Ligand effects in the non-alternating CO/ethene copolymerisation reaction

Abstract

This chapter describes the synthesis of two novel bis(*o*-methoxyphenyl) phosphinoalkylsulfonate (P-O) ligands through a new and sustainable synthetic route as well as the synthesis of new neutral and anionic palladium (II) complexes. Furthermore, it deals with the effects of the rigidity of the anionic phosphine sulfonate ligands in neutral palladium(II) complexes on the catalytic outcome of the non-alternating CO-ethene copolymerisation in terms of catalytic productivity and the extra-ethene insertion into the polymeric chain. To this purpose neutral palladium(II) complexes bearing P-O ligands containing a 2-phenylidene and an ethylidene back-bone are compared from both a catalytic and a mechanistic point of view.

4.1.1. Introduction

The development of novel late transition metal catalysts for the synthesis of new copolymers containing a controlled amount of polar monomer is of considerable interest to both academia and industry.[1]

As it has been discussed in *chapter 1*, chelating anionic P-O ligands constitute a class of ligands that has much less been studied in catalytic reactions than their diphoshine counterparts. Apart from oligomerisation and polymerisation reactions,[2] very few homogeneous processes are efficiently catalysed by metal complexes with anionic P-O ligands. One of these is the palladium catalysed copolymerisation of carbon monoxide and ethene that gives perfectly alternating polyketones with diphosphine ligands and non-alternating polyketones with P-O ligands.[3]

Within the field of polar copolymers, the carbon monoxide and ethene copolymerisation, catalysed by cationic palladium (II) complexes bearing chelating diphosphine ligands is one of the most studied reaction.[4] These catalytic CO-ethene copolymerisation reactions are known to provide polyketones with strictly alternating CO and ethene units, due to the lack of the double CO insertion (thermodynamic control) and the difference in binding affinity of CO and ethene to cationic palladium centres (kinetic control). Furthermore coordination of an oxygen atom from the growing polymeric chain to the palladium centre takes place, increasing the activation barrier for the ethene incorporation into a metal-alkyl bond.[5]

The production of non-perfectly alternating carbon monoxide and ethene copolymers is one of the aims in polyketone research in order to obtain new materials with desirable properties. The architecture of randomly extra-ethene

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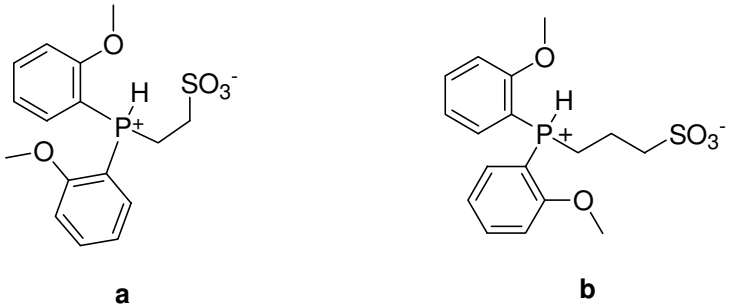
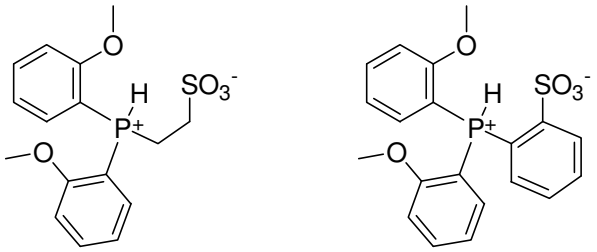
incorporated into a linear CO-ethene copolymer is obtained by employing neutral Pd(P-O) complexes (P-O = anionic chelating ligand) as precatalysts.[6]
Since the non-alternating polyketones might exhibit improved thermal stability, while retaining the excellent engineering properties of the strictly alternating polyketones, the development of highly efficient catalytic systems for the non-alternating CO-ethene copolymerisation, based on the knowledge of the key-steps of the catalytic copolymerisation cycle, are subject of experimental[6a,6b,6c] and theoretical[6d,6e] studies.

This chapter is focused on an alternative synthesis of two new phosphine-sulfonate ligands **a** and **b** (**Figure 1**) and on the comparison of neutral palladium(II)(P-O) complexes bearing the two phosphine sulfonate ligands **a** and **c**[6a] featured by a different rigidity of the carbon-backbone (**Figure 2**) in the non-alternating CO-ethene copolymerisation reaction from a catalytic and a mechanistic point of view.



a **b**

Figure 1. New phosphine sulfonate ligands



a **c**

Figure 2. Phosphine sulfonate ligands used for comparative purposes in the CO-ethene copolymerisation reaction

4.1.2. Results and discussion

Syntheses of the phosphine sulfonated ligands

The synthesis of two novel diaryl alkyl phosphine sulfonate ligands was carried out applying a modified synthetic protocol.

Synthetic routes for related phenyl derivates reported in the literature involve the use of ammonia as solvent[7] or sultones as reactants.[8] Indeed, all attempts to synthesise phosphinoalkylsulfonate ligands without either ammonia or sultones reported so far were unsuccessful.[9]

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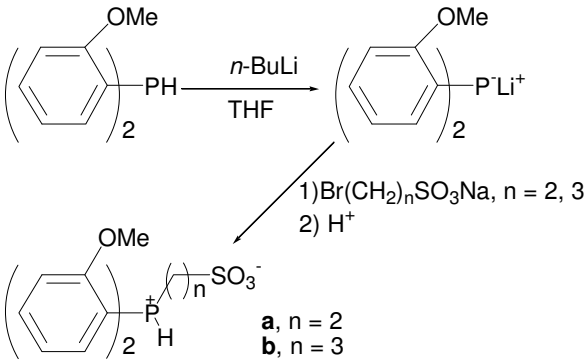

Scheme 1. Synthetic route for the syntheses of ligands **a** and **b**

Ligands **a** and **b** were synthesised by a new synthetic route that involves the reaction of *n*-butyllithium with bis(*o*-mehoxyphenyl)phosphine in THF[10] in order to obtain the corresponding lithium salt, followed by the reaction of the latter salt with the appropriate bromoalkylsulfonate derivate as shown in **Scheme 1**. Both ligands were isolated as zwitterions in 54% and 43% yield, respectively and characterised in solution by multinuclear NMR spectroscopy and in addition ligand **b** was also characterised in the solid state by a single crystal X-ray structure analysis. Both ligands resulted to be water soluble as well as air stable.

Single crystals of ligand **b** were obtained by diffusion of diethyl-ether into a $CHCl_3$ solution of **b**. An ORTEP drawing of ligand **b** is shown in **Figure 3**. The crystal structure of **b**.H_2O shows one molecule of **b** along and one molecule of H_2O per asymmetric unit. Crystallographic data and selected bond distances and angles for **b**.H_2O are reported in **Table 1** and **Table 2,** respectively.

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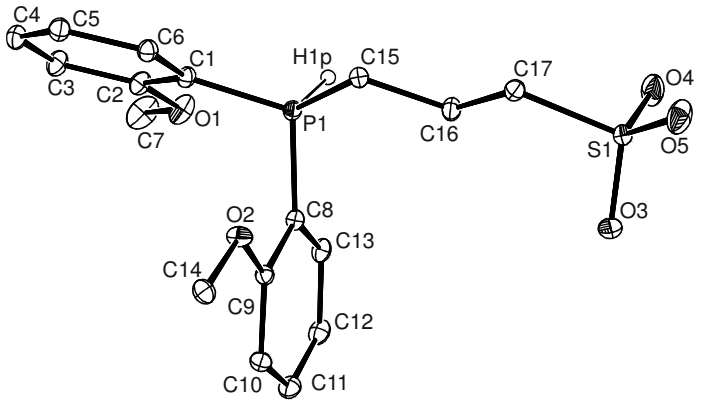


Figure 3. ORTEP drawing of ligand **b**. The solvent molecule as well as the hydrogen-atoms, except the one attached to P(1) have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level

Table 1. Summary of crystallographic data for ligand **b**.H_2O

Empirical formula	$C_{17}\ H_{21}\ O_5\ PS.H_2O$
Formula weight	386.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*2(1)/c
a	10.717(2) Å
b	15.216(3) Å
c	12.173(2) Å
α	90^o
β	112.803(4)°
γ	90^o
Volume	1829.8(5) $Å^3$
Z	4
Density (calculated)	1.403 Mg/m^3
Absorption coefficient	0.294 mm^{-1}
F(000)	816
Crystal size	0.20 x 0.10 x 0.02 mm^3
Theta range for data collection	3.44 to 39.58°.

Index ranges	-18<=h<=19 -26<=k<=23 -19<=l<=21
Reflections collected	36864
Independent reflections	10350 [R(int) = 0.0318]
Completeness to theta = 39.55°	93.9 %
Absorption correction	SADABS (Bruker-Nonius)
Max. and min. transmission	0.9941 and 0.9435
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10350 / 0 / 240
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.1115
R indices (all data)	R1 = 0.0442, wR2 = 0.1165
Largest diff. peak and hole	1.417 and -0.512 e.Å^{-3}

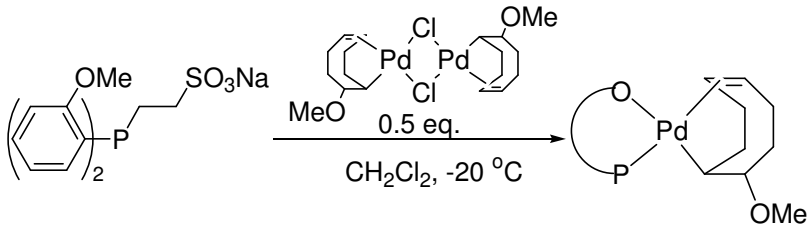
Table 2. Selected bond distances (Å) and angles (^{o}) for ligand **b**.H_2O

P(1)-C(1)	1.7813(8)
P(1)-C(8)	2.7853(8)
P(1)-C(15)	1.7980(8)
S(1)-C(17)	1.7865(8)
S(1)-O(3)	1.4534(7)
S(1)-O(4)	1.4566(8)
S(1)-O(5)	1.4537(8)
C(1)-P(1)-C(8)	109.42(4)
C(1)-P(1)-C(15)	112.60(4)
C(8)-P(1)-C(15)	110.99(4)
C(16)-C(17)-S(1)	112.24(6)

The zwitterionic structure of ligands **a** and **b** was unambiguously determined by low temperature ^{31}P NMR spectroscopy, showing in the corresponding ^{31}P NMR spectra a characteristic $^1J_{PH}$ coupling constants of 545 Hz, respectively. In the case of ligand **b** the presence of the P-H bond was also confirmed by its X-ray structure (**Figure 3**).

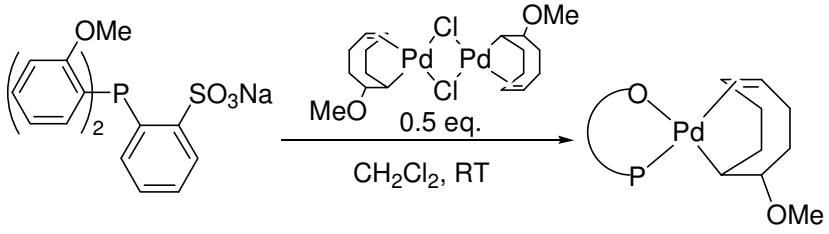
Syntheses of the neutral complexes

The neutral palladium(II) complex Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_2H_4SO_3$) (COD-OMe = 2-methoxycyclooct-5-enyl) (**1a**) containing the more flexible zwitterionic P-O ligand {bis-(2-methoxyphenyl)phosphonium}ethanesulfonate (**a**) was obtained upon reaction of the dimeric palladium (II) complex [Pd_2(μ-Cl)$_2${η^1,η^2-C_8H_{12}OMe}$_2$][11] with the sodium salt of ligand **a** at -20 ^oC, which was formed by the reaction of ligand **a** with NaH in CH_2Cl_2 (**Scheme 2**).



Scheme 2. Synthesis of the palladium(II) complex **1a**

Analogously, Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_6H_4SO_3$) (**1c**) was obtained upon reaction of the dimeric palladium (II) complex [Pd(μ-Cl){η^1,η^2-C_8H_{12}OMe}$_2$][11] with the Na-salt of the zwitterionic P-O ligand {bis-(2-methoxyphenyl)phosphonium}benezenesulfonate (**c**)[6a] in CH_2Cl_2 at room temperature (**Scheme 3**).



Scheme 3. Synthesis of the palladium(II) complex **1c**

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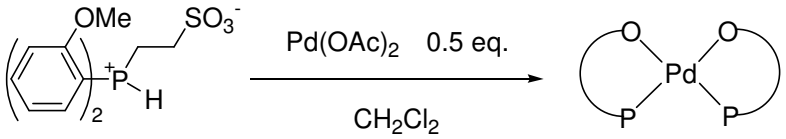
Both complexes were characterised in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis. Unlike compound **1c**, **1a** shows a much lower stability in most organic solvents. Indeed, a methanol solution of **1a** decomposes within one day at room temperature to yield the neutral bis-chelate complex Pd(**a**)$_2$ (**2a**), which was also obtained upon reaction of a CH_2Cl_2 solution of $Pd(OAc)_2$ with ligand **a** in a 1:2 molar ratio (**Scheme 4**). This latter complex is almost insoluble in most common organic solvents as reported for the analogous palladium compound with ligand **c**.[6b] Nevertheless the latter complex has been characterised in solution by ^1H and $^{31}P\{^1H\}$NMR spectroscopy and in the solid state by elemental analysis and a single X-ray structure analysis.



Scheme 4. Synthesis of complex **2a**

The reaction of the triethylammonium salt of ligands **a** and **c** with the neutral palladium(II) complex PdClMe(COD) (COD = cycloocta-1,5-diene) yields the anionic palladium complexes of the type [PdClMe(**L**)](NHEt$_3$) (**L** = **a** (**3a)**, **c** (**3c**)[12]). Both complexes were prepared following the synthetic procedure reported by Nozaki et al.,[12] which comprises the deprotonation of the zwitterionic P-O ligand with triethylamine in CH_2Cl_2, followed by the reaction of the obtained ammonium-salt with PdClMe(COD) in the same solvent (**Scheme 5**).

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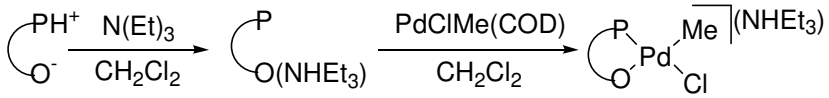
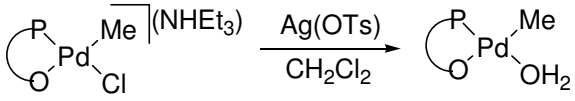


a, c **3a, 3c**

Scheme 5. General procedure for the syntheses of the anionic palladium complexes **3a** and **3c**

In both cases an off-white semi-crystalline powder was obtained, which was analysed in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis. The reaction of these latter palladium complexes with Ag(OTs) (OTs = *p*-toluenesulfonate) in CH_2Cl_2 yields the corresponding neutral palladium complexes PdMe(**L**)(H_2O) (**L** = **a** (**4a**), **c** (**4c**)) (**Scheme 6**), which were separated from the inorganic salt upon a CH_2Cl_2/water extraction. Since both latter complexes are slightly soluble in water, the yield of both complexes were rather low (around 38% in both cases).



3a, 3c **4a, 4c**

Scheme 6. Syntheses of the neutral complexes **4a** and **4c**

It is important to stress at this point that the low Lewis-acidity of the neutral palladium complexes brings about a weak coordination of the solvent molecule to the metal centre. Thus, the complete evaporation of a CH_2Cl_2 solution of **4a** and **4c** yields probably dimeric pallladium species, featured by intra-molecular palladium-oxygen (sulfonate) interactions (**Figure 4**). This latter dimeric species are not soluble in CH_2Cl_2 but show and excellent solubility in methanol. The formation of similar dimeric complexes has also been described for neutral Ni(P-O) complexes.[13]

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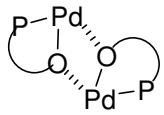


Figure 4

X-ray structures of compounds 1a and 2a

Suitable crystals of compound **1a** were obtained by a slow diffusion of diethyl-ether into a chloroform solution of compound **1a**, while crystals of complex **2a** were obtained by diffusion of a methanol solution of $Pd(OAc)_2$ into a dichloromethane solution of ligand **a**. Experimental X-ray diffraction parameters and selected bond length and angles for both complexes are reported in **Table 3** and **Table 4,** respectively. An ORTEP drawing of compounds **1a** and **2a** is shown in **Figure 5** and **Figure 6**, respectively.

Table 3. Experimental X-ray diffraction parameters and crystal data for compounds **1a** and **2a**

Compound	**1a**	**2a**
Empirical formula	$C_{25}H_{33}O_6PPdS$	$C_{32}H_{36}O_{10}P_2PdS_2$
Formula weight	598.94	813.07
Temperature	100(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a	9.4428(3) Å	9.403(5) Å
b	14.8530(5) Å	19.844(5) Å
c	17.7593(6) Å	10.566(5) Å
α	90°	90°
β	100.5950(10)º.	114.647(5)º
γ	90°	90°
Volume	2448.35(14) $Å^3$	1791.9(14) $Å^3$
Z	4	2
Density (calculated)	1.625 Mg/m^3	1.507 Mg/m^3

Absorption coefficient	0.948 mm^{-1}	0.777 mm^{-1}
F(000)	1232	832
Crystal size	0.20 x 0.10 x 0.10 mm^3	0.40 x 0.30 x 0.25 mm^3
Theta range for data collection	3.75 to 25.00°	2.36 to 24.97°
Index ranges	-11<=h<=11 0<=k<=17 0<=l<=21	-11<=h<=10 0<=k<=23 0<=l<=9
Reflections collected	4275	2982
Independent reflections	4275	2803
Data / restraints /	4275 / 0 / 310	2803 / 0 / 428
Goodness-of-fit on F^2	1.100	1.081
R indices (all data)	R1 = 0.0297, wR2 = 0.0701	R1 = 0.0306, wR2 = 0.0832
Largest diff. peak and hole	1.755 and -1.447 e/$Å^{-3}$	0.086 and -0.417 $Å^{-3}$

Table 4. Selected Bond length (Å) and angles (°) of compounds **1a** and **2a**

Compound	**1a**	**2a**
Pd(1)-P(1)	2.2836(7)	2.241(1)
Pd(1)-P(2)		2.340(1)
Pd(1)-O(4)	2.161(2)	
Pd(1)-O(5)		2.105(4)
Pd(1)-O(8)		2.103(4)
Pd(1)-C(15)	2.044(3)	
Pd(1)-C(18)	2.274(3)	
Pd(1)-C(19)	2.276(3)	
P(1)-Pd(1)-P(2)		102.97(6)
P(1)-Pd(1)-O(4)	96.78(6)	
P(1)-Pd(1)-C(15)	89.87(8)	
C(15)-Pd(1)-C(18)	80.98(11)	
C(15)-Pd(1)-C(19)	88.93(11)	
O(5)-Pd(1)-O(8)		87.29(17)
P(1)-Pd(1)-O(5)		85.30(12)
P(2)-Pd(1)-O(8)		84.44(13)

Intramolecular distances (Å)		
Pd(1)-O(1)	3.829(2)	5.083(5)
Pd(1)-O(2)	5.207(2)	3.679(4)
Pd(1)-O(3)		3.783(5)
Pd(1)-O(4)		5.018(4)
Pd(1)-H(9)	2.935	2.720
Pd(1)-H(25)		2.756

Complex **1a** (**Figure 5**) exhibits a distorted square-planar coordination geometry with the phosphine sulfonate ligand coordinating to the palladium atom in a bidentate fashion. Very few examples of metal complexes containing a direct M-oxygen (SO_3) bond are reported in the literature, due to the poor coordination properties of this latter group. The Pd(1)-O(4) bond length of 2.161(2) Å and the P(1)-Pd(1)-O(4) bite angle of 96.78(6)^o are comparable to related palladium structures.[12,6b]

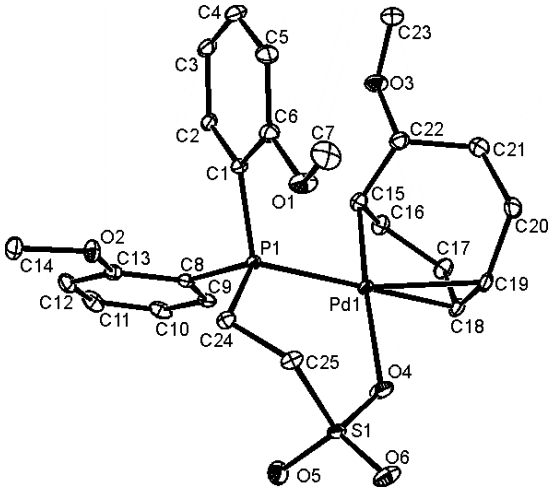


Figure 5. ORTEP drawing of compound **1a**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are shown at a 30% probability level

The crystal structure of the neutral palladium(II) bis-chelate complex **2a** (**Figure 6**) shows a square planar coordination sphere with a *cis* coordination of the

phosphorus atoms belonging to two different P-O ligands.[6b,14] The two remaining coordination sites are occupied by two oxygen atoms stemming from sulfonate units. The palladium atom shows no significant deviation from the best coordination plane, which is defined by the atoms P(1), P(2), O(5) and O(8). The molecule shows almost C_2-symmetry, with the C_2 axis bisecting the P(1)-Pd(1)-P(2) angle of 102.97(6)°. The bite angles of the two coordinating P-O ligands of 85.30(12)° (P(1)-Pd(1)-O(5)) and of 84.44(13)° (P(2)-Pd(1)-O(8)) are only slightly different from each other. While both Pd-O bonds of 2.105(4) Å (Pd(1)-O(5)) and of 2.103(4) Å (Pd(1)-O(8)) are identical, the Pd-P bond lengths of 2.241(1) Å (Pd(1)-P(1)) and of 2.340(1) Å (Pd(1)-P(2)) are significantly different, which may be accounted for by the steric pressure, which exert the two equatorial 2-methoxyphenyl units on each other. The intra-molecular palladium methoxy-oxygen distances range from 3.679(4) Å to 5.083(5) Å and are thus far from being bonding interactions.[15] Unlike the intra-molecular palladium methoxy-oxygen distances, the intra-molecular palladium-hydrogen distances of 2.720 Å (Pd(1)-H(9)) and of 2.756 Å (Pd(1)-H(25)) evidence interactions between the palladium atom and two *ortho*-hydrogen atoms, which belong to the axial 2-methoxyphenyl units of both P-O ligands. These latter interactions are retained also in solution at room temperature, which is evidenced by ^{1}H-NMR spectroscopy, showing a broad singlet centred at 9.10 ppm in the corresponding ^{1}H NMR spectrum. Such down-field shifts of ^{1}H-NMR signals of *ortho*- phenyl hydrogen atoms, due to interactions with the palladium atom has also been observed in 2-methoxy modified Pd(P-P) complexes (see *chapter 2*, sections 2.1 and 2.2).[15]

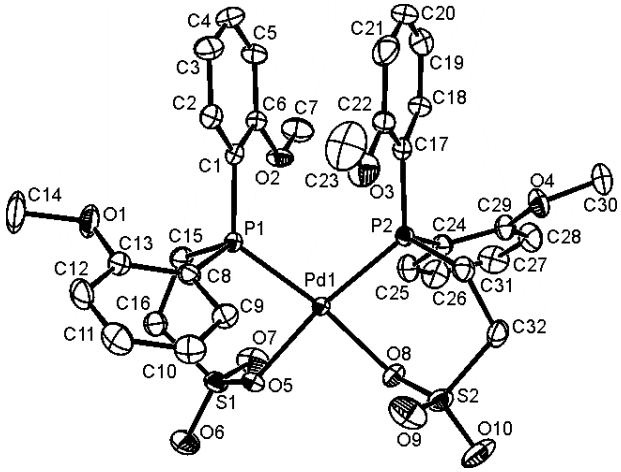


Figure 6. ORTEP drawing of compound **2a**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at a 30% probability level

Catalytic study

Non-alternating CO-ethene copolymerisation reactions, catalysed by the neutral Pd(P-O) complexes **1a**, **1c**, **4a** and **4c** were carried in methanol and 2,2,2-trifluoroethanol at 110 and 120 ^{o}C in the presence of different CO-ethene gas ratios. The results of the catalytic study are reported in **Table 5**.

A perusal of **Table 5** shows that irrespective of the catalytic conditions chosen, the precatalysts bearing the more rigid ligand **c** are much more productive than those bearing the flexible counterpart. A comparable trend has been observed in oligo-and polymerisation reactions, catalysed by neutral Ni(P-O) complexes.[13] Performing the catalytic reactions in the presence of 1,4-benzoquinone (BQ) leads to an increase of the catalytic productivity, being more pronounced in those catalytic reactions, performed with the rigid pre-catalysts.

The addition of Broensted-acid to the catalytic system has an enhancing effect on the productivity of those pre-catalyst, which bear the flexible ligand **a**, which

might be explained by the lower stability of the corresponding Pd-H species formed during the catalytic process, while for the rigid pre-catalyst, the opposite applies. Indeed, a negative acid effect on the catalytic productivity has already been observed in CO-ethene copolymerisation reactions, catalysed by Pd-diphosphine complexes, bearing 2-methoxyphenyl groups at the phosphorus donor atoms (see *chapter 2*, section 2.1).[15a] This latter phenomenon has been rationalised by the formation of a net of strong hydrogen-bond interactions between the acid and the *ortho*-methoxy-oxygen atoms.

Irrespective of the pre-catalyst employed, the CO-ethene gas-ratio steers the catalytic productivity significantly. In fact, on increasing the partial pressure of ethene going from a 1/3 to a 1/20 CO-ethene gas-ratio, the catalytic productivity decreases significantly (entries 31 *vs* 39, 32 *vs* 40 and 33 *vs* 38), which might be accounted for by the CO assisted insertion of ethene into Pd-γ-chelate complexes, which was postulated as the rate determining step in the propagation of the CO-ethene copolymerisation reaction.[16]

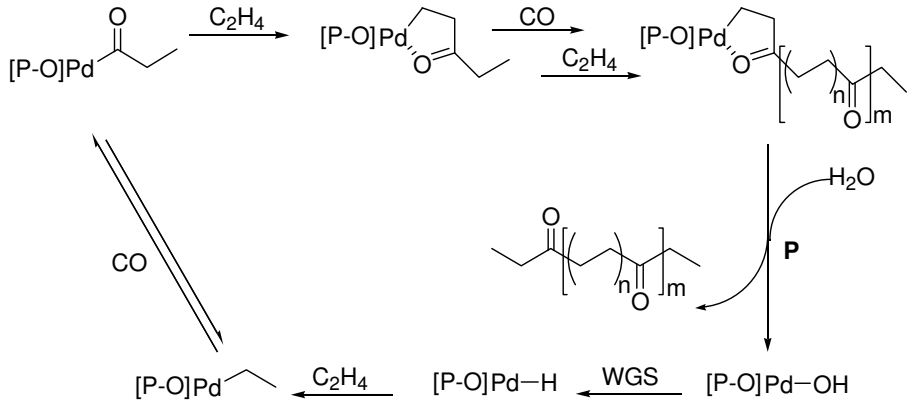
Performing analogous catalytic reactions in 2,2,2-trifluoroethanol shows with both types of pre-catalysts a positive effect on the catalytic productivity, being more pronounced in those cases were high molecular weight non-alternating copolymers were obtained, thus indicating the importance of the reaction to be carried out in a homogeneous phase, which is provided by the excellent solubilising properties of fluorinated solvents for polymeric materials.[17] As far as the molecular weight of the copolymers is concerned, two different ranges of average molecular weight were observed. While the pre-catalysts bearing the rigid ligand **c** produce high molecular weight copolymers (>300.000),[6b] the flexible counterparts produce low molecular weight non-alternating copolymers (**Table 5**), indicating the prevalence of the termination over the propagation reactions in the latter case.

Table 5. Non-alternating copolymerisation of CO and ethene, catalysed by the neutral Pd(P-O) complexes **1a**, **1c**, **4a** and **4c**[a]

Entry	Precat	t(h)	T (°C)	p(CO)/ $p(C_2H_4)$	Acid/BQ	Productivity[b]	M_n[c]	Extra-C_2H_4 (%)
1	**1a**	6	100	1/3	80/0	1.3		
2	**1a**	6	110	1/1	20/0	4		
3	**1a**	3	110	1/3		0.6		
4	**1a**	6	110	1/3		0.4	5.3	0.3
5	**4a**	6	110	1/3		0.4		
6	**1a**	12	110	1/3		0.1		
7[†]	**1a**	6	110	1/3		0.6	4.3	0.5
8	**1a**	6	110	1/3	0/80	1.3		
9	**1a**	6	110	1/3	20/0	1.9	5.2	3.0
10	**1a**	6	110	1/3	80/0	5.4	5.4	6.6
11[e]	**1a**	6	110	1/3	80/0	0.7	8.0	3.2
12	**1a**	12	110	1/3	80/0	2.5		
13	**1a**	6	110	1/3	160/0	1.8	8.4	23.2
14[e]	**1a**	6	110	1/3	160/0	0.7		
15	**1a**	6	110	1/6	20/0	0.6	2.3	8.2
16	**1a**	6	120	1/3	20/0	0.6	5.6	9.9
17	**1a**	6	120	1/3	80/0	1.3	4.8	13.7
18	**1c**	1	110	1/3		153	n.d.	3.2
19[d]	**1c**	1	110	1/3	0/80	210		
20	**4c**	1	110	1/3		150		
21[d,f]	**1c**	1	110	1/3		390	n.d.	2.5
22	**1c**	1	110	1/3	20/0	58	n.d.	3.2
23	**1c**	1	110	1/6		92	n.d.	5.4
24[d]	**1c**	1	110	1/6	0/80	133		
25	**1c**	1	110	1/20		44	n.d.	22.2
26[d]	**1c**	1	110	1/20	0/80	83		
27[g]	**1c**	1	110	0/1		340		
28	**1c**	1	120	1/1		254	n.d.	1.5
29[d]	**1c**	1	120	1/1	0/80	490	n.d.	1.1
30	**1c**	1	120	1/3		175	n.d.	6.0
31[d,f]	**1c**	1	120	1/3		337		3.4
32[d,f]	**1c**	1	120	1/3	0/80	607		
33[d]	**1c**	1	120	1/3	0/80	337		
34	**1c**	1	120	1/6		125	n.d.	9.9
35[d]	**1c**	1	120	1/6	0/80	190		
36	**1c**	1	120	1/20		40.8		27.8
37[d]	**1c**	1	120	1/20	0/80	133		
38[d]	**1c**	2	120	1/20	0/80	95		
39[d,f]	**1c**	1	120	1/20		77	n.d.	23.8
40[d,f]	**1c**	1	120	1/20	0/80	130		

[a]Catalytic conditions: pre-catalyst (0.012 mmol), p(total) (800psi), MeOH (50 mL), [b]Productivity expressed as g × (mmol (Pd) × h)$^{-1}$, [c]M_n (kg × mol^{-1}), [d]precatalyst (0.003 mmol), [e] HBF_4, [f]CF_3CH_2OH (50 mL), [g]ethene (600 psi).

End-group analyses of the non-alternating CO-ethene copolymers, which were carried out in a 1:3 (v:v) mixture of hexafluoropropan-2-ol-d_2 and C_6D_6 by means of ^{1}H NMR spectroscopy show in the case of the low-weight copolymers, which were obtained in the absence of any additives, three types of end-groups, namely ester (E), ketone (K) and vinyl (V) end-groups in a 10:10:1 ratio, while those produced in the presence of acid exhibited only ketone end groups, stemming from protonolysis reaction of Pd-alkyl species.[4] A possible catalytic cycle operative in acidic methanol solution is shown in **Scheme 7**.



P = Protonolysis reaction, WGS = Water Gas Shift reaction

Scheme 7. Proposed catalytic cycle operative in acidic methanol solution

The protonolysis reaction of Pd-alkyl species with water in conjunction with the water gas shift reaction (WGS) generates the Pd-H species, which inserting ethene starts the propagation of a new polymeric chain. The fast protonolysis reaction of Pd-alkyl species bearing the flexible Pd(P-O) moiety, might be rationalised by a fast coordination-de-coordination equilibrium of the sulfonate group to and from the palladium centre, increasing thus the Lewis acidity of the metal centre upon de-coordination of the sulfonate unit from the metal centre and therefore accelerating the β-hydride elimination reaction, which is followed by a protonation step. The extra-ethene insertion into the growing polymeric

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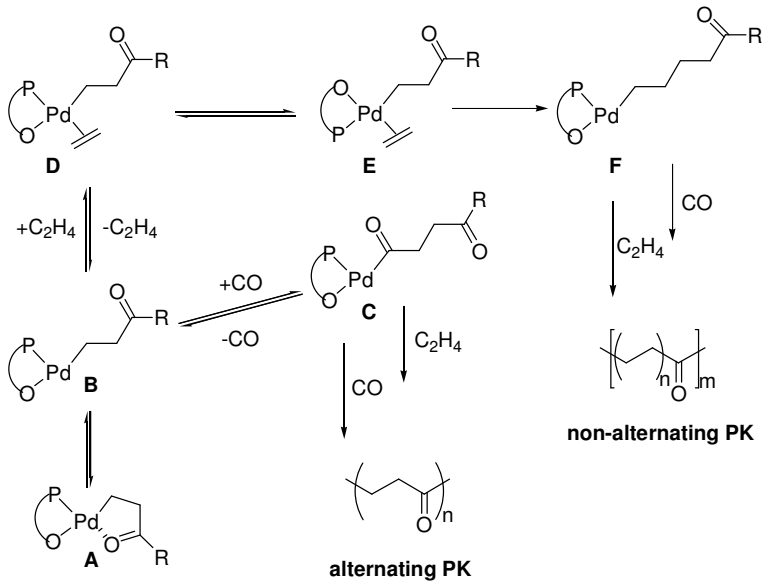
chain is mainly influenced by the coordinating P-O ligand, by the reaction temperature, by the CO-ethene gas-pressure ratio.

Theoretical studies of the catalytic cycle concerning the non-alternating CO-ethene copolymerisation reaction, catalysed by neutral Pd(P-O) complexes, revealed that the rate controlling step of the chain-propagation is the insertion of ethene into a palladium-alkyl bond (**Scheme 8**, **E**-**F**).[6d,6e] The Pd(ethene)-alkyl species (**E**) shows the migrating alkyl group in *trans*-position to the phosphine unit lowering the activation energy for the migration step significantly, due to the higher trans influence of the phosphorus donor atom compared to the oxygen atom, favour the extra-ethene insertion into the growing polymeric chain.[6d,6e]



Scheme 8. Proposed mechanism for the production of non-alternating CO-ethene copolymers

The concentration of latter compound **E** increases with **a**) the temperature, due to the decarbonylation of the palladium acyl complex **C** (**Scheme 8**), shifting the

equilibrium versus the open form of the Pd-β-chelate (**B**); **b**) the ethene partial pressure, shifting the equilibrium between compound **B** and **D** versus the latter compound on increasing the ethene partial pressure; **c**) the bulkiness of the phosphorus-substitutens of the P-O ligand, shifting the isomerisation equilibrium between the two Pd(ethene)-alkyl species **D** and **E**, versus the latter one on increasing the steric congestion at the phosphorus donor atom of the ligand.[6d,6e]

Indeed, the catalytic study shows very clearly an increase of the extra-ethene insertion on increasing the temperature and the ethene partial pressure. Furthermore catalytic reactions under identical conditions for both types of precatalysts show, that an increase of the ligand rigidity brings about a higher degree of extra-ethene incorporation into the polymeric chain (**Table 5**, entry 4 vs entry 18). While the presence of 1,4-benozquinone in catalytic non-alternating copolymerisation reactions showed no effect on the extra-ethene incorporation, an increase of the amount of *p*-toluenesulfonic acid show only in those copolymerisation reactions, catalysed by the flexible pre-catalysts a significant increase of extra-ethene incorporation. This positive effect on the extra-ethene incorporation vanishes on employing HBF_4 instead of *p*-toluenesulfonic acid (**Table 5**, entry 10 *vs* 11), evidencing, that the coordination of the tosylate plays a crucial role in the overall mechanism of extra-ethene incorporation.

Irrespective of the pre-catalyst and catalytic conditions employed for the copolymerization reactions, all non-alternating CO-ethene copolymers exhibit a linear structure, which was confirmed by $^{13}C\{^1H\}$NMR spectroscopy, evidencing a step-wise ethene insertion into the growing polymeric chain and thus excluding the incorporation of ethene-oligomers, stemming from a parallel ethene-oligomerisation reaction.[6a] Reactions, catalysed by the pre-catalysts containing the rigid ligand **c** employing only ethene, brings about the formation

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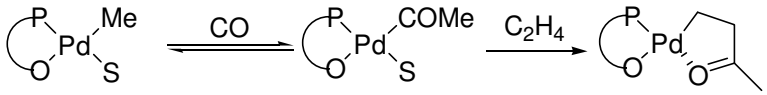
of polyethylene, while analogous reactions, catalysed by the flexible pre-catalysts containing ligans **a** leads to the formation of traces butenes and hexenes, evidencing a fast β-hydride-elimination reaction in the latter case.

NMR Model study

In order to identify metallorganic species, which might be formed during the catalytic non-alternating CO-ethene copolymerisation reaction in MeOH, catalysed by neutral palladium complexes, the neutral Pd-Me complexes **4a** and **4c** were used as starting compounds for the step-wise insertion of CO and ethene, which was carried out in CD_3OD as outlined in **Scheme 9**.



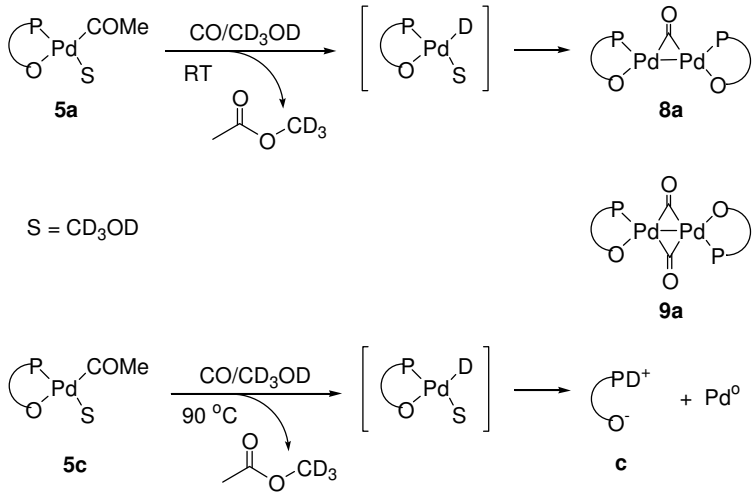
4a, 4c **5a, 5c** **6a, 6c**

S = CD_3OD

Scheme 9. Step-wise insertion of CO and ethene into Pd-alkyl and Pd-acyl bonds, respectively

On bubbling CO through a CD_3OD solution of the neutral Pd-Me complexes **4a** and **4c**, the corresponding Pd-acyl complexes **5a** and **5c** were formed. Like the former complexes, the Pd-acyl complexes **5a** and **5c** exhibit a *cis* coordination of the coordinating carbon atom with respect to the phosphine moiety, which is evidenced by $^{13}C\{^1H\}$NMR spectra, showing a singlet centred at 223.34 ppm and a doublet centred at 222.58 ppm ($^2J_{PC}$ = 8.0 Hz) for **5a** and **5c**, respectively. Interestingly, even in the presence of a (1:9) $^{13}CO/^{12}CO$ gas-mixture (total pressure (200 psi)), no $^{13}C\{^1H\}$ NMR signal, due to CO coordination to the palladium centre was observed. While compound **5c** undergoes methanolysis reaction at 90 ^oC, yielding methyl-acetate and the zwitterionic ligand **c**, which is

evidenced by a $^{31}P\{^{1}H\}$ NMR spectra, showing in CD_3OD a broad hump centred at -9.20 ppm at 90° C and in CD_2Cl_2 a 1:1:1 triplet centred at -10.80 ppm with a $^{1}J_{PD}$ of 92.0 Hz, **5a** undergoes methanolysis reaction already at room temperature yielding methyl-acetate and dimeric CO-bridged palladium(I) complexes. Based on $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra, structures as shown in **Scheme 10** are assigned to compounds **8a** and **9a**, respectively.

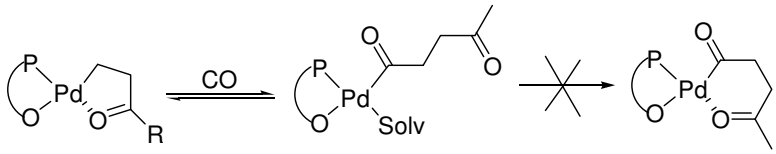


Scheme 10. Methanolysis reaction of compounds **5a** and **5c**

Once the CD_3OD solution of compound **5c** was obtained, excess CO was eliminated upon bubbling nitrogen through the solution, followed by bubbling ethene through the same solution for 10 minutes at room temperature yielding the first-generation Pd-β-chelate (**6c**) quantitatively as the only phosphorus containing compound (**Scheme 9**). The same synthetic procedure was employed for the 2:1:1 mixture of **5a**/**8a**/**9a** yielding a 1:1 mixture of **6a**/**8a**.

The NMR-spectroscopic data for both Pd-β-chelate complexes **6a** and **6c**, are in line with a *trans*-coordination of the carbonyl oxygen atom to the phosphorus

atom of the ligand, as shown in **Scheme 9**. The coordination of the carbonyl unit to the palladium atom is clearly evidenced by singlets in the $^{13}C\{^1H\}$ NMR spectra centred at 230.86 and 231.59 ppm for **6a** and **6c**, respectively. Furthermore concentrating the CD_3OD solution of both Pd-β-chelate complexes to dryness and acquiring IR spectra in CH_2Cl_2 shows in both cases a carbonyl stretching band at 1641 cm^{-1}, which clearly underscores the formation of Pd-β-chelates. Complex **6c** was then further converted into the second-generation Pd-acyl complex **7c** on successively bubbling nitrogen and CO through a CD_3OD solution of **6c** (**Scheme 11**).



6c **7c**

Solv = CD_3OD

Scheme 11. *in situ* synthesis of the second generation Pd-acyl complex **7c**

Compound **7c** is characterised by a singlet in the $^{31}P\{^1H\}$NMR spectrum, centred at 14.53 ppm, which is similar to the ^{31}P chemical shift obtained for the Pd-acyl complex **5c** at 13.60 ppm. The $^{13}C\{^1H\}$NMR spectrum shows for compound **7c** two signals, namely a doublet centred at 221.44 ppm with a $^2J_{PC}$ of 7.5 Hz, which corresponds to the carbonyl-unit directly bond to palladium and a singlet centred at 210.18 ppm, which corresponds to the carbonyl-unit, which is not directly bond to palladium, evidencing the lack of Pd-γ-chelate formation, due to the low Lewis acidity of the palladium centre in neutral Pd(P-O) complexes. As a consequence the de-carbonylation of Pd-acyl complexes yielding Pd-alkyl complexes is facilitated **Scheme 8** (**C**-**B**).[6d,6e]

Operando HP-NMR study

In an attempt of intercepting metallorganic species formed during the non-alternating CO-ethene copolymerisation reaction, catalysed by neutral Pd(P-O) complexes, *operando* HP-NMR experiments were carried out, employing the Pd-Me complexes **4a** and **4c** in the presence of a CO-ethene gas-ratio of 1:3. While a HPNMR experiment with pre-catalyst **4a** was carried out in CD_3OD, an analogous experiment was performed with pre-catalyst **4c** in the presence of a 3:1 (v:v) solvent-mixture of CF_3CH_2OH and C_6D_6 in order to avoid the precipitation of the polymeric material during the NMR experiment. A sequence of selected $^{31}P\{^1H\}$ NMR spectra for both studies are shown in **Figure 7** (for **4a**) and **Figure 8** (for **4c**).

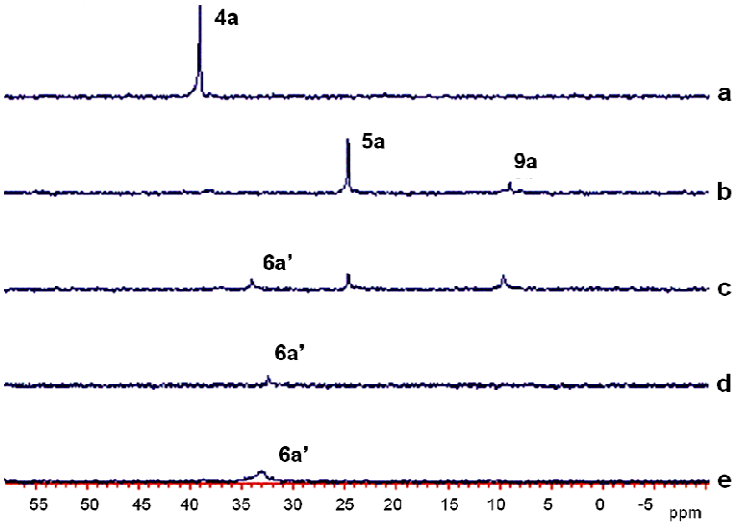


Figure 7. Variable–temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_3OD, 81.01 MHz) of the non-alternating CO-ethene copolymerisation reaction catalysed by pre-catalyst **4a**: (**a**) compound **4a** under nitrogen at RT; (**b**) under CO (200 psi) at RT.; (**c**) under CO (200 psi) and C_2H_4 (600 psi) at RT; (**d**) after 10 min at 110 ^oC; (**e**) after cooling to RT.

The $^{31}P\{^{1}H\}$ HP-NMR experiment carried out in CD_3OD with the neutral complex **4a** (**Figure 7**) shows for the latter complex a singlet, centred at 38.00 ppm at room temperature (**Figure 7**, trace **a**). On pressurising the solution with 200 psi of CO leads after 15 min at room temperature to a complete conversion of **4a** into the Pd-acyl complex **5a** and the dimeric palladium(I) complex **9a** (**Scheme 10)**. This latter complex stems from the methanolysis reaction of the Pd-acyl complex **5a**. Charging the sapphire tube with 600 psi of ethene at room temperature brings about the conversion of the Pd-acyl compound **5a** into Pd-β-chelates (**6a'**), featured by polymeric chains of different length, showing in the $^{31}P\{^{1}H\}$NMR spectrum a singlet, centred at 34.00 ppm (**Figure 7**, trace **c**), which resembles that found for the first-generation Pd-β-chelate (**6a**) (**Scheme 9**). Heating the NMR solution to 110 ^{o}C, shows the complete conversion of **5a** and **9a** into **6a'** (**Figure 7**, trace **d**), indicating that the dimeric Pd(I) complex is not a dead end of the CO-ethene copolymerisation reaction.[18] On cooling the NMR solution to room temperature the $^{31}P\{^{1}H\}$ NMR spectrum shows **6a'** as the only phosphorus containing compound. Performing an identical HP-NMR experiment in the presence of 20 equivalents of *p*-toluenesulfonic acid, shows the same sequence of metallorganic species during the HP-NMR study as in the absent of it.

An analogous HP-NMR experiment carried out with compound **4c** in a 3:1 solvent mixture of CF_3CH_2OH/C_6D_6 shows in the $^{31}P\{^{1}H\}$ NMR spectrum for **4c** a singlet centred at 27.9 ppm (**Figure 8**, trace **a**) at room temperature. On charging the sapphire tube with CO (200 psi) at room temperature brings about the complete conversion of the latter compound into the Pd-acyl complex **5c** (**Figure 8**, trace **b**),which shows a $^{31}P\{^{1}H\}$NMR signal centred at 0.20 ppm. At this point it is important to emphasis the fact that both the $^{31}P\{^{1}H\}$ and the $^{13}C\{^{1}H\}$NMR (Pd-*C*OCH_3) signal for the latter complex are shifted up-filed in this solvent mixture compared to the analogous chemical shifts observed in CD_3OD (TFE/C_6D_6: $^{31}P\{^{1}H\}$NMR: δ 0.2 ppm (s), $^{13}C\{^{1}H\}$NMR: δ 211.49 ppm (d),

^{2}J(PC) of 8.0 Hz; CD_3OD: $^{31}P\{^{1}H\}$NMR: δ 13.60 ppm (s), $^{13}C\{^{1}H\}$NMR: δ 222.58 ppm (d), ^{2}J(PC) of 8.0 Hz. Furthermore a parallel HPNMR experiment in the same solvent mixture employing a (1:10) gas-ratio between ^{13}CO and ^{12}CO at a total pressure of 200 psi, gives no hint for CO coordination to the metal centre of complex **5c**. Once compound **5c** was formed, the sapphire tube was pressurised with 600 psi of ethene, which brings about the conversion of the latter compound into Pd-β-chelates (**6c'**), featured in the $^{31}P\{^{1}H\}$NMR spectrum by a singlet, centred at 21.50 ppm (**Figure 8**, trace **c**). The $^{31}P\{^{1}H\}$NMR chemical shift of these latter species is almost identical to that observed for the first generation Pd-β-chelate (**6c**) (**Scheme 9**) in CD_3OD. Heating the solvent mixture to 110 ^{o}C (**Figure 8**, trace **d**) and then cooling it to room temperature (**Figure 8**, trace **e**) shows the Pd-β-chelates (**6c'**) as the only phosphorus containing species.

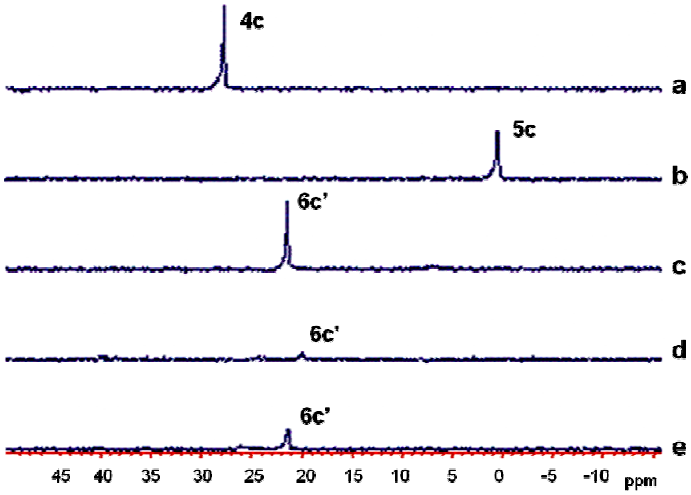


Figure 8. Variable–temperature $^{31}P\{^{1}H\}$ NMR study (sapphire tube, CF_3CH_2OH/C_6D_6 (v:v) (3:1), 81.01 MHz) of the non-alternating CO-ethene copolymerisation reaction catalysed by pre-catalyst **4c**: (**a**) compound **4c** under nitrogen at RT; (**b**) under CO (200 psi) at RT; (**c**) under CO (200 psi) and C_2H_4 (600 psi) at RT; (**d**) after 10 min at 110 ^{o}C; (**e**) after cooling to RT.

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4.1.3. Conclusions

The zwitterionic phosphine sufonate ligands 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulfonic acid (**a**) and 3-{bis(*o*-methoxyphenyl)phosphino}propanesulfonic acid (**b**) were prepared using a simple synthetic procedure.

A comparison of the catalytic CO-ethene copolymerisation reactions, catalysed by neutral Pd(P-O) complexes bearing the flexible 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulfonate and the rigid 2-{bis(*o*-methoxyphenyl)phosphino}benzenesulfonate, show that the former complexes lead to the formation of low-molecular weight copolymers, due to fast chain-transfer reactions, with an extra-ethene content in the polymeric chain up to 23.2 % on addition of *p*-toluensulfonic acid to the catalytic system, while the latter complexes are orders of magnitude more active yielding non-alternating CO-ethene copolymers with an extra-ethene incorporation up to 27.8 %.

Operando HP-NMR experiments of the copolymerisation reactions, catalysed by neutral Pd(P-O) complexes show the corresponding Pd-β-chelates as resting state of the copolymerisation reaction. Since Pd-γ-chelates are not formed in methanol with neutral Pd(P-O) complexes and CO does not coordinate to the palladium centre of Pd-acyl complexes, the decarbonylation reaction of the latter complexes increases with temperature favouring extra-ethene insertion into the growing polymeric chain and thus yielding non-strictly alternating polyketones.

4.1.4. Experimental section

General considerations

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 deareated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. Ligand **c**[6a], PdCl(Me)(COD)[19] (COD = cycloocta-1,5-diene), [Pd(μ-Cl){η^1,η^2-C_8H_{12}OMe}$_2$][11] and **3c**[12] were prepared according to literature methods. All 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 200 mL stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a home made temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure during the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP2010S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25 μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{31}P NMR spectra were obtained on a Bruker ACP 200 and a Bruker Avance DRX-400 spectrometers or on a Varian Mercury VX 400 MHz and Varian Gemini 300 MHz spectrometers. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (^{1}H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). High pressure NMR experiments (HP-NMR) were carried out on Bruker ACP 200 using a 10mm sapphire NMR tube, which was purchased from Saphikon (Milford, NH), while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Florence-Italy).[20] Elemental analyses were performed using either a Carlo Erba

Model 1106 or Model 1108 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer).

Syntheses

Synthesis of 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulfonic acid (a)

To a solution of bis(*o*-methoxy)phenylphosphine[10] (1.00 g, 4.07 mmol) in deareated THF (50 ml) was added dropwise *n*-BuLi (3.1 mL, 4.9 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and was further stirred for 1 h in order to form the corresponding lithium salt. Afterwards the THF solution of the lithium salt was added to a flask containing the sodium salt of 2-bromoethane sulfonic acid (0.83 g, 3.9 mmol). The mixture was then allowed to stir for 1.5 h at room temperature. The reaction was quenched with water and the solvent evaporated to yield a slightly yellow solid, which was dissolved in water (20 ml) and then acidified with HCl (37% in water) to pH 2. The acqueous phase was extracted with dichloromethane (3 x 80 mL). Afterwards the combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield a white powder.

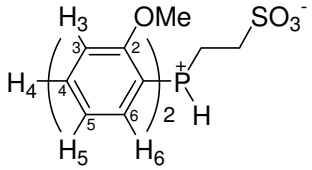

Figure 9. Ligand **a**

Ligand a: 746.3 mg (54%). $C_{16}H_{19}O_5PS.H_2O$ (372.35 g/mol): calc. C 51.61, H 5.68, S 8.61; found: C 52.11, H 5.42, S 8.49. $^{31}P\{^1H\}$ NMR (δ, 121.50 MHz, CD_2Cl_2, 21 °C) 0.5 (br s); ^{31}P NMR (δ, 121.5 MHz, CD_2Cl_2, -60 °C) 2.86 (d, $^1J_{PH}$ = 544,9 Hz); ^1H NMR (δ, 300.13 MHz, CD_2Cl_2, 21 °C) 2.96 (m, 1H, SCH_2), 3.04

(m, 1H, SCH_2), 3.17 (m, 2H, PCH_2), 3.90 (s, 6H, OCH_3), 7.08 (m, 2H, *H*-3), 7.19 (m, 2H, *H*-5), 7.60 (m, 2H, *H*-6), 7.72 (m, 2H, *H*-4); $^{13}C\{^1H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21º C)16.7 (d, $^1J_{PC}$ = 56.1Hz, P*C*H_2), 44.2 (d, $^2J_{PC}$ = 3.9Hz, S*C*H_2), 56.7 (s, O*C*H_3), 104.4 (d, $^1J_{PC}$ = 90.25 Hz, *ipso*-*C*), 111.9 (d, $^3J_{PC}$ = 6.1Hz, *C*-3), 122.5 (d, $^3J_{PC}$ = 12.9Hz, *C*-5), 135.3 (d, $^2J_{PC}$ = 7.6Hz, *C*-6), 137.2 (s, *C*-4), 161.7 (s, *C*-2). See **Figure 9**

Synthesis of 3-{bis(*o*-methoxyphenyl)phosphino}propanesulfonic acid (b)

To a solution of bis(*o*-methoxy)phenylphosphine[10] (1.00 g, 4.07 mmol) in THF (50 ml) was added dropwise *n*-BuLi (3.1 mL, 4.9 mmol) at 0 ^oC. The reaction mixture was allowed to warm to room temperature and was further stirred for 1h in order to form the corresponding lithium salt. The THF solution of the latter salt was added to a flask containing the sodium salt fo 3-bromopropane sulfonic acid (0.88 g, 3.9 mmol).The mixture was then allowed to stir for 1.5 h at room temperature. The reaction was quenched with water and the solvent evaporated to yield a slightly yellow solid, which was dissolved in water (20 ml). The obtained solution was then acidified with HCl (37% in water) to pH 2 and extracted with dichloromethane (3 x 80 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield a white powder, which was recrystallised from MeOH.

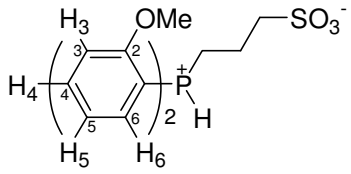

Figure 10. Ligand **b**

Ligand b: 589.1 mg (41%). $C_{17}H_{21}O_5PS$ (368.39 g/mol): calc. C 55.43, H 5.75, S 8.70; found: C 55.67, H 5.22, S 8.56. $^{31}P\{^1H\}$ NMR (δ, 121.5 MHz, $CDCl_3$, 21

^{o}C) -3.94 (br s); ^{31}P NMR (δ, 121.5 MHz, $CDCl_3$, -60 ^{o}C) -2.73 (d, $^{1}J_{PH}$ = 532.89 Hz); ^{1}H NMR (δ, 300.13 MHz, $CDCl_3$, 21 ^{o}C) 2.14 (m, 2H, PCH_2CH_2), 2.99 (t, $^{3}J_{HH}$ = 6.3 Hz, 2H, SCH_2), 3.10 (m, 2H, PCH_2), 3.87 (s, 6H, OCH_3), 7.00 (m, 2H, *H*-3), 7.10 (m, 2H, *H*-5), 7.59 (m, 2H, *H*-4), 7.79 (m, 2H, *H*-6); $^{13}C\{^{1}H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21 ^{o}C) 17.94 (d, $^{1}J_{PC}$ = 49 Hz, PCH_2), 19.6 (s, PCH_2CH_2) 50.6 (d, $^{3}J_{PC}$ = 15.9, SCH_2), 56.9 (s, OCH_3), 105.2 (d, $^{1}J_{PC}$ = 83.4 Hz, *ipso-C*), 112.0 (d, $^{3}J_{PC}$ = 5.9 Hz, *C*-3), 122.3 (d, $^{3}J_{PC}$ = 12.9 Hz, *C*-5), 135.3 (d, $^{2}J_{PC}$ = 8.4 Hz, *C*-6), 135.8 (s, *C*-4), 161.9 (s, *C*-2). See **Figure 10**

Synthesis of Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_2H_4SO_3$) (1a)

NaH (3.6 mg, 0.15 mmol) was added to a Schlenk flask containing a solution of ligand **a** (49.6 mg, 0.14 mmol) in deareated dichloromethane (5 ml). After this solution had been stirred for 30 minutes [$Pd_2(\mu$-$Cl)_2\{\eta^1,\eta^2$-$C_8H_{12}OMe\}_2$] (39.2 mg, 0.07 mmol) was added under stirring at -20 ^{o}C. The reaction mixture was allowed to stir for 1h at RT, followed by concentration of the solution to a small volume (2 ml) and on addition of diethyl-ether (10 mL) compound **1a** precipitated as yellow solid, which was filtered off and dried under a flow of nitrogen.

Complex 1a: 51.2 mg (57%). $C_{25}H_{33}O_6PdPS$ (598.9 g/mol): calc. C 50.09, H 5.51, S 5.34; found: C 50.27, H 5.22, S 5.23. $^{31}P\{^{1}H\}$ NMR (δ, 121.5 MHz, $CDCl_3$, 21 ^{o}C) 20.3 (s); ^{1}H NMR (δ, 300.13 MHz, CD_2Cl_2, 21 ^{o}C) 1.79-2.82 (m, 10H, (COD)), 2.37 (s, 3H, OCH_3, (COD)), 3.01-3.12 (m, 4H, PCH_2CH_2S), 3.76 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.20 (m, 1H, PdC*H*), 6.45 (m, 1H, C*H,* (COD*)*), 6.92 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 7.42 (m, 2H, Ar-H), 7.62 (m, 2H, Ar-H); $^{13}C\{^{1}H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21 ^{o}C) 23.50 (d, $^{1}J_{PC}$ = 29.6Hz, PCH_2), 25.25 (s, CH_2(COD)), 29.07 (s, CH_2(COD)), 31.58 (s, CH_2(COD)), 35.41 (s, CH_2(COD)), 41.4 (s, *C*H(COD)), 46.92 (s, SCH_2), 55.61 (s, OCH_3), 55.72 (s, OCH_3), 55.81 (s, OCH_3), 82.06 (s, Pd*C*H), 111.5 (d, $^{1}J_{PC}$ = 19.5Hz, *C*-ipso, Ar),

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120.30 (*C*, Ar), 121.24 (d, $^2J_{PC}$ = 7.95Hz, *C*, Ar), 121.63 (d, $^2J_{PC}$ = 10.8Hz, *C*, Ar), 122.20 (d, $^2J_{PC}$ = 7.35Hz, *C*, Ar), 133.25 (s, *C*, Ar), 134.57 (s, *C*, Ar), 161.9 (s, *C*, Ar)

Synthesis of Pd[(*o*-MeO-C_6H_4)$_2$$PC_2H_4SO_3$]$_2$ (2a)

In a Schlenk tube was dissolved $Pd(OAc)_2$ (11.3 mg, 0.05 mmol) in deareated MeOH (2 mL). To this solution was added ligand **a** (35.4 mg, 0.10 mmol) and the solution was then stirred at room temperature for 3 hours, during which the product precipitated as yellow powder, which was filtered off, washed with diethyl-ether (5 mL) and dried in a stream of nitrogen. The product was insoluble in common organic solvents. Even in DMSO a very low solubility of the compound was obtained.

Complex 2a: 26.4 mg (65%). $C_{32}H_{36}O_{10}P_2PdS_2$ (813.08 g/mol): cal. C 49.16, H 4.60; found: C 49.01, H, 4.58. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, $(CD_3)_2SO$, 21 ^oC) 32.28 (br s); ^1H NMR (δ, 400.13 MHz, $(CD_3)_2SO$, 21 ^oC) 2.80 (br m, 4H, CH_2P), 3.10 (br s, 4H, CH_2SO_3), 3.55-4.09 (br s, 12H, OCH_3), 6.15-7.74 (m, 14H, Ar-H), 9.10 (br. s, 2H, *o-H*)

Synthesis of Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_6H_4SO_3$) (1c)

NaH (8.9 mg, 0.37 mmol) was added to a Schlenk flask containing a solution of ligand **c** (148.9 mg, 0.37 mmol) in deareated dichloromethane (5 ml). After stirring the reaction solution for 30 minutes [$Pd_2(\mu$-Cl)$_2${η^1,η^2-C_8H_{12}OMe}$_2$] (100.8 mg, 0.18 mmol) was added at RT. The reaction mixture was allowed to stir for 1h at RT, followed by concentration of the solution to a small volume (2 ml) and addition of *n*-pentane (10 mL) in order to precipitate the product, which was filtered off, washed with *n*-pentane and dried under a flow of nitrogen, yielding complex **1c** as a pale yellow semi-crystalline solid.

Complex 1c: 162.9 mg (67%). $C_{29}H_{33}O_6PPdS$ (657.02 g/mol): calc. C 53.86, H 5.10; found: C 53.42, H, 5.01. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, $CDCl_3$, 21 °C) 8.20 (s); ^1H NMR (δ, 400.13 MHz, $CDCl_3$, 21 °C) 1.70-2.72 (m, 13H, (COD) + OC*H*$_3$), 2.42 (s, overlapped), 3.59 (s, 3H, OC*H*$_3$), 3.65 (s, 3H, OC*H*$_3$), 6.04 (m, 1H, (COD)), 6.72 (m, 1H, (COD)), 6.92-7.51 (m, 10H, Ar) 8.07 (dd, $^3J_{PH}$ = 12.4 Hz, $^3J_{HH}$ = 10.0 Hz, 1H, *o-H*), 8.16 (dd, $^3J_{PH}$ = 20.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, *o-H*); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, $CDCl_3$, 21 °C) 25.37 (s, *C*H$_2$(COD)), 28.62 (s, *C*H$_2$(COD)), 30.72 (s, *C*H$_2$(COD)), 35.26 (s, *C*H$_2$(COD)), 40.72 (s, *C*H(COD)), 54.82 (s, O*C*H$_3$), 55.27 (s, O*C*H$_3$), 55.54 (s, O*C*H$_3$), 81.55 (s, Pd*C*H), 111.24 (s, *C*, Ar), 114.70 (d, $^1J_{PC}$ = 52.0 Hz, *ipso-C*), 115.37 (d, $^1J_{PC}$ = 52.0 Hz, *ipso-C*), 117.08 (d, $^3J_{PC}$ = 9.2 Hz, *C*H), 120.85 (s, *C*, Ar), 121.14 (s, *C*, Ar), 121.42 (d, $^2J_{PC}$ = 12.1 Hz, *C*H), 127.85 (d, $^2J_{PC}$ = 10.62 Hz, *C*, Ar), 128.45 (s, *C*, Ar), 130.27 (s, *C*, Ar), 132.93 (s, *C*,Ar), 134.27 (s, *C*, Ar), 134.90 (s, *C*, Ar), 140.47 (d, $^2J_{PC}$ = 27.8 Hz, *C*, Ar), 147.90 (s, *C*, Ar), 160.04 (s, *C*, Ar), 161.06 (s, *C*, Ar).

Synthesis of [PdClMe(*o*-MeO-C$_6$H$_4$)$_2$PC$_2$H$_4$SO$_3$)](NHEt$_3$) (**3a**)

In a Schlenk flask containing deareated CH_2Cl_2 was added triethylamine (97.6 µL, 0.70 mmol) and ligand **a** (49.6 mg, 0.14 mmol). This solution was stirred for 15 min. at room temperature, followed by the addition of PdClMe(COD) (37.1 mg, 0.14 mmol). The reaction solution was allowed to stir for one hour at room temperature. Then the solution was filtered through a plug of celite, followed by the addition of *n*-hexane (20 mL) to cause the precipitation of the product, which was filtered off, washed with *n*-hexane and dried in a flow of nitrogen, yielding an off-white semi-crystalline product.

Complex 3a: 59.4 mg (73%). $C_{23}H_{37}ClNO_5PdPS$ (581.50 g/mol): cal. C 45.13, H 6.04: found: C 45.01, H 5.97. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 31.44 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 0.37 (d, $^3J_{PH}$ = 2.2 Hz, 3H, PdC*H*$_3$), 1.33 (t, $^3J_{HH}$ = 7.2 Hz, 9H, NCH$_2$C*H*$_3$), 3.02 (m, 2H, SC*H*$_2$), 3.12 (m, 2H,

PCH_2), 3.22 (q, $^3J_{HH}$ = 7.2 Hz, 6H, NCH_2), 3.91 (s, 6H, OCH_3), 7.05 (m, 2H, Ar), 7.15 (m, 2H, Ar), 7.57 (m, 2H, Ar), 7.68 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) -0.20 (br s, PdCH$_3$), 7.87 (s, CH_2CH_3), 22.32 (d, $^1J_{PC}$ = 33.7 Hz, CH_2P), 46.48 (s, CH_2N), (SCH_2, overlapped signal), 55.12 (s, OCH$_3$), 111.31 (d, $^3J_{PC}$ = 4.3 Hz, *m-C*, Ar), 111.59 (d, $^1J_{PC}$ = 53.7 Hz, *ipso-C*, Ar),120.55 (d, $^3J_{PC}$ = 11.2 Hz, *m-C*, Ar), 133.25 (s, *o-C*, Ar), 135.81 (s, *p-C*, Ar); 160.62 (s, *C*, Ar).

Synthesis of [PdMe(L)]$_2$ (L = a, (4a); c, (4c))

In a Schlenk flask compounds (**3a**) or (**3c**) (0.20 mmol) were dissolved in deareated CH_2Cl_2 (5mL), followed by the addition of Ag(OTs) (OTs = *p*-toluenesulfonate) (58.6 mg, 0.21 mmol) at room temperature. The suspension was allowed to stir for half an hour and was then filtered through celite. The CH_2Cl_2 solution was washed with deareated water (3×5 mL) and then the organic phase separated, dried over Mg_2SO_4 and concentrated to dryness by means of a vacuum pump, obtaining an off-white solid in both cases. Both complexes were characterised in CD_3OD, were both of them a monomeric complexes, best described as PdMe(L)(CD_3OD).

Complex 4a: 37.9 mg (40%). $C_{34}H_{42}O_{10}Pd_2P_2S_2$ (949.58 g/mol): calc. C 43.02, H 4.42; found: C 42.91, H 4.37%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 37.67 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 0.11 (d, $^3J_{PH}$ = 1.2 Hz, 3H, PdCH_3), 3.06 (m, 2H, CH_2S), 3.12 (m, 2H, CH_2P), 3.90 (s, 6H, OCH_3), 7.04-7.65 (m, 8H, Ar); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) -2.22 (s, PdCH$_3$), 22.99 (d, $^1J_{PC}$ = 35.2 Hz, PCH$_2$), 46.84(s, CH_2S), 54.78 (s, OCH$_3$), 111.31 (d, $^3J_{PC}$ = 4.3 Hz, *m-C*, Ar), 115.32 (d, $^1J_{PC}$ = 53.7 Hz, *ipso*-C, Ar),120.55 (d, $^3J_{PC}$ = 11.2 Hz, *m-C*, Ar), 133.25 (s, *o-C*, Ar), 136.91 (s, *p-C*, Ar), 160.36 (s, *C*, Ar)

Complex 4c: 36.6 mg (35%). $C_{42}H_{42}O_{10}Pd_2P_2S_2$ (1045.66 g/mol): calc. C 48.26, H 4.02; found: C 48.15, H 3.90%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C)

26.98 (s); ^{1}H NMR (δ, 400.13 MHz, CD_3OD, 21 ^{o}C) 0.18 (d, $^{3}J_{PH}$ = 0.8 Hz, 3H, PdCH_3), 3.69 (s, 6H, OCH_3), 7.05-7.61 (m, 11H, Ar), 8.02 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 4.8 Hz, 1H, *o-H*); ^{13}C{^{1}H}NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) -0.63 (s, PdCH_3), 54.31 (s, OCH_3), 111.33 (d, $^{3}J_{PC}$ = 4.3 Hz, *m-C*, Ar), 115.37 (d, $^{1}J_{PC}$ = 61.4 Hz, *ipso-C*, Ar), 120.20 (d, $^{3}J_{PC}$ = 12.5 Hz, *m-C*, Ar), 126.80 (d, $^{3}J_{PC}$ = 8.3 Hz, *C*, Ar), 127.84 (d, $^{1}J_{PC}$ = 53.0 Hz, *ipso-C*, Ar), 128.74 (d, $^{3}J_{PC}$ = 8.2 Hz, *C*, Ar), 129.99 (s, *C*, Ar), 133.56 (s, *o-C*, Ar), 134.92 (s, *C*, Ar), 137.40 (s, *p-C*, Ar), 146.87 (d, $^{2}J_{PC}$ = 14 Hz, *C*, Ar), 160.44 (s, *C*, Ar)

***In situ* synthesis of Pd(COMe)(L)(CD_3OD) (L = a, (5a); b, (5c))**

In a Schlenk tube compounds **4a** and **4c** (0.05 mmol) were dissolved in deareated CD_3OD (1.5 mL). These solutions were transferred into a 5 mm NMR tube followed by bubbling CO through the solution at room temperature. In the case of **4a**, complete transformation into compound **5a** was achieved after 40 minutes under a concomitant formation of two palladium(I) complexes (**8a**/**9a**), while the analogous procedure applied to **4c**, yielded **5c** quantitatively after 10 minutes.

Selected spectroscopic data for 5a: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21º C) 23.66 (s); ^{1}H NMR (δ, 400.13 MHz, CD_3OD, 21 ^{o}C) 1.84 (d, $^{4}J_{PH}$ = 0.4 Hz, 3H, COCH_3); ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) 32.38 (d, $^{3}J_{PC}$ = 28.1 Hz, CO*C*H_3), 223.34 (s, *C*OCH_3).
Selected spectroscopic data for 8a: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21 ^{o}C) 8.09 (s); ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) 227.60 (s, *C*O).
Selected spectroscopic data for 9a: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21 ^{o}C) 8.55 (s); ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) 225.36 (s, *C*O).
Selected spectroscopic data for 5c: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21 ^{o}C) 13.60 (s); ^{1}H NMR (δ, 400.13 MHz, CD_3OD, 21 ^{o}C) 1.85 (d, $^{4}J_{PH}$ = 0.4 Hz,

3H, COCH_3); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) 34.24 (d, $^3J_{PC}$ = 29.2 Hz, CO*C*H_3), 222.58 (d, $^2J_{PC}$ = 8.0 Hz, *C*OCH_3).

***In situ* syntheses of PdCH$_2$CH$_2$COMe(L) (L = a, (6a); b, (6c))**

In a Schlenk tube compound **4a** and **4c** (0.05 mmol) were dissolved in deareated CD_3OD (1.5 mL). These solutions were transferred into 5 mm NMR tubes. While the CD_3OD solution of ob **4a** was bubbled successively with CO for 40 min, with nitrogen for 2 min. and then with ethene for 20 min. obtaining a 1:1 mixture of **6a** and **8a**, the solution of **4c** was successively bubbled with CO for 10 min., with nitrogen for 2 min. and then with ethene for 2 min. to quantitatively transform the latter compound into **6c**. IR-spectroscopic data for **6a** and **6c** were obtained by evaporating the CD_3OD solutions of **6a**/**8a** and **6c** to dryness and dissolving the residuals in CH_2Cl_2.

Selected spectroscopic data for 6a: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 32.80 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 1.21 (td, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 2.4 Hz, 2H, PdCH_2), 2.30 (s, 3H, COCH_3), 2.81 (t, $^3J_{HH}$ = 6.2 Hz, 2H, COCH_2); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) 19.80 (s, PdCH_2), 26.02 (s, CO*C*H_3), 49.47 (s, CO*C*H_2), 230.86 (s, *C*OCH_3); IR (CH_2Cl_2): ν(CO) = 1641 cm^{-1}.

Selected spectroscopic data for 6c: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 21.73 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 1.33 (td, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 2.6 Hz, 2H, PdCH_2), 2.36 (s, 3H, COCH_3), 2.84 (t, $^3J_{HH}$= 6.2 Hz, 2H, COCH_2); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) 20.63 (s, PdCH_2), 26.34 (s, CO*C*H3), 49.80 (s, CO*C*H_2), 231.59 (s, *C*OCH_3); IR (CH_2Cl_2): ν(CO) = 1641 cm^{-1}.

***In situ* synthesis of $PdCOCH_2CH_2COMe(L)(CD_3OD)$ (L = c, (7c))**

A CD_3OD solution (1.5 mL) of compound **6c**, which was obtained as described above, was transferred into a 5 mm NMR tube. The solution was bubbled successively with nitrogen for 2 min. and CO for 10 minutes.

Selected spectroscopic data for 7c: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 ^oC) 14.53 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 ^oC) 2.02 (s, 3H, $COCH_3$), 2.18 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2CO), 2.61 (t, $^3J_{HH}$ = 6.6 Hz, 2H, $COCH_2$); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 ^oC) 28.28 (s, $COCH_3$), 36.97 (s, CH_2CO), 39.92 (d, $^3J_{PC}$ = 26.3 Hz, $PdCOCH_2$), 210.18 (s, $COCH_3$), 221.44 (d, $^2J_{PC}$ = 7.5 Hz, $COCH_2$)

Catalytic reactions

Catalytic reactions in MeOH or 2,2,2-trifluoroethanol (TFE) employing 1a, 1c, 4a and 4c as pre-catalysts

Typically, MeOH (50 mL) or TFE (50 mL), was introduced by suction into an autoclave (200 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.012 mmol). When the catalytic reaction was performed in the presence of 1,4-benzoquinone (BQ) or *p*-toluenesulfonic acid, these latter compounds and the catalytic precursors were added together in the autoclave. The autoclave was then charged with the desired CO/C_2H_4 mixture to 600 psi at room temperature followed by heating to the desired temperature. Once the desired temperature was reached the total pressure of the gas mixture was equilibrated to 800 psi and stirring (1300 rpm) was started. After the desired reaction time, the autoclave was cooled by means of an ice-water bath and the gases released. Due to the much higher solubility of the copolymers in TFE compared to MeOH, two different work-up procedures were employed. While for

the catalytic experiments carried out in MeOH, the insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 °C to constant weight, for the catalytic experiments carried out in TFE, the catalysis mixture was poured into a flask containing 100 mL of MeOH, followed by stirring the suspension for half an hour. Then the solid polymeric material was filtered off and dried under vacuum at 60 °C to constant weight.

Characterisation of the non-alternating CO-ethene copolymer

While the low-molecular weight copolymers were characterised by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy in a 1:3 (v:v) solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2 and C_6D_6, the high molecular weight non-alternating copolymers were analysed only by $^{13}C\{^{1}H\}$ NMR spectroscopy in a 1:3 (v:v) solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol and C_6D_6. The assignment of $^{1}H$and ^{13}C chemical shifts were based on literature reports.[6a]

NMR studies

***Operando* HP-NMR studies of 4a and 4c in CD_3OD and TFE/C_6D_6, respectively**

A 10 mm sapphire tube was charged with a solution of compound **4a** (**4c**) (0.03 mmol) in CD_3OD (2.0 mL) or a 3:1(v:v) mixture of TFE/C_6D_6 under nitrogen at room temperature and placed into a NMR probe at 20 °C. After $^{31}P\{^{1}H\}$ and ^{1}H (only for the study in CD_3OD) NMR spectra had been recorded, the sapphire tube was removed from the NMR probe, charged with CO to 200 psi, and then placed again into the NMR probe at 20 °C. After the NMR spectra had been recorded, the sapphire tube was removed from the NMR probe and charged with ethene to 800 psi, and placed again into the NMR probe at 20 °C. The reaction was followed by variable-temperature NMR spectroscopy in the

temperature range from 20 to 110 °C. After heating the NMR solution for 10 min at 110 °C, the sapphire was cooled to 20 °C, followed by the acquisition of NMR spectra. Once the sapphire tube was removed from the NMR probe, in the case of **4a** a layer of grey copolymer and a dark solution was observed while in the case of the NMR study employing **4c** as pre-catalyst an off-white layer of copolymer over a yellow solution was observed.

X-Ray crystallography

While suitable crystals of ligand **b** and compound **1a** were obtained by diffusion of diethylether in a saturated CH_3Cl solution of the corresponding compounds, crystals of compound **2a** were obtained by a slow diffusion of a methanol solution of $Pd(OAC)_2$ (0.05 mmol) into a CH_2Cl_2 solution of ligand **a** (0.1 mmol) at room temperature. Diffraction data of compounds **b** and **1a** were collected on a Bruker-Nonius diffractometer equipped with APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = 100 K), while for the collection of diffraction data for compound **2a** an Enraf Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation and graphite monochromator was employed. The absorption correction was carried out for compounds **b** and **1a** were carried out using SADABS v.2.10 (2003) while for compound **2a** *psi*-scans were applied. The structures were solved by direct methods and refined by full-matrix F^2 refinement. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, while hydrogen atoms were introduced in their calculated positions. All calculations were performed on a PC using SIR97[21a], SHELXL-97[21b] and ORTEP-3[21]

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4.1.5. References

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