collection and refinement of the structures

The crystallographic data for (*S,S*)-**1a** are summarised in **Table 1**. Graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) was used. The data collection was performed on a Oxford Diffraction CCD diffractometer using ω-scans for (*S*,*S*)-**1a**, respectively. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS[27a] for (*S,S*)-**1a**. All structure determination calculations for (*S,S*)-**1b**. were performed with WINGX package[27b] with SIR-97,[27c] SHELXL-97 and ORTEP-3 programs.[27d] Final refinements on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were included using a riding model with isotropic U values depending on the Ueq of the adjacent carbon atoms. CCDC reference number 293489 for (*S,S*)-**1a**

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