

**The *o*-methoxy groups on the P-aryl rings effect in the carbon monoxide and ethene copolymerisation reaction by palladium(II)-diphosphine catalysts. A catalytic study in different reaction media**

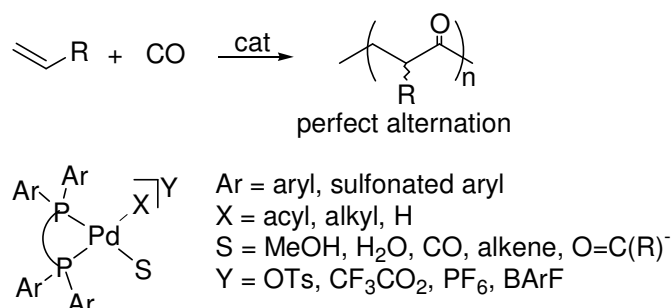
**Abstract**

Neutral and bis-cationic palladium(II) complexes with 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp) have been synthesised and employed to catalyse the CO-ethene copolymerisation reaction in either protic or aprotic solvents. A comparison of the catalytic performance of these complexes with that of analogous precursors stabilised by 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) ligands have shown significant differences in terms of catalytic productivity and molecular weight. *In situ* and *operando* high-pressure NMR experiments have provided valuable information on catalysis resting states and intermediates and have contributed to rationalise the observed productivity as well.

### 2.1.1. Introduction

As previous mentioned in *chapter 1*, polyketones are a family of high-performance thermoplastics featured by excellent resistance to solvents as well as good mechanical properties. Unlike many other engineering plastics, perfectly alternating polyketones such as Shell's Carilon are relatively easy to synthesise and are derived from inexpensive monomers such as ethene and CO.<sup>1</sup> A small fraction of the ethene can be replaced with propene to reduce the melting point and improve the stability and rheology of the materials. Low molecular weight Carilon is known with the name Carilite and is currently used as wood-binding adhesive.<sup>2</sup>

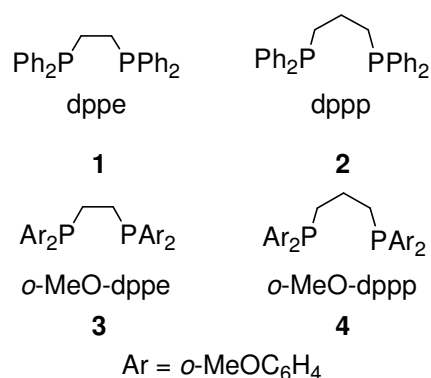
Polyketones (alt-ethene-CO) are made with palladium(II) catalysts modified with chelating diphosphines bearing various substituents on the phosphorus aryl rings (**Scheme 1**). Either protic (alcohols, preferentially methanol) or aprotic (toluene, dichloromethane, THF (tetrahydrofurane)) solvents can be used depending on the structure of the metal precursors that can generate the catalysts by a number of pathways. Sulfonation of the aryl rings is a common procedure to have water soluble catalysts.



**Scheme 1.** Copolymerisation reaction with palladium(II)(P-P) complexes

A major drawback to the large scale commercialisation of alt-ethene-CO materials is provided by the low catalytic productivity which seldom exceeds 20-30 kg polyketone (g Pd x h)<sup>-1</sup>. The productivity is particularly low for low molecular weight materials such as Carilite. Studies aimed at improving the performance of the palladium catalysts are therefore under way in many laboratories. Since catalyst degradation to inactive species, including black palladium, is the major cause of the low productivity, much research efforts are being directed to design both diphosphine ligands and reaction media capable of stabilising mononuclear palladium(II) under the copolymerisation conditions.

It is now established that the introduction of an *ortho*-methoxy substituent on the P-aryl rings of the diphosphine greatly enhances the productivity as compared to the unsubstituted ligands.<sup>3</sup> Two such ligands are shown in **Figure 1** together with their unsubstituted counterparts.



**Figure 1**

Both steric and electronic factors have been proposed to be responsible for the positive effect of the *ortho*-methoxy groups on catalyst activity: lower tendency to form inactive bis-chelates and dimers, reduced tendency to phosphine oxidation,<sup>4a</sup> a increased basicity of the metal center,<sup>4b</sup> reduced stability of relevant catalyst resting states such as  $\beta$ -keto alkyl chelates.<sup>4c</sup>

Besides the P-aryl substituents, the productivity of palladium(II) copolymerisation catalysts is affected remarkably by the reaction media as well as by added co-reagents. The latter include protic acid and organic oxidants,<sup>1</sup> while protic solvents such as alcohols and water are much better media than aprotic organic solvents. As a matter of fact, the highest productivities of both Carilon and Carilite have been obtained in water in the presence of added protic acid by means of water-soluble diphosphines bearing *o*-methoxy groups.<sup>2</sup>

Despite the undoubted qualities of *o*-methoxy substituted diphosphines and the many papers assessing these qualities, we are not aware of a study where such ligands are employed, in conjunction with palladium(II) salts, to copolymerise ethene and CO in reaction media other than MeOH or water.

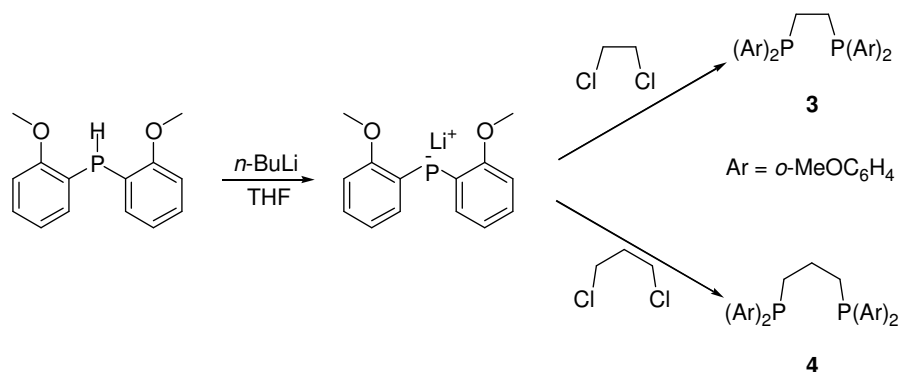
In this chapter, we report a new synthetic protocol for the synthesis of 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) (**3**) (**Figure 1**) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp) (**4**) (**Figure 1**) the synthesis and characterisation of various palladium(II) neutral and cationic catalyst precursors and their use to catalyse the CO/C<sub>2</sub>H<sub>4</sub> copolymerisation in different solvents such as MeOH, 2,2,2-Trifluoroethanol (TFE), water-AcOH (acetic acid) mixtures, CH<sub>2</sub>Cl<sub>2</sub>, and toluene. For comparative purposes all catalytic reactions have also been performed with the classical ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylphosphino)propane (dppp).

*In situ* and *operando* high-pressure NMR experiments carried out on selected reactions have provided valuable information on catalysis resting states and intermediates as well as have contributed to rationalise the observed productivity.

## 2.1.2. Results and discussion

### Synthesis of ligands and complexes

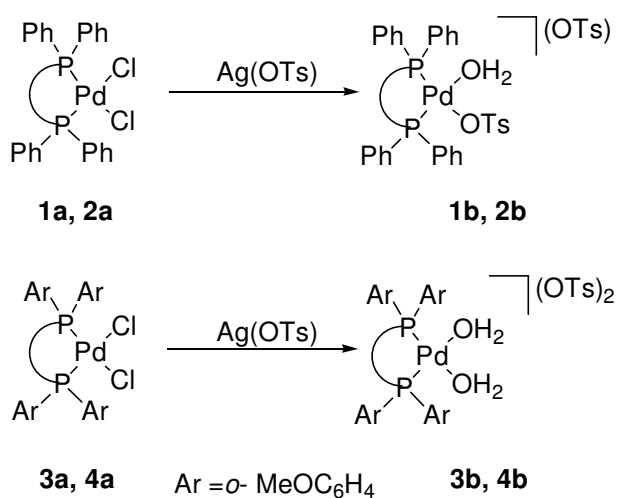
The known diphosphines *o*-MeO-dppe<sup>5a,5b</sup> and *o*-MeO-dppp<sup>5c</sup> were synthesised by a new synthetic route, illustrated in **Scheme 2**, which is simpler and more efficient as compared with the procedures reported in the literature.



**Scheme 2.** New synthetic route for the synthesis of *o*-MeO-dppe and *o*-MeO-dppp

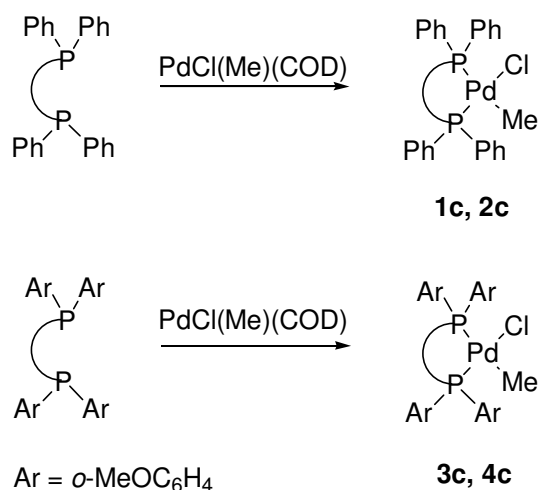
The new synthetic protocol involves the deprotonation of the stable and isolable secondary phosphine bis(2-methoxyphenyl)phosphine<sup>6a</sup> with *n*-BuLi in THF, followed by addition of the corresponding dichloride reagent. Both ligands were isolated as microcrystalline solids in good yields (78% *o*-MeO-dppe; 68% *o*-MeO-dppp). The reaction of either ligand with PdCl<sub>2</sub>(COD) in CH<sub>2</sub>Cl<sub>2</sub> gave the complexes PdCl<sub>2</sub>(*o*-MeO-dppe) (**3a**) and PdCl<sub>2</sub>(*o*-MeO-dppp) (**4a**) as yellow crystalline compounds, which were characterised in solution by multinuclear NMR spectroscopy and in the solid state by single crystal X-ray structure analyses.

The reaction of **3a** or **4a** with AgOTs led to the formation of the bis-cationic tosylate derivatives  $[\text{Pd}(\text{H}_2\text{O})_2(o\text{-MeO-dppe})](\text{OTs})_2$  (**3b**) and  $[\text{Pd}(\text{H}_2\text{O})_2(o\text{-MeO-dppp})](\text{OTs})_2$  (**4b**) (**Scheme 3**). The authentication of these complexes was achieved in solution by multinuclear NMR spectroscopy where both complexes behave as 1:2 electrolytes (conductivity measurements in nitroethane). Notably, the known and isostructural compounds  $[\text{Pd}(\text{OTs})(\text{H}_2\text{O})(\text{dppe})]\text{OTs}$  (**1b**) and  $[\text{Pd}(\text{OTs})(\text{H}_2\text{O})(\text{dppp})]\text{OTs}$  (**2b**) (**Scheme 3**) behave as 1:1 electrolytes in the same solvent, which is consistent with the coordination of a tosylate ion to palladium.



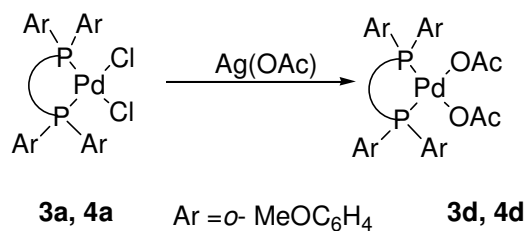
**Scheme 3**

The neutral complexes  $\text{PdCl}(\text{Me})(\text{P-P})$  (P-P = *o*-MeO-dppe, **3c**; *o*-MeO-dppp, **4c**) were prepared by reaction of the appropriate ligand with  $\text{PdCl}(\text{Me})(\text{COD})$  in  $\text{CH}_2\text{Cl}_2$  in good yield (78%, **3c**; 68%, **4c**) (**Scheme 4**).



Scheme 4

The reaction of complexes **3a** and **4a** with Ag(OAc) in dichloromethane brought about the formation of the neutral palladium(II)-acetate complexes **3d** or **4d**, which were isolated as yellow microcrystalline compounds in good yield (62%, **3d**; 71%, **4d**) (Scheme 5). Both latter complexes were characterised in solution by multinuclear NMR spectroscopy and in the solid state by single crystal X-ray structure analyses.



Scheme 5

### Crystal structure determination of **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub>, **4a**, **3d** and **4d**

Single crystals of **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub> and **4a** were obtained by slow diffusion of *n*-hexane into CH<sub>2</sub>Cl<sub>2</sub> solutions of **3a** and **4a**, while suitable single crystals of compounds **3d** and **4d** were obtained by a slow diffusion of toluene into a dichloromethane solution of the corresponding compounds. Crystallographic details for **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub>, **4a** are reported in **Table 1**, while those for **3d** and **4d** are shown in **Table 3**. Selected bond distances and angles are reported for the Pd-dichloride complexes in **Table 2** and for the Pd-acetate complexes in **Table 4**. An ORTEP drawing of **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub>, **4a**, **3d** and **4d** is shown in **Figures 2**, **3**, **4** and **5**, respectively.

**Table 1.** Summary of crystallographic data

Compound	<b>3a</b> ·2.3 CH <sub>2</sub> Cl <sub>2</sub>	<b>4a</b>
Empirical formula	C <sub>32.20</sub> H <sub>36.60</sub> Cl <sub>6.60</sub> O <sub>4</sub> P <sub>2</sub> Pd	C <sub>31</sub> H <sub>34</sub> Cl <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Pd
Formula weight	891.13	709.82
Temperature (K)	203(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pcca</i>
<i>a</i> (Å)	19.386(5)	23.432(5)
<i>b</i> (Å)	12.616(5)	9.059(2)
<i>c</i> (Å)	16.485(5)	14.876(5)
$\alpha^\circ$	90.00	90.00
$\beta^\circ$	97.655(5)	90.00
$\gamma^\circ$	90.00	90.00
Volume (Å <sup>3</sup> )	3996(2)	3157.7(14)
Z	4	4
$\rho_{\text{calc}}$ (gcm <sup>-3</sup> )	1.481	1.493
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.019	0.892
Diffraction radiation (Å)		$\lambda$ (MoK $\alpha$ )= 0.71069
<i>F</i> (000)	1802.4	1448
Crystal size (mm)	0.22 × 0.05 × 0.02	0.25 × 0.20 × 0.18
$\Theta$ range (°)	4.10-25.00	2.77-25.00



	-23<= <i>h</i> <=23	0<= <i>h</i> <=27
Index ranges	14<= <i>k</i> <=14	0<= <i>k</i> <=10
	19<= <i>l</i> <=19	0<= <i>l</i> <=17
Reflections collected	3464	2759
Independent reflections	2912	2759
Refined parameters	212	186
<i>R</i> 1 (2 $\sigma$ ( <i>I</i> ))	0.0688	0.0274
<i>R</i> 1 (all data)	0.0875	0.0384
<i>wR</i> 2 (all data)	0.1518	0.0789
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.167	1.015
Largest diff. peak and hole (eÅ <sup>-3</sup> )	1.005/-0.834	0.414/-0.480

The crystal structure of **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub> shows half molecule of **3a** and 1.15 molecules of disordered CH<sub>2</sub>Cl<sub>2</sub> per asymmetric unit. The palladium centre is square planar coordinated with *cis* phosphorus atoms.

**Table 2.** Selected bond lengths (Å), bond angles (°), and intramolecular Pd-O and Pd-H distances (Å)

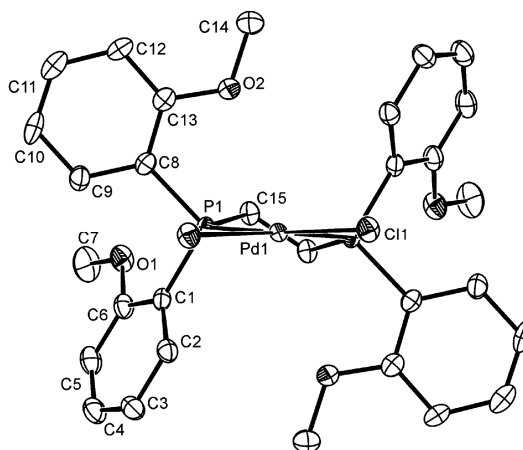
Complex	<b>3a</b> 2.3 CH <sub>2</sub> Cl <sub>2</sub>	<b>4a</b>
Pd(1)-P(1)	2.239(2)	2.250(1)
Pd(1)-Cl(1)	2.366(2)	2.362(1)
P(1)-Pd(1)-P(1)#1 <sup>a</sup>	86.55(8)	90.09(4)
P(1)-Pd(1)-Cl(1)	174.43(5)	88.88(3)
Cl(1)-Pd(1)-Cl(1)#1 <sup>a</sup>	93.00(8)	92.70(4)
Pd(1)...O(1)	5.173(4)	3.435(2)
Pd(1)...O(2)	3.482(4)	5.193(2)
Pd(1)...H(2)	2.877	
Pd(1)...H(9)		2.871

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: -x+1, y, -z+1/2

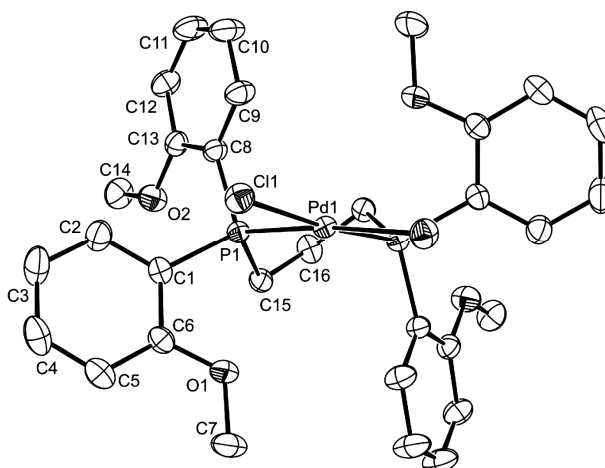
The Pd-P bond length of 2.239(2) Å and the P-Pd-P bite angle of 86.55(8)° are comparable to the values found for the dppe analogue **1a**.<sup>7</sup> The four *o*-methoxy

oxygen atoms are disposed around the palladium centre in such a way that two of them occupy a *pseudo*-apical position of the metal coordination sphere (Pd...O distance of 3.482(4) Å) while the other two symmetry-related *o*-methoxy oxygen atoms are close to *pseudo*-equatorial positions (Pd...O distance of 5.173(4) Å). However, all of these Pd...O distances are too large to consider an electrostatic interaction between the palladium and the *o*-methoxy groups. In contrast, the *o*-hydrogen atoms of two axial aryl ring groups interact with the palladium centre (Pd(1)...H(2) distance of 2.877 Å). Very similar structure features were already observed for the related complex NiI<sub>2</sub>(*o*-MeO-dppe).<sup>4a</sup>

The asymmetric unit of **4a** contains half molecule and the coordination geometry about the palladium centre is square planar. The P-Pd-P angle of 90.09(4)<sup>o</sup> is comparable to that found for the related dppp complex **2a** of 90.58(5)<sup>o</sup>.<sup>7</sup> Likewise, the Pd-P bond distance of 2.250(1) Å is very close to those observed in **2a** of 2.244(1) and 2.249(2) Å.<sup>7</sup> The major difference between **4a** and **2a** is provided by the conformation of the six-member PdP<sub>2</sub>C<sub>3</sub> ring. Indeed, in **2a** the three bridging carbon atoms are located at the same side of the coordination plane, while **4a** exhibits a symmetrical twisting of the ligand with a deviation of C(15) of 0.878(2) Å in direction of O(1) from the coordination plane defined by the atoms Pd(1), Cl(1), and P(1). Like **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub>, **4a** exhibits two rather long Pd...O distances of 3.435(2) and 5.193(2) Å and one short intramolecular Pd(1)...H(9) distance of 2.871 Å per asymmetric unit, which was already observed in the structure of the nickel complex NiCl<sub>2</sub>(*o*-MeO-dppp).<sup>8</sup> The short Pd...H intramolecular interactions observed in the structures of both **3a**·2.3 CH<sub>2</sub>Cl<sub>2</sub> and **4a** have been found to persist in solution as shown by <sup>1</sup>H NMR spectroscopy.



**Figure 2.** ORTEP plot of **3a**·2.3·CH<sub>2</sub>Cl<sub>2</sub>. Solvent molecules and hydrogen atoms are omitted for clarity. Only the asymmetric unit of the molecule is labelled. Thermal ellipsoids are shown at the 30% probability level



**Figure 3.** ORTEP plot of **4a**. Solvent molecules and hydrogen atoms are omitted for clarity. Only the asymmetric unit of the molecule is labelled. Thermal ellipsoids are shown at the 30% probability level

**Table 3.** Summary of crystallographic data for **3d** and **4d**

Complex	3d	4d
empirical formula	C <sub>34</sub> H <sub>38</sub> O <sub>8</sub> P <sub>2</sub> Pd	C <sub>35</sub> H <sub>40</sub> O <sub>8</sub> P <sub>2</sub> Pd
<i>Fw</i>	742.98	757.01
Cryst. size (mm)	0.30 x 0.30 x 0.20	0.30 x 0.30 x 0.20
Cryst. system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	10.430(5)	14.065(3)
<i>b</i> (Å)	10.536(5)	16.297(2)
<i>c</i> (Å)	18.933(5)	15.385(2)
$\alpha^\circ$	78.820(5)	90.00
$\beta^\circ$	81.260(5)	92.420(15)
$\gamma^\circ$	77.060(5)	90.00
<i>V</i> (Å <sup>3</sup> )	1976.4(14)	3523.4(10)
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.248	1.427
<i>Z</i>	2	4
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )		0.666
$\mu$ (Cu K $\alpha$ ) (mm <sup>-1</sup> )	4.905	
Diffraction radiation (Å)	$\lambda$ (Cu K $\alpha$ ) = 1.54180	$\lambda$ (Mo K $\alpha$ ) = 0.71069
<i>F</i> (000)	764	1560
temp (K)	293(2)	293(2)
$\Theta$ range for data collec (deg)	4.37-55.0	2.00-22.97
index range	-1 <= <i>h</i> <= 11 -10 <= <i>k</i> <= 11 -19 <= <i>l</i> <= 20	-15 <= <i>h</i> <= 15 0 <= <i>k</i> <= 17 0 <= <i>l</i> <= 16
N <sup>o</sup> . of reflns collected	4913	5102
N <sup>o</sup> . of independent reflns	4576	4896
N <sup>o</sup> . of refined params	412	421
<i>R</i> 1 (2 $\sigma$ ( <i>I</i> ))	0.0369	0.0331
<i>R</i> 1 (all data)	0.0402	0.0617
<i>wR</i> 2 (all data)	0.0955	0.0805
goodness of fit on <i>F</i> <sup>2</sup>	1.053	0.998
Largest diff peak and hole (e/ Å <sup>3</sup> )	0.063/-0.890	0.372/-0.448

**Table 4.** Selected Bond lengths (Å), bond angles (°) and intra-molecular Pd-O and P-H distances(Å) for **3d** and **4d**

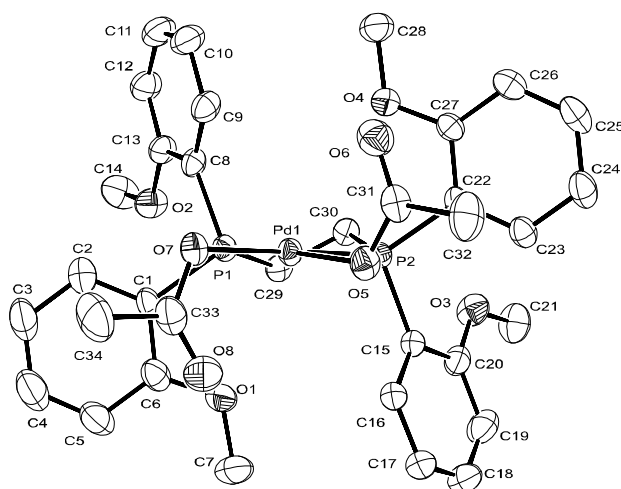
Complex	<b>3d</b>	<b>4d</b>
Pd(1)-P(1)	2.229(1)	2.223(1)
Pd(1)-P(2)	2.221(1)	2.226(1)
Pd(1)-O(5)	2.108(3)	2.092(2)
Pd(1)-O(7)	2.104(3)	2.109(3)
P(1)-Pd(1)-P(2)	85.42(4)	95.30(4)
O(5)-Pd(1)-O(7)	92.83(11)	87.00(10)
P(1)-Pd(1)-O(5)	174.56(8)	174.31(7)
P(2)-Pd(1)-O(7)	176.86(8)	172.18(7)
<b>Intramolecular Pd-oxygen distances in (Å)</b>		
Pd(1)...O(1)	3.732(3)	5.144(3)
Pd(1)...O(2)	5.163(3)	3.564(3)
Pd(1)...O(3)	5.102(4)	3.699(3)
Pd(1)...O(4)	3.604(3)	5.106(3)
Pd(1)...H(2)		2.716
Pd(1)...H(23)		2.695
Pd(1)...H(9)	2.855	
Pd(1)...H(16)	2.778	

The crystal structure of **3d** shows a square planar coordination geometry for palladium with a slight displacement of the Pd(1) from its coordination plane, defined by P(1), P(2), O(5) and O(7), by 0.035(2) Å in direction of O(2). The conformation of the five membered ring is puckered, as typically found in complexes bearing dppe as ligand. The P(1)-Pd(1)-P(2) bite angle is 85.42(4)°, is comparable with that observed in Pd(OAc)<sub>2</sub>(dppe).<sup>11a</sup> The same is valid for the Pd-P bond length of 2.229(1) and 2.221(1) Å in **3d** and of 2.218(2) and 2.225(2) Å in the analogous dppe complex.

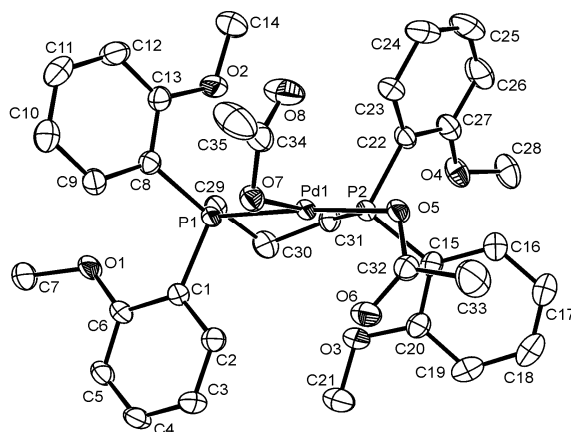
The crystal structure of **4d** shows a typical square planar coordination geometry. The Pd-P bond distances of 2.223(1) and 2.226(1) Å are significantly shorter than those of the analogous PdCl<sub>2</sub> compound (**4a**) of 2.250(1) and

2.244(1) Å, due to the weaker *trans* influence of acetate compared to chloride. Compound **4d** shows thus a significantly larger P(1)-Pd(1)-P(2) bite angle of 95.30(4)° compared to that of **4a**, which is significantly larger than that found for **4a** of 90.09(4)°.

Like the crystal structures of both PdCl<sub>2</sub> complexes **3a** 2.3 CH<sub>2</sub>Cl<sub>2</sub> and **4a**, also the crystal structures of the Pd-acetate complexes **3d** and **4d** show intra-molecular palladium methoxy-oxygen distances, which range from 3.604(3) to 5.163(3) for **3d** and 3.699(3) to 5.144(3) Å for **4d** and palladium *ortho*-hydrogen atom interactions of less than 3.0 Å. The intra-molecular distances are reported in **Table 4**. This typical pair-wise orientation of the *o*-methoxy groups around the metal centre has been observed also by Bouwman in comparable nickel complexes.<sup>8</sup>



**Figure 4.** ORTEP plot of **3d**. Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level



**Figure 5.** ORTEP plot of **4d**. Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level

#### Variable-temperature NMR studies of **3a**, **4a**, and **4b** in $\text{CD}_2\text{Cl}_2$

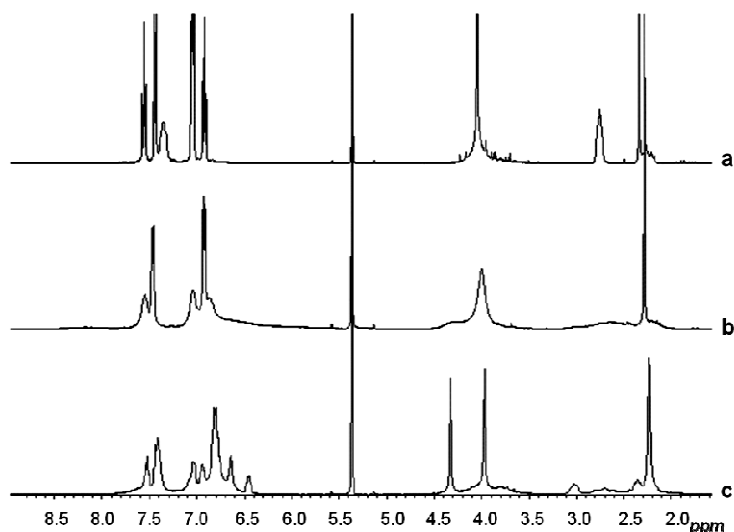
In an attempt of elucidating the solution structure of the palladium(II) complexes with the *o*-methoxy ligands, (*o*-MeO-dppe and *o*-MeO-dppp)  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR studies were carried out on  $\text{CD}_2\text{Cl}_2$  solutions of **3a**, **4a**, and **4b** in the temperature range from 20 to  $-80$  °C. Complexes **3a** and **4a** exhibit fluxional behaviour on the NMR time-scale. The  $^1\text{H}$  NMR spectrum at 20 °C of either complex displayed one set of resonances for the aryl hydrogen ( $\delta$  6.96-7.95 and 6.97-7.60, respectively) and one singlet for the *o*-methoxy groups ( $\delta$  3.61 and 3.75, respectively), which indicates the equivalence of all four aryl groups in the *o*-MeO-ligands. Decreasing the temperature led to a progressive broadening of all resonances. At  $-80$  °C, the  $^1\text{H}$  NMR spectra of **3a** and **4a** contained a couple of singlets at  $\delta$  3.75 and 3.42 and  $\delta$  3.73 and 3.68 for the *o*-methoxy groups, respectively. This pattern can be safely attributed to the formation of couples of axially and equatorially oriented methoxy groups as shown also by the crystal structures of **3a**·2.3· $\text{CH}_2\text{Cl}_2$  and **4a**. Notably, the  $^1\text{H}$  NMR spectra of **3a** and **4a** at  $-80$  °C showed a significant downfield shift of the resonances of two aryl

hydrogen ( $\delta$  8.85 and 8.95, respectively), which suggests that the interactions between the *o*-hydrogen atoms of the aryl groups and the metal centre, observed in the crystal structures of **3a**·2.3·CH<sub>2</sub>Cl<sub>2</sub> and **4a**, are maintained in solution.<sup>9</sup> An analogous fluxional behaviour has been reported for NiCl<sub>2</sub>(*o*-MeO-dppp) whose crystal structure closely resembles those of **3a**·2.3·CH<sub>2</sub>Cl<sub>2</sub> and **4a**.<sup>8</sup>

Like the bis-chloride complexes **3a** and **4a**, the tosylate complex **4b** is fluxional in CD<sub>2</sub>Cl<sub>2</sub> solution at room temperature due to the exchange of equatorial and axial aryl groups. The temperature-dependent <sup>1</sup>H NMR spectra of **4b** are reported in **Figure 6**. Analogously to **3a** and **4a**, the spectrum at 20 °C (trace **a**) showed a singlet at  $\delta$  4.05 which resolved at -80 °C into two singlets at  $\delta$  3.97 (equatorial) and 4.32 (axial) (trace **c**). Unlike **3a** and **4a**, the <sup>1</sup>H NMR spectrum of **4b** at -80 °C contained no downfield shifted resonance, consistent with no interaction between the metal centre and the *o*-hydrogen atoms of the aryl groups.

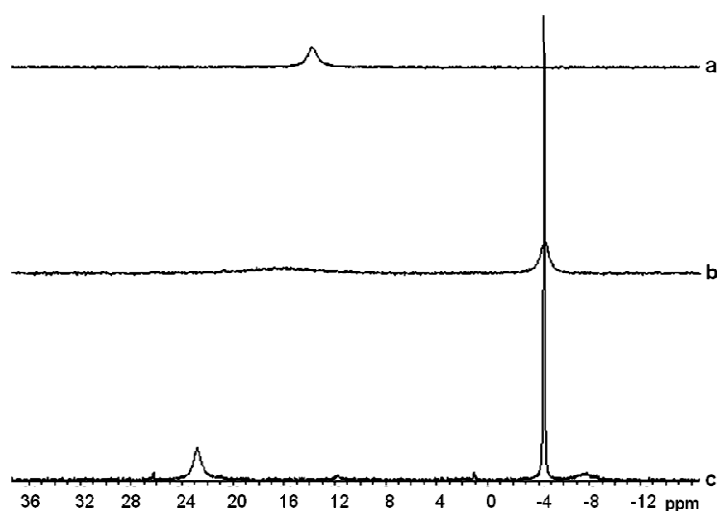
The NMR pattern observed for **4b** is in perfect agreement with that exhibited by the nickel derivative [Ni(H<sub>2</sub>O)<sub>2</sub>(*o*-MeO-dppp)](PF<sub>6</sub>)<sub>2</sub> whose X-ray crystal structure analysis revealed the absence of any interaction between nickel and the *o*-hydrogen with all four *o*-methoxy groups pointing towards palladium.<sup>8</sup> It is therefore most likely that **4b** and [Ni(H<sub>2</sub>O)<sub>2</sub>(*o*-MeO-dppp)](PF<sub>6</sub>)<sub>2</sub> adopt the same structure in both the solid state and solution.





**Figure 6.** Variable-temperature  $^1\text{H}$  NMR study of **4b** ( $\text{CD}_2\text{Cl}_2$ , 400.13 MHz): (a) 20 °C; (b) -40 °C; (c) -80 °C.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **3a**, **4a**, and **4b** at 20 °C consist of a single relatively sharp resonance at  $\delta$  69.02, 16.30, and 13.72, respectively. A sharp resonance was also observed at -80 °C for **3a** ( $\delta$  68.97) and **4a** ( $\delta$  17.63), while the spectrum of **4b** showed a quite different behaviour with the temperature (**Figure 7**). At -80 °C the initial  $^{31}\text{P}\{^1\text{H}\}$  NMR singlet was split into two resonances at  $\delta$  -4.46 and 22.78 in a 5:1 ratio (trace **c**). The chemical shifts of these two resonances as well as their line-shape do not appear to be consistent with a slow exchange regime of a unique fluxional species: It is much more likely that new species are formed at low temperature where tosylate ions may compete with water molecules for coordination.



**Figure 7.** Variable temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR study of **4b** ( $\text{CD}_2\text{Cl}_2$ , 400.13 MHz): (a) 20 °C; (b) -40 °C; (c) -80 °C.

### Catalytic copolymerisation of CO and ethene

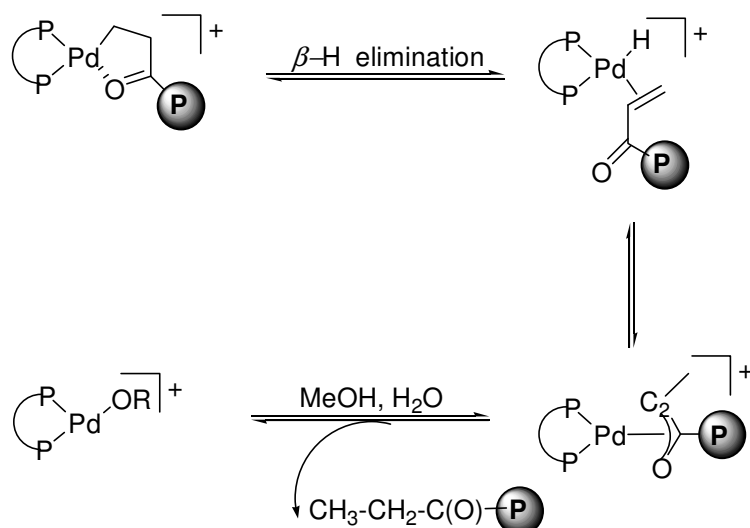
Both neutral and cationic Pd(II) complexes, with either *ortho*-methoxy modified ligands *o*-MeO-dppe and *o*-MeO-dppp or with the unmodified dppe and dppp ligands, were employed to catalyse CO-ethene copolymerisation reactions in five different solvents: MeOH, TFE, water-AcOH mixtures,  $\text{CH}_2\text{Cl}_2$  and toluene. All reactions in protic solvents were performed at 85 °C and with a 1:1 CO/ $\text{C}_2\text{H}_4$  pressure of 40 bar. Lower temperatures (50-60 °C) were used for the reactions in aprotic solvents. No optimisation of the catalytic activity was attempted. The results obtained are summarised in **Table 5-8**.

Prior to the presentation and discussion of the catalytic results, it may be useful to anticipate that, with the only exception of the reactions carried out in TFE, higher productivities as well as higher molecular weights of the polyketone products were observed both for the dppp-like catalysts in comparison with the

corresponding dppe-like catalysts (i.e., dppp > dppe and *o*-MeO-dppp > *o*-MeO-dppe) as well as for the *ortho*-methoxy modified catalysts as compared to the corresponding unmodified catalysts (i.e., *o*-MeO-dppp > dppp and *o*-MeO-dppe > dppe).<sup>10</sup>

The different catalytic activities exhibited by the palladium precursors with diphosphine chelating ligands bearing CH<sub>2</sub> spacers between the phosphorus donor atoms have been subject of many studies.<sup>11,12</sup> According to several authors, the Pd(P-P) chelate ring is the main factor that effectively controls the catalytic activity.<sup>1</sup> In particular, the formation of a more stable  $\beta$ -keto alkyl metallacycle, involving intramolecular interaction between the  $\beta$ -carbonyl group of the propagating chain and the palladium centre (**Scheme 6**) has been suggested to account for the lower activity of the dppe-like catalysts as compared to the dppp-like ones.<sup>11a</sup> In a similar way, the higher productivity exhibited in most solvents by the catalysts with the *ortho*-methoxy substituted ligands can be related to the capability of such nucleophilic groups to stabilise, by virtue of the oxygen donor atoms, coordinatively unsaturated intermediates as well as destabilise the  $\beta$ -keto alkyl metallaring favouring its opening by CO and thus speeding up the propagation process.<sup>3</sup>

Protonolysis and/or  $\beta$ -hydride elimination are the unique or largely prevailing chain termination processes operative in the copolymerization reactions investigated in this work. **Scheme 6** illustrates the generally accepted mechanism by which diphosphine palladium(II) propagating species undergo chain transfer mechanism.<sup>13</sup> This mechanism, experimentally demonstrated by van Leeuwen et al.,<sup>13</sup> involves equilibrium between the  $\beta$ -keto alkyl metallacycle and its enolate. However, since the overall protonolysis rate depends on the rate of the  $\beta$ -hydride elimination,<sup>13</sup> the polyketone molecular weight is determined by the kinetics of the  $\beta$ -hydride elimination step: the lower the rate of the  $\beta$ -H elimination, the higher the molecular weight.



Scheme 6

$\beta$ -H elimination reactions involving organometallic complexes are steered by both electronic and steric factors.<sup>14</sup> In particular, it is agreed that the agostic interaction between the metal and a  $\beta$ -hydrogen (precursor to hydrogen transfer) is disfavoured both by a high electron density at the metal centre and by the presence of groups on the supporting ligand which can compete with the  $\beta$ -hydrogen for interaction with the metal center.<sup>14</sup> Within this picture, it is apparent that highly basic phosphines bearing also two potential donor atoms such as *o*-MeO-dppe and *o*-MeO-dppp are more appropriately design suited than their unsubstituted counterparts dppe and dppp to retard  $\beta$ -H elimination paths.

### Catalytic reactions with the tosylate complexes **1b-4b** as catalyst precursors in either MeOH or TFE

The bis-cationic complexes **3b** and **4b** and the mono-cationic complexes **1b** and **2b** were employed to catalyse the CO-ethene copolymerisation in MeOH

with or without added *p*-toluensulfonic acid (TsOH) and/or 1,4-benzoquinone (BQ) (**Table 5**). The latter oxidant is commonly used for the re-generation of the catalytically active palladium(II) species by oxidation of catalytically inactive Pd(I) and Pd(0) species, that may form under the reducing conditions of the copolymerisation reactions. In turn, the protic acid serves to generate Pd-H moieties by oxidative addition to Pd(0) species as well as to convert catalytically inactive  $\mu$ -OH dimers (generated by adventitious moisture) into active mononuclear species.<sup>11</sup> Irrespective of the catalyst precursor employed, the alt-ethene-CO copolymers obtained in MeOH were featured by ketone and ester end groups in a 1:1 ratio, which is typical for CO-ethene copolymerisation in MeOH where initiation involves both Pd-OMe or Pd-H species and termination, may occur *via* either protonolysis or methanolysis.<sup>1</sup>

The highest productivities (up to 17-18 kg alt-ethene-CO (g Pd x h)<sup>-1</sup>) were obtained with the *o*-MeO catalyst precursors **3b** ([Pd(H<sub>2</sub>O)<sub>2</sub>(*o*-MeO-dppe)](OTs)<sub>2</sub>) and **4b** ([Pd(H<sub>2</sub>O)<sub>2</sub>(*o*-MeO-dppp)](OTs)<sub>2</sub>) without any acid co-catalyst and, under these conditions, the productivity gap between the *o*-MeO substituted catalysts and the unsubstituted congeners reached its maximum. Irrespective of catalyst and acidity of the reaction medium, a beneficial effect on the polymerisation rate was produced by the addition of 80 equiv of BQ. As an example, productivities of 18.1 vs 13.6 and 11.2 vs 9.1 were obtained for the **4b**-derived catalyst with or without BQ. Notably, the addition of increasing amounts of TsOH produced a significant increase in the productivity and stability of the unsubstituted catalysts (for **2b**, 3.5 / 4.2 / 4.4), whereas a negative effect was observed for the *o*-MeO-substituted ones (for **4b**, 13.6 / 11.0 / 9.1).

**Table 5.** Productivities (Kg alt-ethene-CO(g Pd x h)<sup>-1</sup>) and  $M_n$  (Kg mol<sup>-1</sup>) of [Pd(H<sub>2</sub>O)<sub>2-x</sub>(OTs)<sub>x</sub>(**P-P**)](OTs)<sub>2-x</sub> precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in MeOH.<sup>a</sup>

Entry	( <b>P-P</b> )	BQ(equiv.)	TsOH(equiv.)	Productivity 1h/3h	$M_n$
1	dppe			0.3/0.2	
2 <sup>b</sup>	<i>o</i> -OMe-dppe			12.4/9.6	14.2
3	dppp			3.5/2.5	
4 <sup>b</sup>	<i>o</i> -OMe-dppp			13.6/13.2	
5	dppe	80		0.4/-	
6 <sup>b</sup>	<i>o</i> -OMe-dppe	80		17.4/-	
7	dppp	80		4.1/-	
8 <sup>b</sup>	<i>o</i> -OMe-dppp	80		18.1/-	
9	dppe		2	0.8/0.3	
10	<i>o</i> -OMe-dppe		2	10.8/8.2	
11	dppp		2	4.2/4.0	
12	<i>o</i> -OMe-dppp		2	11.0/7.8	
13	dppe		20	1.9/1.7	4.3
14	<i>o</i> -OMe-dppe		20	8.9/7.2	16.2
15	dppp		20	4.4/4.4	14.9
16	<i>o</i> -OMe-dppp		20	9.1/6.6	>35
17	dppp	80	20	6.2/-	
18	<i>o</i> -OMe-dppp	80	20	11.2/-	

<sup>a</sup>Reaction conditions: catalyst 0.0048 mmol, MeOH 100 mL, P(CO/C<sub>2</sub>H<sub>4</sub>) 40 bar at 85 °C, 1 h and 3 h, 1200 rpm. <sup>b</sup>Catalyst 0.0024 mmol..

The decrease in productivity exhibited by the *o*-MeO catalysts upon increasing the acid concentration may be explained in the light of previous studies of palladium complexes with phosphine ligands bearing *o*-MeO substituted aryl rings.<sup>15</sup> Indeed, it has been reported that the *o*-MeO oxygen atoms act as effective H-bond acceptors, which, in an environment rich of H-bond donors, creates a web of interactions involving the complex, protons, solvent, and counteranions.<sup>16</sup> This would ultimately results in an increase of the steric congestion at the metal centre with negative effects on the monomers uptake and thus on the propagation rate. The substitution of MeOH ( $pK_a = 16$ ) by the

stronger Brønsted acid TFE ( $pK_a = 12.4$ ) was found to affect the catalytic productivity,  $M_n$  as well as the nature of the end groups (**Table 6**).

The data reported in **Table 6** shows, as already anticipated, that TFE depresses the productivity of the *o*-MeO catalysts **3b** and **4b** as compared to MeOH, while it enhances the activity of the catalysts derived from the unsubstituted precursors **1b** and **2b** up to ca. 16 kg alt-ethene-CO (g Pd x h)<sup>-1</sup>.

**Table 6.** Productivities (Kg alt-ethene-CO(g Pd x h)<sup>-1</sup>) and  $M_n$  (Kg mol<sup>-1</sup>) of [Pd(H<sub>2</sub>O)<sub>2-x</sub>(OTs)<sub>x</sub>(**P-P**)](OTs)<sub>2-x</sub> precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in TFE.<sup>a</sup>

Entry	( <b>P-P</b> )	BQ (equiv.)	Productivity 1h/3h	$M_n$
1	dppe		3.5/2.8	4.9
2	<i>o</i> -OMe-dppe		2.1/1.9	6.0
3	dppp		15.9/13.6	23.5
4	<i>o</i> -OMe-dppp		3.0/2.6	29.4
5	dppe	80	3.3/-	4.7
6	<i>o</i> -OMe-dppe	80	2.7/-	
7	dppp	80	15.6/-	
8	<i>o</i> -OMe-dppp	80	2.0/-	

<sup>a</sup>Reaction conditions: catalyst 0.0048 mmol, CF<sub>3</sub>CH<sub>2</sub>OH 100 mL, P(CO/C<sub>2</sub>H<sub>4</sub>) 40 bar at 85 °C, 1 h and 3 h, 1200 rpm.

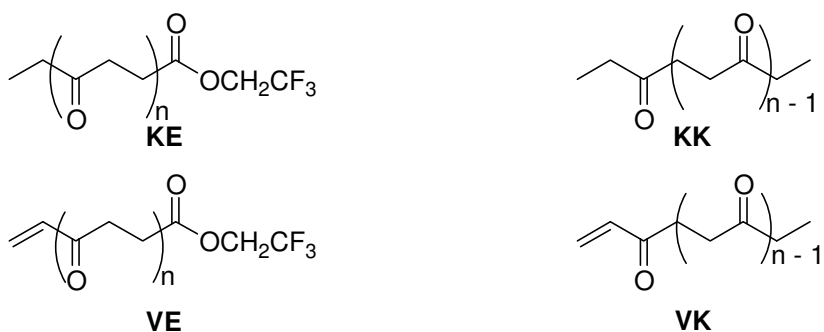
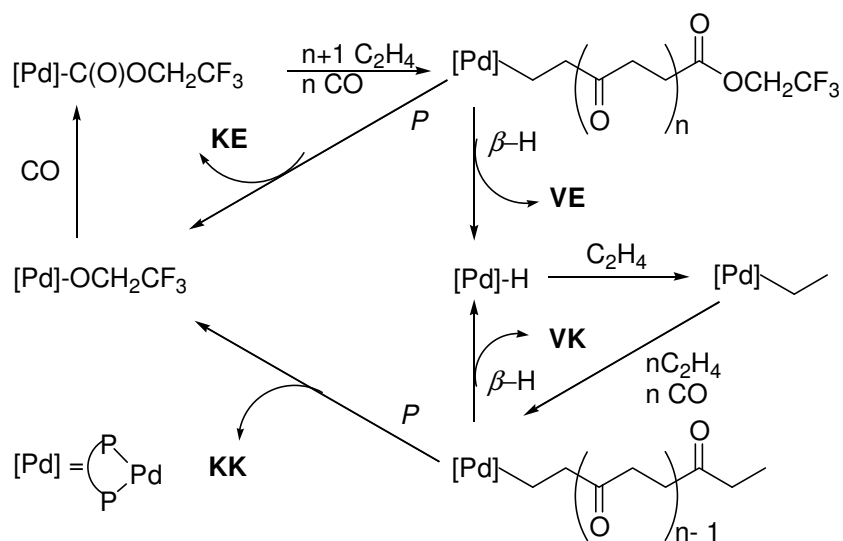
A <sup>13</sup>C{<sup>1</sup>H} and <sup>1</sup>H NMR analysis in 1,1,1,3,3,3-hexafluoroisopropanol-d<sub>2</sub>/C<sub>6</sub>H<sub>6</sub>-d<sub>6</sub> of the products obtained with the catalysts based on C<sub>2</sub>-bridged ligands showed the alt-ethene-CO materials obtained in TFE to have ketone, ester, and vinyl end groups. Since alcoholysis as chain transfer reaction in TFE can be ruled out due to the low nucleophilicity of this alcohol,<sup>17</sup> the only effective termination reactions in this solvent are β-hydride elimination and protonolysis.<sup>1</sup> Accordingly, polymeric materials with keto-ester (**KE**), vinyl-ester (**VE**), vinyl-ketone (**VK**) and diketone (**KK**) end groups may form. On the basis of the <sup>1</sup>H

NMR integration of the corresponding signals, the ratios between vinyl, ester and ketone end groups have been found to be 5:42:53 and <1:46:54 for **1b** and **3b**, respectively. The addition of BQ had no significant influence either on the ratio between the end groups or on the  $M_n$  values of the copolymers. The copolymers obtained with **1b** in the presence of BQ showed a vinyl:ester:ketone end group ratio of 7:40:53 and a  $M_n$  value of 4.7 kg mol<sup>-1</sup>.

Based on the end groups analysis of the polyketone products as well as previous literature reports,<sup>17</sup> a general catalytic mechanism for the CO/ethene copolymerisation in TFE is proposed in **Scheme 7**. Since the keto-ester copolymers are the dominant products, the most frequent initiator (> 85%) should be Pd-OCH<sub>2</sub>CF<sub>3</sub> and protonolysis the most effective termination path.

*Operando* and *in situ* HP-NMR experiments were carried out using either **2b** or **4b** as catalyst precursor and <sup>13</sup>C labelled CO as reagent in a 1:1 (v:v) mixture of CD<sub>2</sub>Cl<sub>2</sub> and TFE. While details of this study will be provided in a following section, it is useful to anticipate here that **4b** was converted under catalytic conditions into at least three dynamic species, likely alkoxycarbonyl and/or carbonyl, whereas no intermediate species was intercepted with **2b**, only a very fluxional species being observed even at low temperature.<sup>18</sup> Although no clear-cut experimental evidence was actually obtained, the <sup>13</sup>C labelling HP-NMR experiments suggest that the *o*-OMe-dppp ligand favour the formation of more stable carbonyl or ester species as compared to dppp, which may account for the lower activity of the catalysts with the former ligand. A largely positive influence of TFE on the CO/styrene copolymerisation by palladium(II) catalysts has been previously demonstrated by Milani et al. and has been attributed to the stabilising effect of TFE on important catalytic intermediates, such as Pd-H species.<sup>17</sup>





Scheme 7

Another positive effect on the catalytic activity is likely provided by the increased diffusion of the monomers in reactions performed in TFE due to capability of this alcohol to dissolve perfectly alternating polyketones as well as propagating Pd-polyketone chains.<sup>19</sup> Since there is no reason to think that these two positive effects are influenced by the presence of *o*-MeO substituted aryl rings in the catalysts precursors as is the case of **3b** and **4b**, the dramatic decrease in productivity observed with these catalysts in TFE must have a specific reason.

We do think that the low catalytic productivity exhibited by the *o*-MeO systems is due to the excellent H-bond donor and poor H-bond acceptor properties of TFE. Indeed, evidence has been provided according to which a web of strong H-bond interactions may be built up on the side of the metal coordination sphere where the *o*-MeO oxygen atoms can act as H-bond acceptors from TFE.<sup>19</sup> As a consequence, the steric congestion around the metal centre would be drastically increased, resulting in a slow diffusion of the monomers towards the metal centre and, hence, in the stabilisation of intermediates, for example alkoxy carbonyl species.

### CO-ethene copolymerisation reactions with the bis-chloride complexes **1a-4a** as catalyst precursors in water-AcOH mixtures

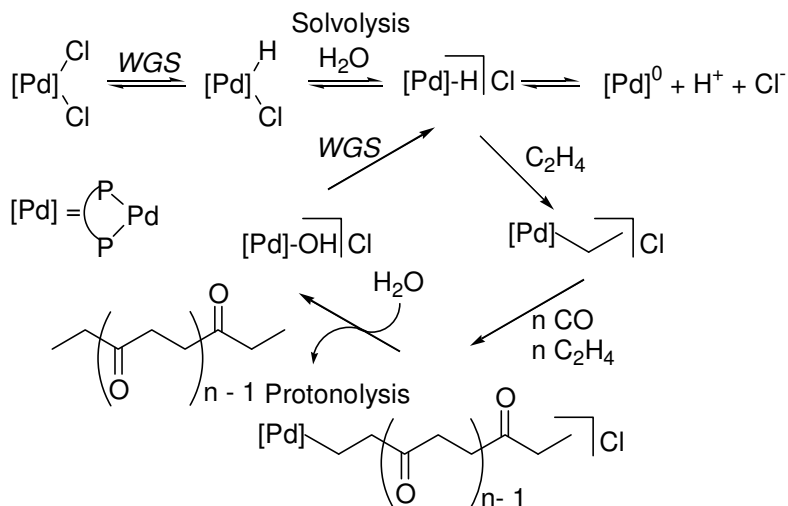
The bis-chloride complexes **1a-4a** were employed as catalyst precursors for the CO-ethene copolymerisation in mixtures of water and AcOH with a water content ranging from 55 to 85 mol% (**Table 7**). Irrespective of the catalyst precursor, the maximum of catalytic productivity was found using a water-AcOH mixture containing 75 mol% water.

**Table 7.** Productivities (Kg alt-ethene-CO(gPdxh)<sup>-1</sup>) and  $M_n$  (Kg mol<sup>-1</sup>) of PdCl<sub>2</sub>(**P-P**) (**1a-4a**) precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in AcOH/H<sub>2</sub>O.<sup>a</sup>

Entry	( <b>P-P</b> )	Productivity 1h/2h	$M_n$
1	dppe	0.8/0.4	3.3
2	<i>o</i> -OMe-dppe	8.9/5.5	5.7
3	dppp	5.6/4.5	14.5
4	<i>o</i> -OMe-dppp	9.1/6.0	> 40

<sup>a</sup>Reaction conditions: catalyst 0.0048 mmol, AcOH/H<sub>2</sub>O 75% mol 100 mL, P(CO/C<sub>2</sub>H<sub>4</sub>) 40 bar at 85 °C, 1 h and 2 h, 1200 rpm.

All of the alt-ethene-CO products obtained were exclusively featured by ketone end groups, which is consistent with the mechanism proposed for CO/ethene copolymerisations catalysed by PdCl<sub>2</sub>(diphosphine) complexes in acidic aqueous media involving Pd-H initiators and chain termination by protonolysis (**Scheme 8**).<sup>15,20</sup>



The neutral palladium(II)-H complexes shown in **Scheme 8** are believed to be generated from the bis-chloride precursors by water gas shift reaction (WGS), and then converted into the catalytically active cationic palladium(II)-H species by a water-controlled solvolysis process.<sup>20a</sup> It has been also demonstrated by Toniolo and Zudin that increasing the water proportion in the water/AcOH mixture increases the concentration of the cationic Pd(II)-H species by speeding up the solvolysis process.<sup>20</sup>

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<sub>2</sub>H<sub>4</sub>.<sup>20</sup> In the case at hand, 75 mo% in water seems to be the best compromise between an efficient solvolysis

process rate and acceptable co monomer solubility. 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.<sup>20</sup>

### **CO-ethene copolymerisation reactions with the methyl complexes 1c-4c as catalyst precursors in both CH<sub>2</sub>Cl<sub>2</sub> and toluene**

A few examples of palladium-catalysed CO-ethene copolymerisation in aprotic solvents such as dichloromethane, THF or acetone have been reported so far.<sup>21</sup> Herrmann has reported the performance of monocationic palladacycles stabilised by dppe and dppp, while Barron has studied the influence of *tert*-butylaluminumoxane co-catalysts on dppp modified catalysts.<sup>22</sup> Under these conditions, the only effective chain termination mechanism is  $\beta$ -H elimination to give high molecular weight copolymers with vinyl end groups. The neutral methyl complexes PdCl(Me)(P-P) **1c-4c** were scrutinised in either CH<sub>2</sub>Cl<sub>2</sub> with NaBARf (ArF = 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) as activator at 50 °C or in toluene in the presence of MAO at 60 °C (**Table 8**). No end-group could be seen by <sup>1</sup>H and <sup>13</sup>C NMR analysis of the copolymers obtained, which indicates the exclusive formation of very high molecular weight copolymers. However, ketone and vinyl end groups were detected in the copolymer samples obtained in CH<sub>2</sub>Cl<sub>2</sub> at higher temperature (85 °C), which is consistent with the formation of Pd-H initiators and  $\beta$ -H transfer as termination path.

**Table 8.** Productivities (Kg alt-ethene-CO(gPdxh)<sup>-1</sup>) of PdCl(Me)(**P-P**) (**1c-4c**) precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup> and Toluene.<sup>b</sup>

Entry	( <b>P-P</b> )	BQ (equiv.)	NaBARF (equiv.)	Productivity
1 <sup>a</sup>	dppe	80	1.5	0.4
2 <sup>a</sup>	<i>o</i> -MeO-dppe	80	1.5	2.9
3 <sup>a</sup>	dppp	80	1.5	2.8
4 <sup>a</sup>	<i>o</i> -MeO-dppp	80	1.5	5.1
5 <sup>b</sup>	dppe			-
6 <sup>b</sup>	<i>o</i> -MeO-dppe			0.4
7 <sup>b</sup>	dppp			0.1
8 <sup>b</sup>	<i>o</i> -MeO-dppp			0.5

<sup>a</sup>Reaction conditions: catalyst 0.01 mmol, CH<sub>2</sub>Cl<sub>2</sub> 75 mL, P(CO/C<sub>2</sub>H<sub>4</sub>) 40 bar at 50 °C, 20 min., 1200 rpm. <sup>b</sup>Reaction conditions: catalyst 0.01 mmol, MAO 100 equiv., Toluene 75 mL, P(CO/C<sub>2</sub>H<sub>4</sub>) 40 bar at 60 °C, 2 h, 1200 rpm.

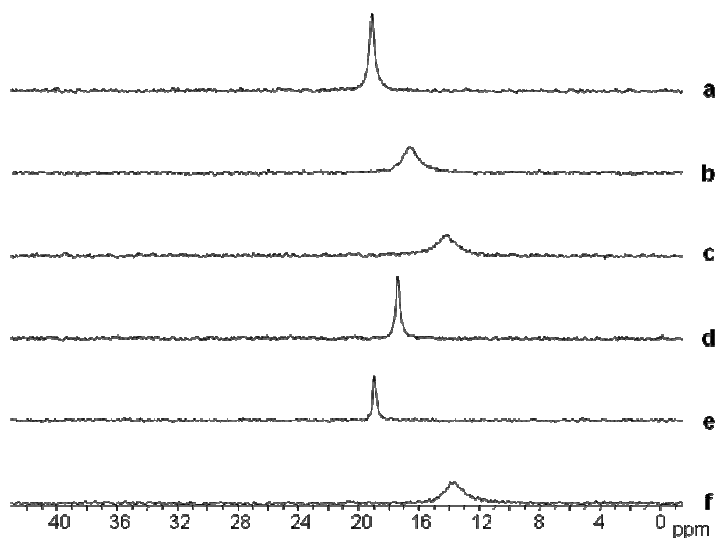
Irrespective of the catalyst precursor, the productivities were generally much lower than those in protic solvents, which may be due to the minor stability of the Pd-H initiator to reduction to Pd(0) and H<sup>+</sup> in aprotic solvents. The catalytic data of **1c** and **2c** in CH<sub>2</sub>Cl<sub>2</sub> are comparable with those reported by Herrmann.<sup>21</sup>

#### **Operando and in situ HP-NMR studies of the CO-ethene copolymerisation with 2b and 4b**

In an attempt to find out a reliable explanation for the low productivity exhibited by the *ortho*-methoxy modified catalysts in TFE, *operando* HP-NMR experiments were carried out in a 1:1 (v:v) mixture of CD<sub>2</sub>Cl<sub>2</sub>/TFE employing **4b** as catalyst precursor. Selected <sup>31</sup>P{<sup>1</sup>H} NMR spectra are reported in **Figure 8**. Pressurising the NMR tube with 20 bar CO converted **4b** ( $\delta$  19.0 in trace **a**) into a species featured by a broad signal centred at  $\delta$  16.5 (trace **b**). The line-shape of the latter resonance suggests that the carbonylation of **4b** is accompanied by fluxional processes. Pressurising the tube with ethene to 40 bar led to the

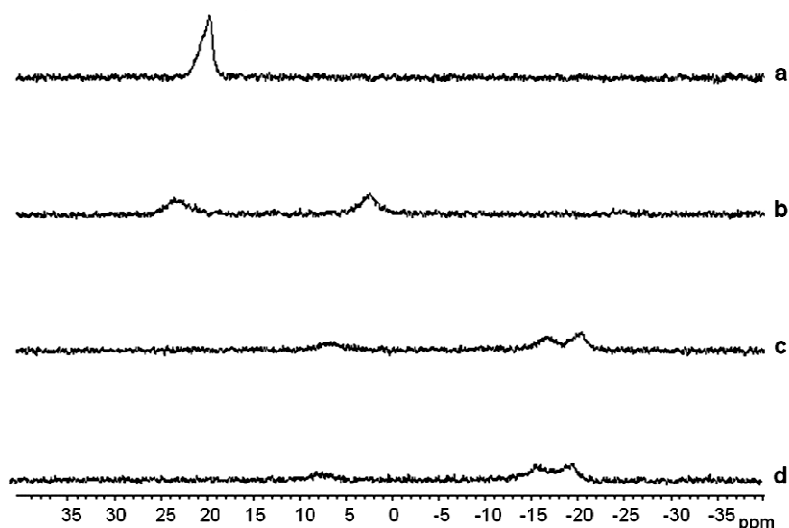
formation of polyketone product while the broad signal moved to ca.  $\delta$  14 (trace **c**). Upon heating, first to 50 °C and then to 85 °C, the signal narrowed and shifted to ca.  $\delta$  19.0 (traces **d** and **e**). After the tube was cooled to 20 °C, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum became similar to that observed before heating (compare traces **f** and **c**).

In line with previously reported studies of CO-ethene copolymerisation by palladium complexes stabilised by dppp-like diphosphines, the resonances shown in traces **C-F** are attributed to a catalyst resting state containing "Pd(P-P) $^{2+}$ " moieties stabilised by OTs $^-$  ligands, eventually in rapid exchange with solvent molecules and/or monomers.<sup>1,12a</sup> In analogous *operando* HP-NMR experiments carried either in CD<sub>2</sub>Cl<sub>2</sub>/TFE with the catalyst precursor **2b** or in MeOD-d<sub>4</sub> with the catalyst precursors **2b** and **4b**, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra showed a single relatively sharp resonance at the chemical shift of the starting complex during all experiments. This evidence suggests that the fluxional species observed in trace **b** of **Figure 8** forms only when the reaction is performed in TFE and the catalyst is modified with a diphosphine ligand containing *o*-OMe-aryl substituents.



**Figure 8.** *Operando*  $^{31}\text{P}\{^1\text{H}\}$  HP-NMR study (sapphire tube, 1:1 (v:v)  $\text{CD}_2\text{Cl}_2/\text{TFE}$ , 81.01 MHz) of the CO-ethene copolymerisation catalysed by **4b**: (a) under nitrogen at room temperature; (b) under 20 bar of CO at room temperature; (c) under 40 bar of 1:1 CO/ethene at room temperature; (d) at 50 °C; (e) at 85 °C; (f) after the sapphire tube was cooled to room temperature

In an attempt of elucidating the structure of the species formed by carbonylation of **4b** (trace **b** in **Figure 8**), a variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR study was performed in a 1:1 (v:v) mixture of  $\text{CH}_2\text{Cl}_2/\text{TFE}$ , using  $^{13}\text{C}$  labeled CO. A selected sequence of  $^{31}\text{P}\{^1\text{H}\}$ NMR spectra is presented in **Figure 9**. Traces (a) (singlet at  $\delta$  19.0) and (b) (broad resonance at ca.  $\delta$  3.0) are consistent with **4b** being in axial/equatorial aryl conformational exchange (see **Figure 6** and **Figure 7**). Upon pressurization to 20 bar with 1:19  $^{13}\text{CO}/^{12}\text{CO}$ , the  $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displayed a hump centred at  $\delta$  16.5 at 20 °C, analogous to that reported in trace (b) of **Figure 9**, which resolved at -40 °C into at least three broad resonances at ca.  $\delta$  7, -16, and -20. (trace c). A quite similar NMR picture was observed at -40 °C when the tube was pressurised with 20 bar ethene (trace d).

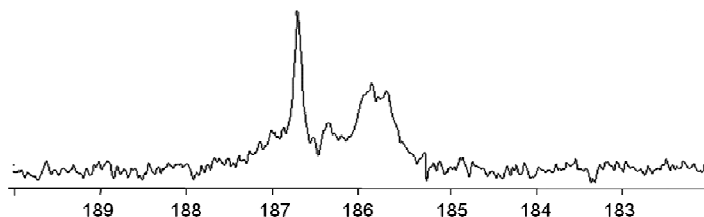


**Figure 9.** *In situ*  $^{31}\text{P}\{^1\text{H}\}$  NMR study (sapphire tube, 1:1 (v:v)  $\text{CD}_2\text{Cl}_2/\text{TFE}$ , 81.01 MHz) of the CO/ethene copolymerisation catalysed by **4b**: (a) under nitrogen at room temperature; (b) under nitrogen at  $-40\text{ }^\circ\text{C}$ ; (c) under 20 bar of 1:19  $^{13}\text{CO}/^{12}\text{CO}$  at  $-40\text{ }^\circ\text{C}$ ; (d) under 20 bar of 1:19  $^{13}\text{CO}/^{12}\text{CO}$  and 20 bar of ethene at  $-40\text{ }^\circ\text{C}$

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the latter reaction mixture were acquired at different temperatures. At room temperature, a rather broad resonance centered at ca  $\delta$  186 was observed, which resolved at low temperature into several resonances between  $\delta$  187 and 185. The spectrum at  $-80\text{ }^\circ\text{C}$  is shown in **Figure 10**. Apart from the sharp signal at  $\delta$  186.7 of free CO, no clear cut assignment of the other resonances was possible due to the broadness of the signals as well as the absence of any well defined multiplicity. The only reliable assumption is that signals in this spectral region are typical of linearly bonded CO as well as other keto ligands such as (alkoxy)carbonyls. It is worth reporting that no copolymer was produced along the whole experiments with **4b**, whereas the formation of polyketone bearing  $-\text{C}(\text{O})\text{OCH}_2\text{CF}_3$  end groups was observed using **2b** under comparable experimental conditions. On the other hand, there was no NMR



evidence whatsoever of the formation of carbonyl or alkoxy carbonyl species<sup>18a</sup> with the dppp-modified catalysts, which is consistent with its much higher activity.



**Figure 10.** High pressure  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4b** under 20 bar of 1:19  $^{13}\text{CO}/^{12}\text{CO}$  at  $-80\text{ }^\circ\text{C}$

### 2.1.3. Conclusions

The results obtained in this work confirm that, irrespective of the reaction medium, the palladium(II) catalysts supported by the dppp-like chelating diphosphines give higher productivities as well as higher molecular weight polyketones as compared to the dppe-like counterparts (i.e., dppp > dppe and *o*-MeO-dppp > *o*-MeO-dppe). Except for the reactions performed in TFE, the *ortho*-methoxy modified catalysts are by far more productive than their unmodified catalysts (*o*-MeO-dppp > *o*-MeO-dppe > dppp > dppe) and also provide higher molecular weight materials.

In TFE, the *ortho*-methoxy oxygen atoms of either *o*-MeO-dppp or *o*-MeO-dppe form an effective web of hydrogen bonding interactions with solvent molecules. As a result of the increased congestion at the metal centre, a slower diffusion of the monomers would take place with a retardant effect on the propagation rate. Organic solvents such as  $\text{CH}_2\text{Cl}_2$  and toluene promote the formation of very high molecular weight materials, yet in unsatisfactory yields.

## 2.1.4. 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 deoxygenated before use. 2,2,2-Trifluoroethanol (TFE) was used as purchased from Aldrich. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise.  $\text{PdCl}_2(\text{COD})$ <sup>23a</sup>,  $\text{PdCl}(\text{Me})(\text{COD})$  (COD = cycloocta-1,5-diene),<sup>23b</sup>  $\text{PdCl}_2(\text{dppe})$  (**1a**),<sup>7</sup>  $\text{PdCl}_2(\text{dppp})$  (**2a**),<sup>7</sup>  $[\text{Pd}(\text{H}_2\text{O})(\text{dppp})](\text{OTs})_2$  (OTs = *p*-toluenesulfonate, **2b**),<sup>24</sup>  $\text{PdCl}(\text{Me})(\text{dppe})$  (**1c**),<sup>11a</sup>  $\text{PdCl}(\text{Me})(\text{dppp})$  (**2**),<sup>11b</sup> and  $\text{NaBArF}$  (ArF = 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sup>25</sup> were prepared according to literature methods. Solid MAO (methylaluminoxane) for the copolymerisation reaction was prepared by removing toluene and  $\text{AlMe}_3$  under vacuum from a commercially available MAO solution (10 wt.% in toluene, Crompton Corp.).<sup>26</sup> 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 during the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP2100S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25 $\mu\text{m}$  film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H} 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 ( $\delta$ ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (<sup>1</sup>H

and  $^{13}\text{C}$  NMR) or 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$  NMR). High pressure NMR (HP-NMR) experiments were carried out on Bruker ACP 200 spectrometer using a 10 mm HP-NMR tube (Saphikon (Milford, NH) sapphire tube; titanium high-pressure charging head constructed at the ICCOM-CNR).<sup>27</sup> 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.<sup>28</sup> Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer).

## Syntheses

### Preparation of 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp)

*n*-BuLi 1.6 M in *n*-hexane (6.80 mL, 10.80 mmol) was slowly added to a stirred solution of bis(2-methoxyphenyl)phosphine<sup>6a</sup> (2.00 g, 8.31 mmol) in THF (150 mL) at 0 °C. The resulting suspension was allowed to warm to room temperature and stirred for further 2 h. A solution of 1,2-dichloroethane or 1,3-dichloropropane, (4.10 mmol) in THF (20 mL) was added drop wise to this suspension that became almost colourless. Afterwards, the reaction mixture was quenched with water (3 mL) and concentrated to dryness under reduced pressure. Treating the residue with a 1:3 (v:v) mixture of water/ethanol (50 mL) under vigorous stirring gave a white solid. Recrystallisation from  $\text{CH}_2\text{Cl}_2$ /ethanol led to the precipitation of *o*-MeO-dppe (or *o*-MeO-dppp) as an off-white powder, which was filtered off, washed with ethanol, and dried under a stream of nitrogen.

***o*-MeO-dppe**: 1.66 g (78%). C<sub>30</sub>H<sub>32</sub>O<sub>4</sub>P<sub>2</sub> (518.52 g/mol): calc. C 69.49, H 6.22; found: C 69.46, H 6.24. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 81.01 MHz, CDCl<sub>3</sub>, 21 °C) -30.80 (s); <sup>1</sup>H NMR (δ, 200.13 MHz, CDCl<sub>3</sub>, 21 °C) 2.20 (t, <sup>2</sup>J<sub>HP</sub> = 3.7 Hz, 4H, PCH<sub>2</sub>), 3.75 (s, 12H, OCH<sub>3</sub>), 6.80-7.35 (m, 16H, Ar)

***o*-MeO-dppp**: 1.48 g (68%). C<sub>31</sub>H<sub>34</sub>O<sub>4</sub>P<sub>2</sub> (532.54 g/mol): calc. C 69.92, H 6.44; found: C 69.94, H 6.47. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 81.01 MHz, CDCl<sub>3</sub>, 21 °C) -36.7 (s); <sup>1</sup>H NMR (δ, 200.13 MHz, CDCl<sub>3</sub>, 21 °C) 1.73 (br s, 2H, CH<sub>2</sub>), 2.23 (m, 4H, PCH<sub>2</sub>), 3.80 (m, 12H, OCH<sub>3</sub>), 6.79-7.05 (m, 16H, Ar)

### Preparation of PdCl<sub>2</sub>(*o*-MeO-dppe) (**3a**) and PdCl<sub>2</sub>(*o*-MeO-dppp) (**4a**)

A solid sample of PdCl<sub>2</sub>(COD) (57.1 mg, 0.20 mmol) was added to a stirred solution of the appropriate diphosphine ligand (0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at room temperature. After 1 h, the reaction mixture was concentrated to ca. 5 mL under reduced pressure. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (20 mL) led to the precipitation of **3a** or **4a** as a yellow solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

**Complex 3a**: 102.9 mg (74%). C<sub>30</sub>H<sub>32</sub>Cl<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Pd (695.84 g/mol): calc. C 51.78, H 4.64; found: C 51.65, H 4.60. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 81.01 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 69.02 (s); <sup>1</sup>H NMR (δ, 200.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 2.78 (m, 4H, PCH<sub>2</sub>), 3.61 (s, 12H, OCH<sub>3</sub>), 6.96-7.95 (m, 16H, Ar); <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) 68.97 (s); <sup>1</sup>H NMR (δ, 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) 3.00 (m, 4H, PCH<sub>2</sub>), 3.42 (s, 6H, Ar<sub>ax</sub>-*o*-OCH<sub>3</sub>), 3.75 (s, 6H, Ar<sub>eq</sub>-*o*-OCH<sub>3</sub>), 6.81-8.81 (m, 14H, Ar), 8.85 (m, 2H, Ar<sub>eq</sub>-*o*-H)

**Complex 4a**: 116.4 mg (82%). C<sub>31</sub>H<sub>34</sub>Cl<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Pd (709.86 g/mol): calc. C 52.45, H 4.83; found: C 52.48, H 4.86. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 81.01 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 16.30 (s); <sup>1</sup>H NMR (δ, 200.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 1.90 (m, 2H, CH<sub>2</sub>), 2.50 (m, 4H, PCH<sub>2</sub>), 3.75 (s, 12H, OCH<sub>3</sub>), 6.97-7.60 (m, 16H, Ar); <sup>31</sup>P{<sup>1</sup>H} NMR (δ,

161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) 17.63 (s); <sup>1</sup>H NMR (δ, 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) 1.92 (m, 2H, CH<sub>2</sub>), 2.45 (m, 4H, PCH<sub>2</sub>), 3.68 (s, 6H, Ar<sub>ax</sub>-*o*-OCH<sub>3</sub>), 3.73 (s, 6H, Ar<sub>eq</sub>-*o*-OCH<sub>3</sub>), 6.82-8.92 (m, 14H, Ar), 8.95 (dd, <sup>3</sup>J<sub>HP</sub> = 16 Hz, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H, Ar<sub>ax</sub>-*o*-H)

### Preparation of [Pd(OTs)(H<sub>2</sub>O)(dppe)]OTs (**1b**)

A solid sample of AgOTs (136.70 mg, 0.49 mmol) was added to a stirred solution of **1a** (138.12 mg, 0.24 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at room temperature. After 3 h, the precipitated AgCl was removed by filtration of the suspension through a celite column and the clear filtrate was concentrated to ca. 3 mL. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (15 mL) led to the precipitation of **1b** as a yellow microcrystalline solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

**Complex 1b**: 145.4 mg (70%). C<sub>40</sub>H<sub>40</sub>O<sub>7</sub>P<sub>2</sub>S<sub>2</sub>Pd (865.23 g/mol): calc. C 55.55, H 4.62; found: C 55.40, H 4.53. ΛM (nitroethane, 26 °C): 65 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 81.01 MHz, CDCl<sub>3</sub>, 21 °C) 71.01 (s); <sup>1</sup>H NMR (δ, 200.13 MHz, CDCl<sub>3</sub>, 21 °C) 2.27 (s, 6H, OTs-CH<sub>3</sub>), 2.69 (m, 4H, CH<sub>2</sub>), 5.15 (br s, 2H, H<sub>2</sub>O), 6.90-7.79 (m, 28H, Ar)

### Preparation of [Pd(H<sub>2</sub>O)<sub>2</sub>(*o*-MeO-dppe)](OTs)<sub>2</sub> (**3b**) and [Pd(H<sub>2</sub>O)<sub>2</sub>(*o*-MeO-dppp)](OTs)<sub>2</sub> (**4b**)

A solid sample of AgOTs (125.54 mg, 0.45 mmol) was added to a stirred solution of **3a** or **4a**, (0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at room temperature. After 3 h, the precipitated AgCl was removed by filtration of the suspension through a celite column and the clear filtrate was concentrated to ca. 3 mL. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (15 mL) led to the precipitation of **3b**

or **4b** as a yellow microcrystalline solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

**Complex 3b:** 145.7 mg (66%). C<sub>44</sub>H<sub>50</sub>O<sub>12</sub>P<sub>2</sub>S<sub>2</sub>Pd (1003.32 g/mol): calc. C 52.70, H 4.98; found: C 52.50, H 4.60.  $\Lambda$ M (nitroethane, 26 °C): 98  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . <sup>31</sup>P{<sup>1</sup>H} NMR ( $\delta$ , 161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 69.73 (s), <sup>1</sup>H NMR ( $\delta$ , 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 2.29 (s, 6H, OTs-CH<sub>3</sub>), 2.78 (m, 4H, PCH<sub>2</sub>), 3.66 (s, 12H, OCH<sub>3</sub>), 4.43 (br s, 4H, H<sub>2</sub>O), 6.97-7.59 (m, 24H, Ar)

**Complex 4b:** 190.3 mg (85%). C<sub>45</sub>H<sub>52</sub>O<sub>12</sub>P<sub>2</sub>S<sub>2</sub>Pd (1017.35 g/mol): calc. C 53.12, H 5.15; found: C 53.14, H 5.18.  $\Lambda$ M (nitroethane, 26 °C): 100  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . <sup>31</sup>P{<sup>1</sup>H} NMR ( $\delta$ , 161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 13.72 (s); <sup>1</sup>H NMR ( $\delta$ , 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 2.27 (m, 2H, CH<sub>2</sub>), 2.34 (s, 6H, OTs-CH<sub>3</sub>), 2.75 (m, 4H, PCH<sub>2</sub>), 4.05 (s, 16H, OCH<sub>3</sub> + H<sub>2</sub>O), 6.90-7.60 (m, 24H, Ar); <sup>31</sup>P{<sup>1</sup>H} NMR ( $\delta$ , 161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) -4.46 (s); <sup>1</sup>H NMR ( $\delta$ , 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) 2.31 (s, 6H, OTs-CH<sub>3</sub>), 2.35 (m, 2H, CH<sub>2</sub>), 3.02 (m, 4H, PCH<sub>2</sub>), 3.97 (s, 6H, Ar<sub>ax</sub>-O-CH<sub>3</sub>), 4.33 (s, 6H, Ar<sub>eq</sub>-O-CH<sub>3</sub>), 6.4-7.8 (m, 24H, Ar), the water resonance was not detected at -80 °C

#### Preparation of PdCl(Me)(*o*-MeO-dppe) (**3c**) and PdCl(Me)(*o*-MeO-dppp) (**4c**)

A solid sample of PdCl(Me)(COD) (52.99 mg, 0.20 mmol) was added to a stirred solution of the appropriate diphosphine ligand *o*-MeO-dppe or *o*-MeO-dppp (0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at room temperature. After 1 h, the resulting colourless solution was concentrated to ca. 5 mL under reduced pressure. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (20 mL) led to the complete precipitation of **3c** or **4c** as an off-white solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

**Complex 3c:** 105.4 mg (78%).  $C_{31}H_{35}ClO_4P_2Pd$  (675.43 g/mol): calc. C 55.13, H 5.22; found: C 55.09, H 5.24.  $^{31}P\{^1H\}$  NMR ( $\delta$ , 161.98 MHz,  $CDCl_3$ , 21 °C) 61.09 (d,  $^2J_{PP} = 22.0$  Hz), 39.07 (d);  $^1H$  NMR ( $\delta$ , 200.13 MHz,  $CDCl_3$ , 21 °C) 0.40 (dd,  $^3J_{HPtrans} = 8.0$  Hz,  $^3J_{HPcis} = 3.2$  Hz, 3H, PdCH<sub>3</sub>), 2.19-2.93 (m, 4H, CH<sub>2</sub>), 3.59 (s, 6H, OCH<sub>3</sub>), 3.60 (s, 6H, OCH<sub>3</sub>), 6.87-7.91 (m, 16H, Ar);  $^{31}P\{^1H\}$  NMR ( $\delta$ , 161.98 MHz,  $CD_2Cl_2$ , -70 °C) 60.70 (d,  $^2J_{PP} = 23.2$  Hz, P<sub>A</sub>), 38.32 (d, P<sub>M</sub>);  $^1H$  NMR ( $\delta$ , 400.16 MHz,  $CD_2Cl_2$ , -70 °C) 0.40 (dd,  $^3J_{HPM} = 8.0$  Hz,  $^3J_{HPA} = 3.0$  Hz, 3H, PdCH<sub>3</sub>), 2.08 (m, 1H, PCHH), 2.38 (m, 1H, P'CHH), 2.91 (dt,  $^2J_{HP} = 56.0$  Hz,  $^3J_{HH} = 13.6$  Hz, 1H, PCHH), 3.08 (dt,  $^2J_{HP} = 56.0$  Hz,  $^3J_{HH} = 13.6$  Hz, 1H, P'CHH), 3.42 (s, 3H, OCH<sub>3</sub>), 3.44 (s, 3H, OCH<sub>3</sub>), 3.76 (s, 6H, OCH<sub>3</sub>), 6.72-7.73 (m, 14H, Ar), 8.45 (dd,  $^2J_{HP} = 15.9$  Hz,  $^3J_{HH} = 7.3$  Hz, 1H, *o*-H-Ar<sub>ax</sub>(P<sub>A</sub>)), 8.61 (dd,  $^2J_{HP} = 15.1$  Hz,  $^3J_{HH} = 7.5$  Hz, 1H, *o*-H-Ar<sub>ax</sub>(P<sub>M</sub>))

**Complex 4c:** 92.4 mg (67%).  $C_{32}H_{37}ClO_4P_2Pd$  (689.46 g/mol): calc. C 55.75, H 5.41; found: C 55.74, H 5.43.  $^{31}P\{^1H\}$  NMR ( $\delta$ , 81.01 MHz,  $CDCl_3$ , 21 °C) 30.80 (d,  $^2J_{PP} = 52.5$  Hz), -0.56 (d);  $^1H$  NMR ( $\delta$ , 200.13 MHz,  $CDCl_3$ , 21 °C) 0.32 (dd,  $^3J_{HPtrans} = 7.9$  Hz,  $^3J_{HPcis} = 3.5$  Hz, PdCH<sub>3</sub>), 1.92 (m, 2H, CH<sub>2</sub>), 2.43 (m, 2H, PCH<sub>2</sub>), 2.57 (m, 2H, PCH<sub>2</sub>), 3.66 (s, 6H, OCH<sub>3</sub>), 3.76 (s, 6H, OCH<sub>3</sub>), 6.87-7.58 (m, 16H, Ar);  $^{31}P\{^1H\}$  NMR ( $\delta$ , 161.98 MHz,  $CD_2Cl_2$ , -70 °C) 30.88 (d,  $^2J_{PP} = 51.4$  Hz, P<sub>A</sub>), -2.42 (d, P<sub>M</sub>);  $^1H$  NMR ( $\delta$ , 400.16 MHz,  $CD_2Cl_2$ , -70 °C) -0.89 (dd,  $^3J_{HPM} = 7.7$  Hz,  $^3J_{HPA} = 3.2$  Hz, PdCH<sub>3</sub>), 1.70 (m, 1H, CHH), 1.92 (m, 1H, CHH), 2.20 (m, 1H, PCHH), 2.30 (m, 1H, P'CHH), 2.48 (m, 1H, PCHH), 2.79 (m, 1H, P'CHH), 3.56 (s, 3H, OCH<sub>3</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.69 (s, 3H, OCH<sub>3</sub>), 3.72 (s, 3H, OCH<sub>3</sub>), 6.67-7.71 (m, 14H, Ar), 8.55 (dd,  $^2J_{HP} = 16.4$  Hz,  $^3J_{HH} = 7.3$  Hz, 1H, *o*-H-Ar<sub>ax</sub>(P<sub>A</sub>)), 8.74 (dd,  $^2J_{HP} = 14.7$  Hz,  $^3J_{HH} = 7.1$  Hz, 1H, *o*-H-Ar<sub>ax</sub>(P<sub>M</sub>))

#### Preparation of Pd(OAc)<sub>2</sub>(*o*-MeO-dppe) (3d) and Pd(OAc)<sub>2</sub>(*o*-MeO-dppp) (4d)

In a Schlenk flask silver acetate (128.5 mg, 0.77 mmol) was added to a solution of complex **3a** or **4a**, (0.35 mmol) in dichloromethane (20 mL). The solution was allowed to stir for half an hour at room temperature. Afterwards AgCl was

removed by filtration of the suspension through a plug of celite. The clear filtrate was concentrated to ca. 3 mL and a solvent mixture of *n*-hexane and diethylether (1:1) (v:v) (20 mL) was added under nitrogen in order to precipitate the product as a yellow solid, which was filtered off and dried under a stream of nitrogen.

**Complex 3d:** 161.1 mg (62%). C<sub>34</sub>H<sub>38</sub>O<sub>8</sub>P<sub>2</sub>Pd (742.42 g/mol): calc. C 54.96, H 5.15; found: C 54.94, H 5.18. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 61.94 (s); <sup>1</sup>H NMR (δ, 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 1.30 (s, 6H, CH<sub>3</sub>COO), 2.77 (m, 4H, CH<sub>2</sub>), 3.73 (s, 12H, OCH<sub>3</sub>), 6.95-8.04 (m, 16H, Ar)

**Complex 4d:** 187.9 mg (71%). C<sub>35</sub>H<sub>40</sub>O<sub>8</sub>P<sub>2</sub>Pd (756.42 g/mol): calc. C 55.53, H 5.33; found: C 55.49, H 5.35. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, 161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 14.40 (s); <sup>1</sup>H NMR (δ, 400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C) 1.25 (br s, 6H, CH<sub>3</sub>COO), 1.98 (m, 2H, CH<sub>2</sub>), 2.40 (m, 4H, CH<sub>2</sub>-P), 3.70 (s, 12H, OCH<sub>3</sub>), 6.90-7.60 (m, 16H, Ar)

## NMR studies

### Variable-temperature <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR studies of 3a, 4a, and 4b in CD<sub>2</sub>Cl<sub>2</sub>

A solution of the appropriate complex (0.015 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.8 mL) was transferred under nitrogen into a 5 mm NMR tube, which was placed into a NMR probe at 20 °C. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were acquired every 10 °C in the temperature range from 20 to -80 °C.



### ***In situ* HP-NMR studies of the CO-ethene copolymerisation with **2b** and **4b** as catalyst precursors in CD<sub>2</sub>Cl<sub>2</sub>/TFE**

A 10 mm sapphire NMR tube was charged with a solution of **2b** or **4b**, (0.02 mmol) in a 1:1 (v:v) mixture of CD<sub>2</sub>Cl<sub>2</sub>/TFE (2 mL) under nitrogen at room temperature and then placed into a NMR probe at 20 °C. <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at this temperature and then at -40 °C. Analogous spectra were recorded at the same temperatures after the sapphire tube was charged first with a 1:19 mixture of <sup>13</sup>CO/<sup>12</sup>CO to 20 bar and then with ethene to 40 bar.

### ***Operando* HP-NMR studies of the CO-ethene copolymerisation with **2b** and **4b** as catalyst precursors in either CD<sub>2</sub>Cl<sub>2</sub>/TFE or MeOD-d<sub>4</sub>**

A 10 mm sapphire NMR tube was charged with a solution of **2b** or **4b**, (0.02 mmol) in either a 1:1 (v:v) mixture of CD<sub>2</sub>Cl<sub>2</sub>/TFE or MeOD-d<sub>4</sub> (2 mL) under nitrogen at room temperature and then placed into a NMR probe at 20 °C. After <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H (only for the study in MeOD-d<sub>4</sub>) NMR spectra were recorded, the sapphire tube was removed from the NMR probe, charged with CO to 20 bar, and placed again into the NMR probe at 20 °C. After the spectra were recorded, the sapphire tube was removed from the NMR probe, charged with ethylene to 40 bar, 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 85 °C. After 1 h at 85 °C, the tube was cooled to 20 °C, which was followed by the acquisition of the last spectra. Once the tube was removed from the probe head, the copolymer appeared as a off-white solid layer over a colourless solution.

## Catalytic reactions

### Catalytic reactions in MeOH or TFE with 1b-4b as catalyst precursors

Typically, MeOH or TFE, (100 mL), was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.0048 mmol). When the catalytic reactions were performed with additives such as *p*-toluenesulphonic acid monohydrate (*p*-TsOH) and 1,4-benzoquinone (BQ), they were added together with the catalyst precursor into the autoclave. The autoclave was charged with a 1:1 CO/C<sub>2</sub>H<sub>4</sub> mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 85 °C and the pressure was equilibrated to 40 bar, stirring (1200 rpm) was started. After the desired time (1 or 3 h), the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. Due to the much higher solubility capacity of TFE for the alt-ethene-CO materials as compared to MeOH, two different procedures were employed to collect the polymer produced in the two solvents. For the experiments in MeOH, the insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 °C to constant weight. For the experiments in TFE, the catalysis mixture, extremely viscous for the dissolved polymer, was concentrated to dryness under vacuum and the residue was then washed and dried as above. In all of the experiments the solutions were analysed by GC/MS.

### Catalytic reactions in water-acetic acid with 1a-4a as catalyst precursors

A mixture of acetic acid (AcOH) and distilled water (100 mL) was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing 0.0048 mmol of catalyst precursor. The autoclave was charged with a 1:1 CO/C<sub>2</sub>H<sub>4</sub> mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 85 °C and the pressure was equilibrated to 40 bar,

stirring (1200 rpm) was started. After the desired time (1 or 2 h), the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with water, and dried under vacuum at 60 °C to constant weight. Experiments were carried out in water-AcOH mixtures with water in the range from 55 to 85 mol%.

#### **Catalytic reactions in CH<sub>2</sub>Cl<sub>2</sub> with 1c-4c as catalyst precursors**

CH<sub>2</sub>Cl<sub>2</sub> (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol) and NaBARF (0.012 mmol). The autoclave was charged with a 1:1 CO/C<sub>2</sub>H<sub>4</sub> mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 50 °C and the pressure was equilibrated to 40 bar, stirring (1200 rpm) was started. After 20 min, the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub>, and dried under vacuum at 60 °C to constant weight.

#### **Catalytic reactions in toluene with 1c-4c as catalyst precursors**

A solution of solid MAO (58.02 mg, 1.0 mmol) in toluene (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol). The autoclave was charged with a 1:1 CO/C<sub>2</sub>H<sub>4</sub> mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 60 °C and the pressure was equilibrated to 40 bar, stirring (1200 rpm) was started. After 2 h, the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The reaction mixture was treated with MeOH acidified with dilute HCl. The insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 °C to constant weight.

## Characterisation of the alt-ethene-CO copolymers obtained in TFE

Polyketone products were analysed by IR,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopies. The NMR measurements were performed in a 1:1 (v:v) mixture of 1,1,1,3,3,3-hexafluoroisopropanol- $d_2$ /C $_6$ H $_6$ - $d_6$  showing a perfectly alternating structure. The entire polymer samples were featured by the presence of four different combinations of end groups in the following order of abundance: keto-ester (**KE**) > diketone (**KK**) >> vinyl-ester (**VE**) > vinyl-ketone (**VK**). The number-average molecular weight ( $M_n$ ) of the copolymers was determined by  $^1\text{H}$  NMR spectroscopy. NMR and IR data for a representative example are reported below:  $^1\text{H}$  NMR ( $\delta$ , 400.13 MHz, 21 °C) 0.93 (t,  $^3J_{\text{HH}} = 7.4$  Hz, C(O)CH $_2$ CH $_3$ ), 2.17 (q,  $^3J_{\text{HH}} = 7.4$  Hz, C(O)CH $_2$ CH $_3$ ), 2.51 (br s, CH $_2$ C(O)CH $_2$ ), 4.25 (q,  $^3J_{\text{HF}} = 8.0$  Hz, C(O)OCH $_2$ CF $_3$ ), 5.68 (m, C(O)CH=CH $_2$ ), 6.06 (m, C(O)CH=CHH), 6.15 (m, C(O)CH=CHH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ , 100.62 MHz, 21 °C) 6.94 (C(O)CH $_2$ CH $_3$ ), 26.80 (CH $_2$ C(O)OCH $_2$ CF $_3$ ), 35.04 (CH $_2$ C(O)CH $_2$ ), 60.27 ( $^2J_{\text{CF}} = 35.9$  Hz, C(O)OCH $_2$ CF $_3$ ), 124.10 ( $^1J_{\text{CF}} = 283.6$  Hz, C(O)OCH $_2$ CF $_3$ ), 172.14 (C(O)OCH $_2$ CF $_3$ ), 209.85 (C(O)CH $_2$ CH $_2$ C(O)OCH $_2$ CF $_3$ ), 210.90 (CH $_2$ C(O)CH $_2$ ), 214.32 (C(O)CH $_2$ CH $_3$ ). The vinyl resonances were not assigned as obscured by other carbons. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3392 (w), 2912 (m), 1695 (vs), 1407 (s), 1332 (s), 1259 (m), 1165 (m), 1055 (s), 809 (m), 592 (m)

## X-Ray crystallography

Suitable crystals of **3a**·2.3 CH $_2$ Cl $_2$  and **4a** for single crystal X-ray structure analysis were obtained by slow diffusion of *n*-hexane into a saturated CH $_2$ Cl $_2$  solution of either **3a** or **4a**, while crystal of compounds **3d** and **4d** were obtained by diffusion of toluene into a saturated dichloromethane solution of **3d** and **4d**. X-ray diffraction intensity data were collected on Oxford Diffraction diffractometers, equipped with a graphite monochromator and a CCD area detector. While for **3a**·2.3 CH $_2$ Cl $_2$ , **4a** and **4d** Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) was

employed, for **3d** Cu<sub>K $\alpha$</sub>  radiation ( $\lambda = 1.54180 \text{ \AA}$ ) was employed. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS.<sup>29a</sup> All structure determination calculations were performed with the WINGX package<sup>29b</sup> with SIR-97,<sup>29c</sup> SHELXL-97<sup>29d</sup> and ORTEP-3 programs.<sup>29e</sup> Final refinements based on  $F^2$  were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic U values depending on the U<sub>eq</sub> of the adjacent carbon atoms.

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