

CO-ethylene copolymerization reactions in different reaction media catalyzed by palladium(II) complexes with chelating diphosphines bearing *ortho*-methoxy-substituted aryl groups

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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 synthesized and employed to catalyze the CO-ethylene copolymerization reaction in either protic or aprotic solvents. A comparison of the catalytic performance of these complexes with that of analogous precursors stabilized by 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) ligands has 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 rationalize the observed productivity as well.

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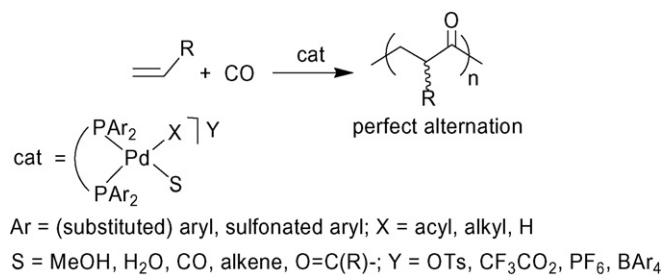
1. Introduction

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 synthesize and are derived from inexpensive monomers such as ethylene and CO [1]. A small fraction of the ethylene 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 [2].

Polyketones (alt-E-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 solvents (toluene,

dichloromethane, THF) 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 2 summarizes the principal steps of the alternating ethylene/CO copolymerization in a generic alcohol by Pd^{II} catalysts modified with chelating diphosphines [1]. Two competing cycles, connected by two cross termination steps, are contemporaneously at work for the production of alt-E-CO, the prevalence of either cycle depending on the experimental conditions. Cycle **B** initiates (*I*) with the insertion of ethylene into a Pd-H bond that can be generated in a variety of ways. Insertion of CO into the resulting alkyl complex is reversible and faster than ethylene insertion, while CO insertion into the Pd-acyl is thermodynamically disfavored. Since ethylene insertion into the Pd acyl is rapid and irreversible, the propagation (*P*) can occur by alternating insertion of CO and ethylene. The copolymer produced by this cycle contains either keto-ester or diketone end groups depending on the termination path: the keto-ester end structure is obtained via alcoholysis (*M*) of a Pd-acyl bond, while the diketone structure occurs by

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Scheme 1.

protonolysis (*H*) of a Pd-alkyl intermediate. A copolymer with keto-ester end groups can be produced also by protonolysis of a Pd-alkyl bond formed during the propagation in the competing cycle **A** that starts with the insertion of CO into a Pd–OR bond to give a Pd alkoxyacetyl complex. The diester structure is obtained via alcoholysis of a Pd-acyl coming from cycle **A**.

Replacing ROH with water does not significantly affect the catalytic cycle of copolymerization, except for the formation of polyketones with diketone and/or acid end groups.

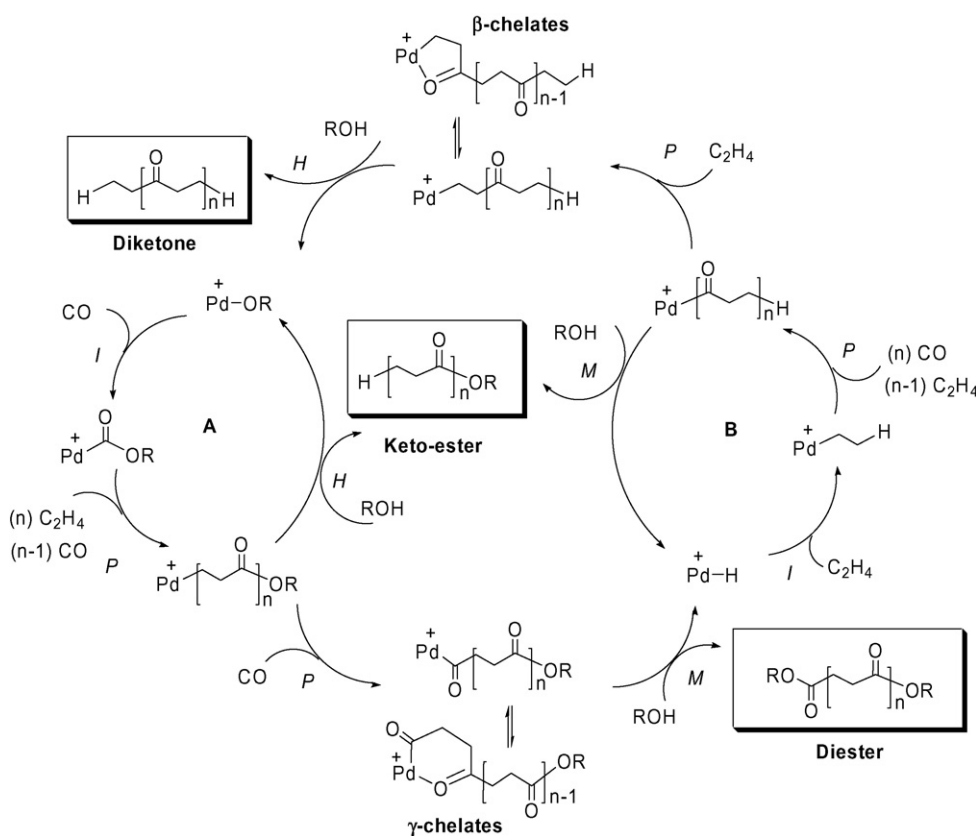
The mechanism of ethylene/CO copolymerization in aprotic solvents is essentially limited to cycle **B** in Scheme 2. The main differences from the reactions in alcohols are constituted by the precursors, that contain already an alkyl ligand to initiate the copolymerization, and by the termination step involving β-H elimination, unless water or a protic acid is present in the reaction in which case protonolysis may also occur. The presence of

water in the organic solvent, even in very low concentration, may lead to chain transfer by protonolysis with formation of mononuclear hydroxo complexes that may convert to μ-OH binuclear species, which, depending on the chelating ligand, may be dead-end for catalysis or resting states capable of re-initiating the copolymerization process [3].

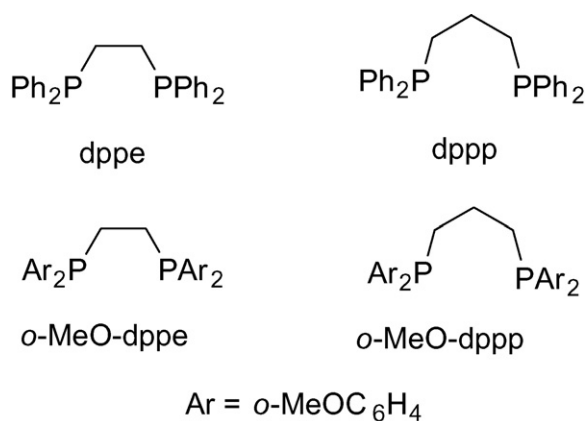
A major drawback to the large scale commercialization of alt-E-CO materials is provided by the low catalytic productivity which seldom exceeds 20–30 kg polyketone (g Pd × h)^{−1}. The productivity is particularly low for low molecular weight materials such as *Carilite*. Studies aimed at improving the 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 stabilizing mononuclear palladium(II) under the copolymerization 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 [4]. Two such ligands are shown in Scheme 3 together with their unsubstituted counterparts.

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 [5a], increased basicity of the metal center [5b], reduced stability of relevant catalyst resting states such as β-keto alkyl chelates [5c].



Scheme 2.



Scheme 3.

Besides the *P*-aryl substituents, the productivity of palladium(II) copolymerization catalysts is affected remarkably by the reaction media as well as by added co-reagents. The latter include protic acid and organic oxidants [1], 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 *ortho*-methoxy groups [2].

Despite the undoubted qualities of *ortho*-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 Pd^{II} salts, to copolymerize ethylene and CO in reaction media other than MeOH or water.

In this paper, we report a new synthetic protocol to 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp), the synthesis and characterization of various Pd^{II} neutral and cationic catalyst precursors and their use to catalyze the CO/C₂H₄ copolymerization in five different solvents: MeOH, TFE, water–AcOH mixtures, CH₂Cl₂, and toluene. For comparative purposes all catalytic reactions have been also performed with the classical ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylphosphino)propane (dppp) (Scheme 3). *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 rationalize the observed productivity.

2. Experimental

2.1. Materials and equipments

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. PdCl₂(COD) [6a] PdCl(Me)(COD) (COD: cycloocta-

1,5-diene) [6b], PdCl₂(dppe) (1a) [7], PdCl₂(dppp) (2a) [7], [Pd(H₂O)(dppp)](OTs)₂ (OTs = *p*-toluenesulfonate, 2b) [8], PdCl(Me)(dppe) (1c) [3a], PdCl(Me)(dppp) (2c) [3b] and NaBAr'₄ (Ar' = 3,5-(CF₃)₂-C₆H₃) [9] were prepared according to literature methods. Solid MAO (methylaluminoxane) for the copolymerization reaction was prepared by removing toluene and AlMe₃ under vacuum from a commercially available MAO solution (10 wt.% in toluene, Crompton Corp.) [10]. All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerization 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 (30 m, 0.25 mm i.d., 0.25 μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ¹H, ¹³C{¹H}, ³¹P{¹H} NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz, respectively). Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (¹H and ¹³C NMR) or 85% H₃PO₄ (³¹P NMR). High-pressure NMR (HPNMR) experiments were carried out on Bruker ACP 200 spectrometer using a 10 mm HPNMR tube (Saphikon (Milford, NH) sapphire tube; titanium high-pressure charging head constructed at the ICCOM-CNR) [11]. 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 [12]. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin-Elmer).

2.2. Syntheses

2.2.1. 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 [13a] (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 dropwise to this suspension that became almost colorless. 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. Recrystallization from CH₂Cl₂/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. Yield: 1.66 g (78%). Anal. Calcd. for C₃₀H₃₂O₄P₂: C, 69.49; H, 6.22. Found: C, 69.46; H, 6.24. ³¹P{¹H} NMR (δ, 81.01 MHz, CDCl₃, 21 °C) −30.80 (s). ¹H NMR (δ, 200.13 MHz, CDCl₃, 21 °C) 2.20 (t, ²J_{HP} = 3.7 Hz, 4H, PCH₂), 3.75 (s, 12H, OCH₃), 6.80–7.35 (m, 16H, Ar).

o-MeO-dppp. Yield: 1.48 g (68%). Anal. Calcd. for C₃₁H₃₄O₄P₂: C, 69.92; H, 6.44. Found: C, 69.94; H, 6.47. ³¹P{¹H} NMR (δ, 81.01 MHz, CDCl₃, 21 °C) −36.7 (s). ¹H NMR (δ, 200.13 MHz, CDCl₃, 21 °C) 1.73 (br s, 2H, CH₂), 2.23 (m, 4H, PCH₂), 3.80 (m, 12H, OCH₃), 6.79–7.05 (m, 16H, Ar).

2.2.2. Preparation of PdCl₂(*o*-MeO-dppe) (**3a**) and PdCl₂(*o*-MeO-dppp) (**4a**)

A solid sample of PdCl₂(COD) (57.10 mg, 0.20 mmol) was added to a stirred solution of the appropriate diphosphine ligand (0.20 mmol) in CH₂Cl₂ (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/diethyl ether (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.

3a. Yield: 102.94 mg (74%). Anal. Calcd. for C₃₀H₃₂Cl₂O₄P₂Pd: C, 51.78; H, 4.64. Found: C, 51.65; H, 4.60. ³¹P{¹H} NMR (δ, 81.01 MHz, CD₂Cl₂, 21 °C) 69.02 (s). ¹H NMR (δ, 200.13 MHz, CD₂Cl₂, 21 °C) 2.78 (m, 4H, PCH₂), 3.61 (s, 12H, OCH₃), 6.96–7.95 (m, 16H, Ar). ³¹P{¹H} NMR (δ, 161.98 MHz, CD₂Cl₂, −80 °C) 68.97 (s). ¹H NMR (δ, 400.13 MHz, CD₂Cl₂, −80 °C) 3.00 (m, 4H, PCH₂), 3.42 (s, 6H, Ar_(ax)-*o*-OCH₃), 3.75 (s, 6H, Ar_(eq)-*o*-OCH₃), 6.81–8.81 (m, 14H, Ar), 8.85 (m, 2H, Ar_(eq)-*o*-H).

4a. Yield: 116.36 mg (82%). Anal. Calcd. for C₃₁H₃₄Cl₂O₄P₂Pd: C, 52.45; H, 4.83. Found: C, 52.48; H, 4.86. ³¹P{¹H} NMR (δ, 81.01 MHz, CD₂Cl₂, 21 °C) 16.30 (s). ¹H NMR (δ, 200.13 MHz, CD₂Cl₂, 21 °C) 1.90 (m, 2H, CH₂), 2.50 (m, 4H, PCH₂), 3.75 (s, 12H, OCH₃), 6.97–7.60 (m, 16H, Ar). ³¹P{¹H} NMR (δ, 161.98 MHz, CD₂Cl₂, −80 °C) 17.63 (s). ¹H NMR (δ, 400.13 MHz, CD₂Cl₂, −80 °C) 1.92 (m, 2H, CH₂), 2.45 (m, 4H, PCH₂), 3.68 (s, 6H, Ar_(ax)-*o*-OCH₃), 3.73 (s, 6H, Ar_(eq)-*o*-OCH₃), 6.82–8.92 (m, 14H, Ar), 8.95 (dd, ³J_{HP} = 16 Hz, ³J_{HH} = 7 Hz, 2H, Ar_(ax)-*o*-H).

2.2.3. Preparation of [Pd(OTs)(H₂O)(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 CH₂Cl₂ (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/diethyl ether (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. Yield: 145.30 mg (70%). Anal. Calcd. for C₄₀H₄₀O₇P₂S₂Pd: C, 55.55; H, 4.62. Found: C, 55.40; H, 4.53. Λ_M (nitroethane, 26 °C): 65 Ω^{−1} cm² mol^{−1}. ³¹P{¹H} NMR (δ, 81.01 MHz, CDCl₃, 21 °C) 71.01 (s). ¹H NMR (δ, 200.13 MHz,

CDCl₃, 21 °C) 2.27 (s, 6H, OTs-CH₃), 2.69 (m, 4H, CH₂), 5.15 (br s, 2H, H₂O), 6.90–7.79 (m, 28H, Ar).

2.2.4. Preparation of [Pd(H₂O)₂(*o*-MeO-dppe)](OTs)₂ (**3b**) and [Pd(H₂O)₂(MeO-dppp)](OTs)₂ (**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 CH₂Cl₂ (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/diethyl ether (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.

3b. Yield: 145.61 mg (66%). Anal. Calcd. for C₄₄H₅₀O₁₂P₂S₂Pd: C, 52.70; H, 4.98. Found: C, 52.50; H, 4.60. Λ_M (nitroethane, 26 °C): 98 Ω^{−1} cm² mol^{−1}. ³¹P{¹H} NMR (δ, 161.98 MHz, CD₂Cl₂, 21 °C) 69.73 (s). ¹H NMR (δ, 400.13 MHz, CD₂Cl₂, 21 °C) 2.29 (s, 6H, OTs-CH₃), 2.78 (m, 4H, PCH₂), 3.66 (s, 12H, OCH₃), 4.43 (br s, 4H, H₂O), 6.97–7.59 (m, 24H, Ar).

4b. Yield: 190.15 mg (85%). Anal. Calcd. for C₄₅H₅₂O₁₂P₂S₂Pd: C, 53.12; H, 5.15. Found: C, 53.14; H, 5.18. Λ_M (nitroethane, 26 °C): 100 Ω^{−1} cm² mol^{−1}. ³¹P{¹H} NMR (δ, 161.98 MHz, CD₂Cl₂, 21 °C) 13.72 (s). ¹H NMR (δ, 400.13 MHz, CD₂Cl₂, 21 °C) 2.27 (m, 2H, CH₂), 2.34 (s, 6H, OTs-CH₃), 2.75 (m, 4H, PCH₂), 4.05 (s, 16H, OCH₃ + H₂O), 6.90–7.60 (m, 24H, Ar). ³¹P{¹H} NMR (δ, 161.98 MHz, CD₂Cl₂, −80 °C) −4.46 (s). ¹H NMR (δ, 400.13 MHz, CD₂Cl₂, −80 °C) 2.31 (s, 6H, OTs-CH₃), 2.35 (m, 2H, CH₂), 3.02 (m, 4H, PCH₂), 3.97 (s, 6H, Ar_(ax)-*o*-OCH₃), 4.33 (s, 6H, Ar_(eq)-*o*-OCH₃), 6.4–7.8 (m, 24H, Ar), the water resonance was not detected.

2.2.5. 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 (0.20 mmol) in CH₂Cl₂ (20 mL) at room temperature. After 1 h, the resulting colorless solution was concentrated to ca. 5 mL under reduced pressure. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethyl ether (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.

3c. Yield: 105.31 mg (78%). Anal. Calcd. for C₃₁H₃₅ClO₄P₂Pd: C, 55.13; H, 5.22. Found: C, 55.09; H, 5.24. ³¹P{¹H} NMR (δ, 161.98 MHz, CDCl₃, 21 °C) 61.09 (d, ²J_{PP} = 22.0 Hz), 39.07 (d). ¹H NMR (δ, 200.13 MHz, CDCl₃, 21 °C) 0.40 (dd, ³J_{HPtrans} = 8.0 Hz, ³J_{HPcis} = 3.2 Hz, 3H, PdCH₃), 2.19–2.93 (m, 4H, CH₂), 3.59 (s, 6H, OCH₃), 3.60 (s, 6H, OCH₃), 6.87–7.91 (m, 16H, Ar).

4c. Yield: 91.92 mg (67%). Anal. Calcd. for C₃₂H₃₇ClO₄P₂Pd: C, 55.75; H, 5.41. Found: C, 55.74; H, 5.43. ³¹P{¹H} NMR (δ, 81.01 MHz, CDCl₃, 21 °C) 30.80 (d, ²J_{PP} = 52.5 Hz), −0.56 (d). ¹H NMR (δ, 200.13 MHz, CDCl₃, 21 °C) 0.32 (dd, ³J_{HPtrans} = 7.9 Hz, ³J_{HPcis} = 3.5 Hz, PdCH₃), 1.92 (m, 2H, CH₂),

2.43 (m, 2H, PCH₂), 2.57 (m, 2H, PCH₂), 3.66 (s, 6H, OCH₃), 3.76 (s, 6H, OCH₃), 6.87–7.58 (m, 16H, Ar).

2.3. Crystallography

Suitable crystals of **3a**·2.3·CH₂Cl₂ and **4a** for single crystal X-ray structure analysis were obtained by slow diffusion of toluene into a saturated CH₂Cl₂ solution of either **3a** or **4a**. X-ray diffraction intensity data were collected on an Oxford Diffraction CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using ω -scans. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS [14a]. All structure determination calculations were performed with the WINGX package [14b] with SIR-97 [14c], SHELXL-97 [14d] and ORTEP-3 programs [14e]. 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_{eq} of the adjacent carbon atoms. Crystallographic data (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre. CCDC-603822 (**3a**·2.3·CH₂Cl₂); CCDC-603821 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

2.4. NMR studies

2.4.1. Variable-temperature ¹H and ³¹P{¹H} NMR studies of **3a**, **4a**, and **4b** in CD₂Cl₂

A solution of the appropriate complex (0.015 mmol) in CD₂Cl₂ (0.8 mL) was transferred under nitrogen into a 5 mm NMR tube, which was placed into a NMR probe at 20 °C. ¹H and ³¹P{¹H} NMR spectra were acquired every 10 °C in the temperature range from 20 to –80 °C.

2.4.2. In situ HPNMR studies of the CO-ethylene copolymerization with **2b** and **4b** as catalyst precursors in CD₂Cl₂/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 CD₂Cl₂/TFE (2 mL) under nitrogen at room temperature and then placed into a NMR probe at 20 °C. ³¹P{¹H} and ¹³C{¹H} 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 ¹³CO/¹²CO to 20 bar and then with ethylene to 40 bar.

2.4.3. Operando HPNMR studies of the CO-ethylene copolymerization with **2b** and **4b** as catalyst precursors in either CD₂Cl₂/TFE or MeOH-*d*₄

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 CD₂Cl₂/TFE or MeOH-*d*₄ (2 mL) under nitrogen at room temperature and then placed into a NMR probe at 20 °C. After ³¹P{¹H} and ¹H (only for the study in MeOH-*d*₄) 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 colorless solution.

2.5. Catalytic reactions

2.5.1. Catalytic reactions in MeOH (or TFE) with **1b–4b** as catalyst precursors

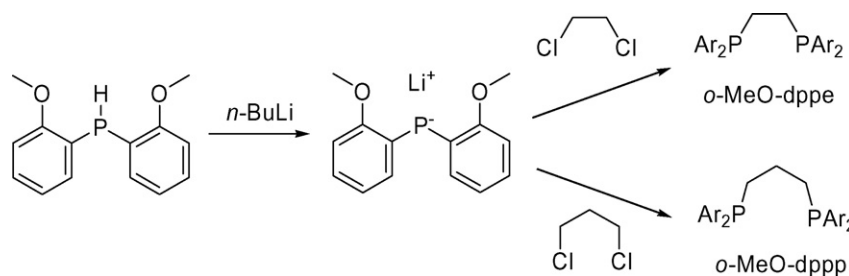
Typically, MeOH (or TFE, 100 mL), was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.0048 mmol). When the catalytic reactions were performed with additives such as *p*-toluenesulfonic acid monohydrate (TsOH) and 1,4-benzoquinone (BQ), they were added together with the catalyst precursor into the autoclave. The autoclave was charged with a 1:1 CO/C₂H₄ 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 solubilizing capacity of TFE for the alt-E-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 analyzed by GC/MS.

2.5.2. 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/C₂H₄ 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%.

2.5.3. Catalytic reactions in CH₂Cl₂ with **1c–4c** as catalyst precursors

CH₂Cl₂ (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously



Scheme 4.

evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol) and NaBAR'_4 (0.012 mmol). The autoclave was charged with a 1:1 $\text{CO}/\text{C}_2\text{H}_4$ 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_2Cl_2 , and dried under vacuum at 60°C to constant weight.

2.5.4. 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 $\text{CO}/\text{C}_2\text{H}_4$ 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.

2.6. Characterization of the alt-E-CO copolymers obtained in TFE

Polyketone products were analyzed by IR, ^1H 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- $d_2/\text{C}_6\text{H}_6-d_6$ showing a perfectly alternating structure. All of the 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) \gg vinyl-ester (VE) > vinyl-ketone (VK). The number-average molecular weight (M_n) of the copolymers was determined by ^1H NMR spectroscopy. NMR and IR data for a representative example are reported below: ^1H NMR (δ , 400.13 MHz, 21°C) 0.93 (t, $^3J_{\text{HH}} = 7.4$ Hz, $\text{C}(\text{O})\text{CH}_2\text{CH}_3$), 2.17 (q, $^3J_{\text{HH}} = 7.4$ Hz, $\text{C}(\text{O})\text{CH}_2\text{CH}_3$), 2.51 (br s, $\text{CH}_2\text{C}(\text{O})\text{CH}_2$), 4.25 (q, $^3J_{\text{HF}} = 8.0$ Hz, $\text{C}(\text{O})\text{OCH}_2\text{CF}_3$), 5.68 (m, $\text{C}(\text{O})\text{CH}=\text{CH}_2$), 6.06 (m, $\text{C}(\text{O})\text{CH}=\text{CHH}'$), 6.15 (m, $\text{C}(\text{O})\text{CH}=\text{CHH}'$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , 100.62 MHz, 21°C) 6.94 ($\text{C}(\text{O})\text{CH}_2\text{CH}_3$), 26.80 ($\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CF}_3$), 35.04 ($\text{CH}_2\text{C}(\text{O})\text{CH}_2$), 60.27 ($^2J_{\text{CF}} = 35.9$ Hz, $\text{C}(\text{O})\text{OCH}_2\text{CF}_3$),

124.10 ($^1J_{\text{CF}} = 283.6$ Hz, $\text{C}(\text{O})\text{OCH}_2\text{CF}_3$), 172.14 ($\text{C}(\text{O})\text{OCH}_2\text{CF}_3$), 209.85 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CF}_3$), 210.90 ($\text{CH}_2\text{C}(\text{O})\text{CH}_2$), 214.32 ($\text{C}(\text{O})\text{CH}_2\text{CH}_3$). The vinyl resonances were not assigned as obscured by other carbons. IR (KBr pellets, cm^{-1}): 3392 (w), 2912 (m), 1695 (vs), 1407 (s), 1332 (s), 1259 (m), 1165 (m), 1055 (s), 809 (m), 592 (m).

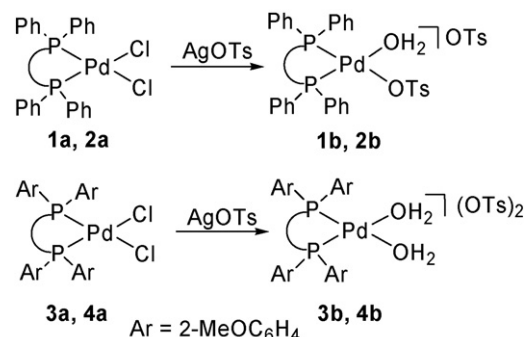
3. Results and discussion

3.1. Synthesis of ligands and complexes

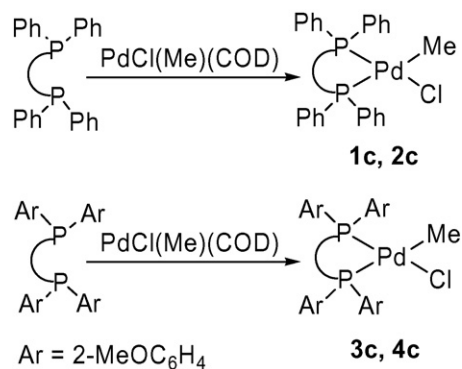
The known diphosphines *o*-MeO-dppe [15a,b] and *o*-MeO-dppp [15c] were prepared by a new synthetic route, illustrated in Scheme 4, which is simpler and more efficient as compared with the procedures reported in the literature.

The new synthetic protocol involves the deprotonation of the stable and isolable secondary phosphine bis(2-methoxyphenyl)phosphine [13a] with 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 $\text{PdCl}_2(\text{COD})$ in CH_2Cl_2 gave the complexes $\text{PdCl}_2(o\text{-MeO-dppe})$ (**3a**) and $\text{PdCl}_2(o\text{-MeO-dppp})$ (**4a**) as yellow crystalline compounds, which were characterized 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 5). The authentication of these complexes was achieved in solution by multinuclear NMR spectroscopy where both complexes behave as 1:2 electrolytes (conduc-



Scheme 5.



Scheme 6.

tivity measurements in nitroethane). Notably, the known and isostructural compounds [Pd(OTs)(H₂O)(dppe)]OTs (**1b**) and [Pd(OTs)(H₂O)(dppp)]OTs (**2b**) (Scheme 5) behave as 1:1 electrolytes in the same solvent, which is consistent with the coordination of a tosylate ion to palladium.

The neutral complexes PdCl(Me)(P–P) (P–P = *o*-MeO-dppe, **3c**; *o*-MeO-dppp, **4c**) were prepared by the plain reaction of the appropriate ligand with PdCl(Me)(COD) in CH₂Cl₂ in good yield (78%, **3c**; 68%, **4c**) (Scheme 6).

3.2. Crystal structure determinations of **3a**·2.3·CH₂Cl₂ and **4a**

Single crystals of **3a**·2.3·CH₂Cl₂ and **4a** were obtained by slow diffusion of *n*-hexane into CH₂Cl₂ solutions of **3a** and **4a**. Crystal data and selected distances and angles for both compounds are reported in Tables 1 and 2, respectively. An ORTEP drawing of the two complexes is shown in Fig. 1.

The crystal structure of **3a**·2.3·CH₂Cl₂ shows half molecule of **3a** and 1.15 molecules of disordered CH₂Cl₂ per asymmetric unit. The palladium centre is square planarly coordinated with *cis* phosphorus atoms. 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** [7]. 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

Table 1
Summary of crystallographic data

	Compound	
	3a ·2.3·CH ₂ Cl ₂	4a
Empirical formula	C _{32.20} H _{36.60} Cl _{6.60} O ₄ P ₂ Pd	C ₃₁ H ₃₄ Cl ₂ O ₄ P ₂ 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	C2/c	Pcca
Unit cell dimensions		
<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)
α (°)	90.00	90.00
β (°)	97.655(5)	90.00
γ (°)	90.00	90.00
Volume (Å ³)	3996(2)	3157.7(14)
Z	4	4
ρ_{calc} (g cm ⁻³)	1.481	1.493
μ (Mo K α) (mm ⁻¹)	1.019	0.892
<i>F</i> (0 0 0)	1802.4	1448
Crystal size (mm)	0.22 × 0.05 × 0.02	0.25 × 0.20 × 0.18
Θ range (°)	4.10–25.00	2.77–25.00
Index ranges	–23 ≤ <i>h</i> ≤ 23, –14 ≤ <i>k</i> ≤ 14, –19 ≤ <i>l</i> ≤ 19	0 ≤ <i>h</i> ≤ 27, 0 ≤ <i>k</i> ≤ 10, 0 ≤ <i>l</i> ≤ 17
Reflections collected	3464	2759
Independent reflections	2912	2759
Refined parameters	212	186
<i>R</i> 1 (2 σ (<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> ²	1.167	1.015
Largest diff. peak and hole (eÅ ⁻³)	1.005/–0.834	0.414/–0.480

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 *ortho*-methoxy groups. In contrast, the *ortho*-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

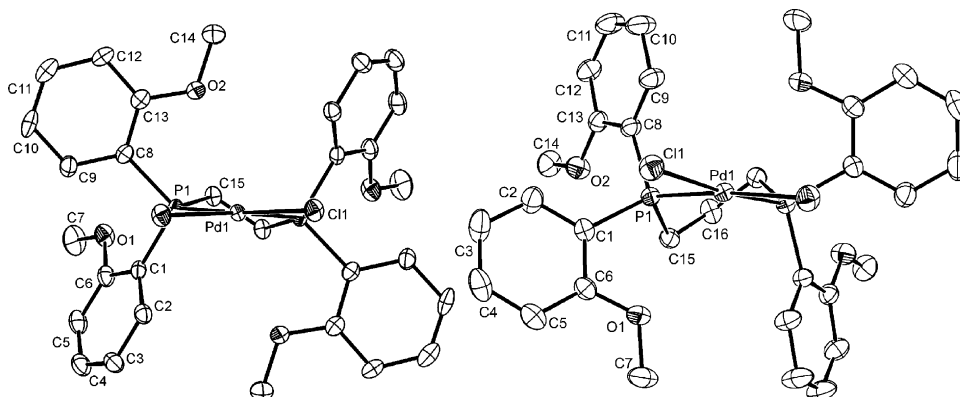


Fig. 1. ORTEP plot of **3a**·2.3·CH₂Cl₂ (left) and **4a** (right). Solvent molecules and hydrogen atoms are omitted for clarity. Only the asymmetric unit of each molecule is labelled. Thermal ellipsoids are shown at the 30% probability level.

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

Complex	3a 2.3-CH ₂ Cl ₂	4a
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 ^a	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 ^a	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

^a Symmetry transformation used to generate equivalent atoms: $-x+1, y, -z+1/2$.

were already observed for the related complex NiI₂(*o*-MeO-dppe) [5a].

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)° is comparable to that found for the related dppe complex **2a** of 90.58(5)° [7]. 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 [7]. The major difference between **4a** and **2a** is provided by the conformation of the six-membered PdP₂C₃ 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-CH₂Cl₂, **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 NiCl₂(*o*-MeO-dppp) [16].

The short Pd ⋯ H intramolecular interactions observed in the structures of both **3a**·2.3-CH₂Cl₂ and **4a** have been found to persist in solution as shown by ¹H NMR spectroscopy (see below).

3.3. Variable-temperature NMR studies of **3a**, **4a**, and **4b** in CD₂Cl₂

In an attempt of elucidating the solution structure of the palladium(II) complexes with the *ortho*-methoxy ligands *o*-MeO-dppe and *o*-MeO-dppp, ³¹P{¹H} and ¹H NMR studies were carried out on CD₂Cl₂ solutions of **3a**, **4a**, and **4b** in the temperature range from 20 to –80 °C.

Complexes **3a** and **4a** exhibit fluxional behavior on the NMR time-scale. The ¹H NMR spectrum at 20 °C of either complex displayed one set of resonances for the aryl hydrogens (δ 6.96–7.95 and 6.97–7.60, respectively) and one singlet for the methoxy groups (δ 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 ¹H NMR spectra of **3a** and **4a** contained a couple of singlets at δ 3.75 and 3.42 and δ 3.73 and 3.68 for the methoxy groups, respectively. This pattern can

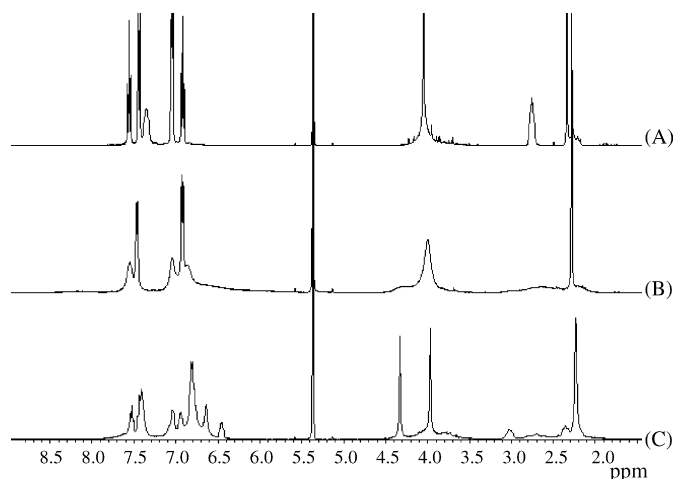


Fig. 2. Variable-temperature ¹H NMR study of **4b** (CD₂Cl₂, 400.13 MHz): (A) 20 °C; (B) –40 °C; (C) –80 °C.

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-CH₂Cl₂ and **4a**. Notably, the ¹H NMR spectra of **3a** and **4a** at –80 °C showed a significant downfield shift of the resonances of two aryl hydrogens (δ 8.85 and 8.95, respectively), which suggests that the interactions between the *ortho*-hydrogen atoms of the aryl groups and the metal centre, observed in the crystal structures of **3a**·2.3-CH₂Cl₂ and **4a**, are maintained in solution [17]. An analogous fluxional behavior has been reported for NiCl₂(*o*-MeO-dppp) whose crystal structure closely resembles those of **3a**·2.3-CH₂Cl₂ and **4a** [16].

Like the bis-chloride complexes **3a** and **4a**, the tosylate complex **4b** is fluxional in CD₂Cl₂ solution at room temperature due to the exchange of equatorial and axial aryl groups. The temperature-dependent ¹H NMR spectra of **4b** are reported in Fig. 2. Analogously to **3a** and **4a**, the spectrum at 20 °C (trace A) showed a singlet at δ 4.05 which resolved at –80 °C into two singlets at δ 3.97 (equatorial) and 4.32 (axial) (trace C). Unlike **3a** and **4a**, the ¹H NMR spectrum of **4b** at –80 °C contained no downfield shifted resonance, consistent with no interaction between the metal centre and the *ortho*-hydrogen atoms of the aryl groups.

The NMR pattern observed for **4b** is in perfect agreement with that exhibited by the nickel derivative [Ni(H₂O)₂(*o*-MeO-dppp)](PF₆)₂ whose X-ray crystal structure analysis revealed the absence of any interaction between nickel and the *ortho*-hydrogen with all four *ortho*-methoxy groups pointing towards palladium [16]. It is therefore most likely that **4b** and [Ni(H₂O)₂(*o*-MeO-dppp)](PF₆)₂ adopt the same structure in both the solid state and solution.

The ³¹P{¹H} NMR spectra of **3a**, **4a**, and **4b** at 20 °C consist of a single relatively sharp resonance at δ 69.02, 16.30, and 13.72, respectively. A sharp resonance was also observed at –80 °C for **3a** (δ 68.97) and **4a** (δ 17.63), while the spectrum of **4b** showed a quite different behavior with the temperature (Fig. 3).

At –80 °C the initial ³¹P{¹H} NMR singlet splits into two major resonances at δ –4.46 and 22.78 in a 5:1 ratio (trace C).

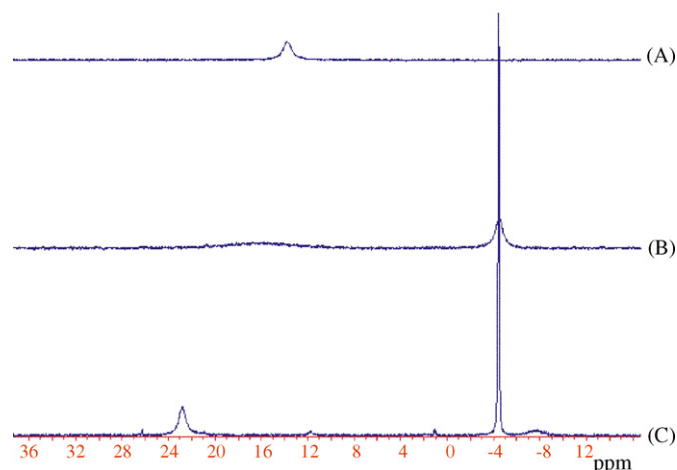


Fig. 3. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR study of **4b** (CD_2Cl_2 , 400.13 MHz): (A) 20 °C; (B) -40 °C; (C) -80 °C.

Two low-intensity humps at ca. -7.8 and 11.8 ppm were also observed. The chemical shifts of these 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.

3.4. Catalytic copolymerization of CO and ethylene

Both neutral and cationic Pd^{II} complexes, either with the *ortho*-methoxy modified ligands *o*-MeO-dppe and *o*-MeO-dppp or with the unmodified ligands dppe and dppp, were employed to catalyze CO-ethylene copolymerization reactions in five different solvents: MeOH, TFE, water-vents were performed at 85 °C and with a 1:1 $\text{CO}/\text{C}_2\text{H}_4$ pressure of 40 bar. Lower temperatures (50–60 °C) were used for the reactions in aprotic solvents. No optimization of the catalytic activity was attempted. The results obtained are summarized in Table 3.

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) [18].

The different catalytic activities exhibited by the palladium precursors with diphosphine chelating ligands bearing CH_2 spacers between the phosphorus donor atoms have been subject of many studies [3,19]. According to several authors, the $\text{Pd}(\text{P}-\text{P})$ chelate ring is the main factor that effectively controls the catalytic activity [1]. In particular, the formation of a more stable β -keto alkyl metallacycle, involving intramolecular interaction between the β carbonyl group of the propagating chain and the palladium center (see Scheme 7) has been suggested to account for the lower activity of the dppe-like catalysts as com-

Table 3
Productivities ($\text{kg alt-E-CO} (\text{g Pd} \times \text{h})^{-1}$) and M_n (kg mol^{-1}) in the CO/ethylene copolymerization reactions catalyzed by Pd^{II} -diphosphine precursors in different solvents

Precursor (solvent)	$[\text{Pd}(\text{H}_2\text{O})_2-\text{x}(\text{OTf})_x(\text{P}-\text{P})](\text{OTf})_{2-\text{x}}$ (1b-4b) ^a		$[\text{Pd}(\text{H}_2\text{O})_2-\text{x}(\text{OTf})_x(\text{P}-\text{P})](\text{OTf})_{2-\text{x}}$ (1b-4b) ^c ($\text{CF}_3\text{CH}_2\text{OH}$)		$[\text{Pd}(\text{H}_2\text{O})_2-\text{x}(\text{OTf})_x(\text{P}-\text{P})](\text{OTf})_{2-\text{x}}$ (1a-4a) ^d ($\text{AcOH}/\text{H}_2\text{O}$ 75% mol)		$\text{PdCl}_2(\text{P}-\text{P})$ (1a-4a) ^e (CH_2Cl_2)		$\text{PdCl}(\text{Me})(\text{P}-\text{P})$ (1c-4c) ^f (toluene)	
	BQ (80 equiv.)	TsOH (2 equiv.)	TsOH (20 equiv.)	TsOH (20 equiv.)	TsOH (20 equiv.)	TsOH (20 equiv.)	TsOH (20 equiv.)	TsOH (20 equiv.)	NaBAI ₄ (1.5 equiv.)	MAO (100 equiv.)
Productivities										
dppe	0.30/2	0.4/-	0.8/0.3	1.9/1.7	-/-	3.5/2.8	3.3/-	0.8/0.4	-	-
dppp	3.5/2.5	4.1/-	4.2/4.0	4.4/4.4	6.2/-	15.9/13.6	15.6/-	5.6/4.5	0.1	0.1
<i>o</i> -OMe-dppe	12.4 ^a /9.6 ^b	17.4 ^b /-	10.8/8.2	8.9/7.2	-/-	2.1/1.9	2.7/-	8.9/5.5	2.9	0.4
<i>o</i> -OMe-dppp	13.6 ^b /13.2 ^b	18.1 ^b /-	11.0/7.8	9.1/6.6	11.2/-	3.0/2.6	2.0/-	9.1/6.0	5.1	0.5
M_n										
dppe	-	-	-	4.3	-	4.9	4.7	3.3	-	-
dppp	-	-	-	14.9	-	23.5	-	14.5	-	-
<i>o</i> -OMe-dppe	14.2	-	-	16.2	-	6.0	-	5.7	-	-
<i>o</i> -OMe-dppp	-	-	-	>35	-	29.4	-	>40	-	-

^a Reaction conditions: catalyst 0.0048 mmol, MeOH 100 mL, $\text{P}(\text{CO}/\text{C}_2\text{H}_4)$ 40 bar at 85 °C, 1 and 3 h, 1200 rpm.

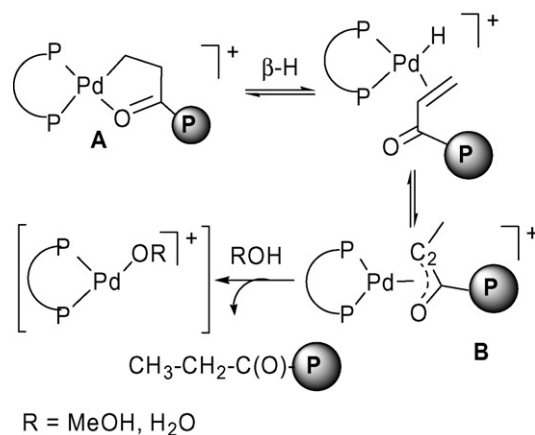
^b Catalyst 0.0024 mmol.

^c Reaction conditions: catalyst 0.0048 mmol, $\text{CF}_3\text{CH}_2\text{OH}$ 100 mL, $\text{P}(\text{CO}/\text{C}_2\text{H}_4)$ 40 bar at 85 °C, 1 and 3 h, 1200 rpm.

^d Reaction conditions: catalyst 0.0048 mmol, $\text{AcOH}/\text{H}_2\text{O}$ 75% mol 100 mL, $\text{P}(\text{CO}/\text{C}_2\text{H}_4)$ 40 bar at 85 °C, 1 and 2 h, 1200 rpm.

^e Reaction conditions: catalyst 0.010 mmol, CH_2Cl_2 75 mL, $\text{P}(\text{CO}/\text{C}_2\text{H}_4)$ 40 bar at 50 °C, 20 min, 1200 rpm.

^f Reaction conditions: catalyst 0.010 mmol, toluene 75 mL, $\text{P}(\text{CO}/\text{C}_2\text{H}_4)$ 40 bar at 60 °C, 2 h, 1200 rpm.



Scheme 7.

pared to the dppp-like ones [3a]. 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 stabilize, by virtue of the oxygen donor atoms, coordinatively unsaturated intermediates as well as destabilize the β -keto alkyl metallacycle favoring its opening by CO and thus speeding up the propagation process [4].

Protonolysis and/or β -hydride elimination are the unique or largely prevailing chain termination processes operative in the copolymerization reactions investigated in this work. Scheme 7 illustrates the generally accepted mechanism by which diphosphine palladium(II) propagating species undergo chain transfer mechanism [20]. This mechanism, experimentally demonstrated by van Leeuwen [20], involves an equilibrium between the β -keto alkyl metallacycle **A** and its enolate form **B**. However, since the overall protonolysis rate depends on the rate of the β -hydride elimination [20], the polyketone molecular weight is determined by the kinetics of the β -hydride elimination step: the lower the rate of the β -H elimination, the higher the molecular weight.

β -H elimination reactions involving organometallic complexes are steered by both electronic and steric factors [21]. In particular, it is agreed that the agostic interaction between the metal and a β -hydrogen (precursor to hydrogen transfer) is disfavored 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 β -hydrogen for interaction with the metal center [21]. 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 β -H elimination paths.

3.4.1. 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 catalyze the CO-ethylene copolymerization in MeOH with or without added *p*-toluenesulfonic acid (TsOH) and/or 1,4-benzoquinone (BQ). The latter oxidant is commonly used for the re-generation of

the catalytically active Pd^{II} species by oxidation of catalytically inactive Pd^I and Pd⁰ species, that may form under the reducing conditions of the copolymerization reactions. In turn, the protic acid serves to generate Pd–H moieties by oxidative addition to Pd⁰ species as well as to convert catalytically inactive μ -OH dimers (generated by adventitious moisture) into active mononuclear species [3]. Irrespective of the catalyst precursor employed, the alt-E-CO copolymers obtained in MeOH were featured by ketone and ester end groups in a 1:1 ratio, which is typical for CO-ethylene copolymerization in MeOH where initiation involves either Pd–OMe or Pd–H species and termination may occur via either protonolysis or methanolysis [1].

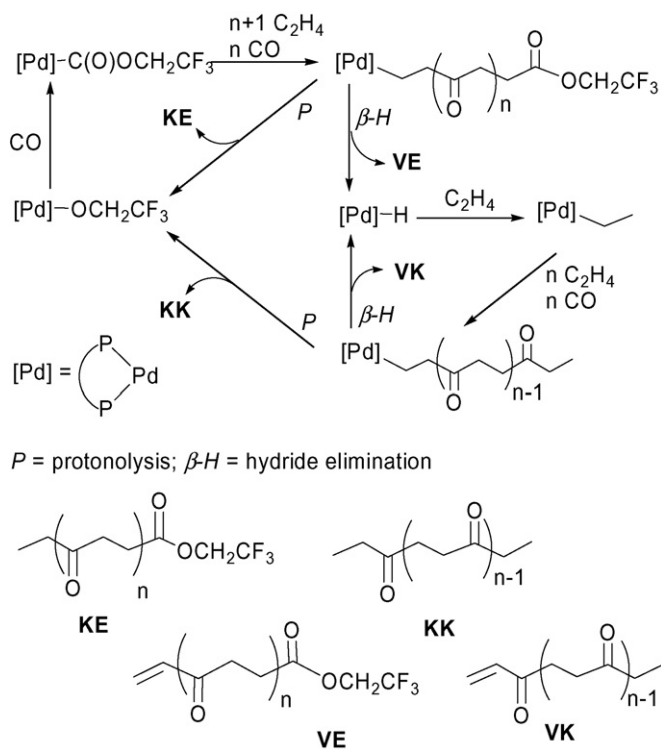
The highest productivities (up to 17–18 kg alt-E-CO (g Pd \times h)⁻¹) were obtained with the *o*-MeO catalyst precursors **3b** and **4b** without any acid co-catalyst and, under these conditions, the productivity gap between the *o*-MeO substituted catalysts and the unsubstituted congeners reached its maximum. Irrespective of catalyst and acidity of the reaction medium, a beneficial effect on the polymerization rate was produced by the addition of 80 equiv. of BQ. As an example, productivities of 18.1 versus 13.6 and 11.2 versus 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).

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 [22]. 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 [23]. 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.

A perusal of the data reported in Table 3 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-E-CO (g Pd \times h)⁻¹.

A ¹³C{¹H} and ¹H NMR analysis in 1,1,1,3,3,3-hexafluoroisopropanol-*d*₂/C₆H₆-*d*₆ of the products obtained with the catalysts based on C₂-bridged ligands showed the alt-E-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 [24], the only effective termination reactions in this solvent are β -hydride elimination and protonolysis [1]. 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 ¹H NMR integration of the corresponding signals, the ratios between vinyl, ester and ketone end groups have been



Scheme 8.

found to be 5:42:53 and <1:45:54 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^{-1} .

Based on the end groups analysis of the polyketone products as well as previous literature reports [24], a general catalytic mechanism for the CO/ethylene copolymerization in TFE is proposed in Scheme 8. Since the keto-ester copolymers are the dominant products, the most frequent initiator (>85%) should be Pd-OCH₂CF₃ and protonolysis the most effective termination path.

Operando and *in situ* HPNMR experiments were carried out using either **2b** or **4b** as catalyst precursor and ¹³C labeled CO as reagent in a 1:1 (v:v) mixture of CD₂Cl₂ 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 alkoxy carbonyl and/or carbonyl, whereas no intermediate species was intercepted with **2b**, only a very fluxional species being observed even at low temperature [25]. Although no clear-cut experimental evidence was actually obtained, the ¹³C labeling HPNMR experiments suggest that the *o*-OMe-dppp ligand favor 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.

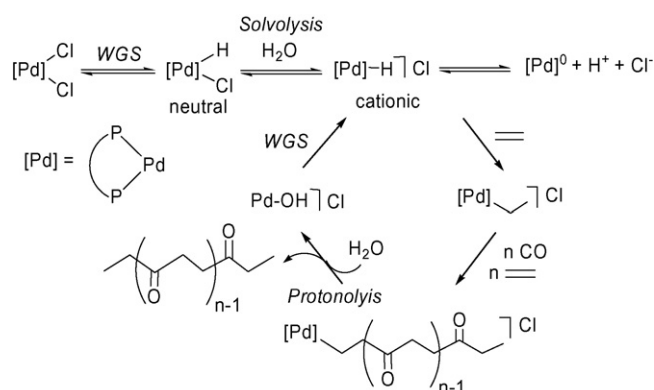
A largely positive influence of TFE on the CO/styrene copolymerization by palladium(II) catalysts has been previously demonstrated by Milani et al. and has been attributed to the stabilizing effect of TFE on important catalytic intermediates,

such as Pd-H species [24]. 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 [26]. 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, to a web of strong H-bond interactions [26]. 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 stabilization of intermediates, for example alkoxy carbonyl species.

3.4.2. CO-ethylene copolymerization 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-ethylene copolymerization in mixtures of water and AcOH with a water content ranging from 55 to 85 mol%. Irrespective of the catalyst precursor, the maximum of catalytic productivity was found using a water–AcOH mixture containing 75 mol% water. All of the alt-E-CO products obtained were exclusively featured by ketone end groups, which is consistent with the mechanism proposed for CO/ethylene copolymerizations catalyzed by PdCl₂(diphosphine) complexes in acidic aqueous media involving Pd-H initiators and chain termination by protonolysis (Scheme 9) [22,27].

The neutral Pd^{II}-H complexes shown in Scheme 9 are believed to be generated from the bis-chloride precursors by water gas shift (WGS), and then converted into the catalytically active cationic Pd^{II}-H species by a water-controlled solvolysis process [27a]. 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. On the other hand, a too large proportion of water has been found to have a detrimental effect on the solubility of CO and C₂H₄ [27]. In



Scheme 9.

the case at hand, 75 mol% water seems to be the best compromise between an efficient solvolysis process rate and an acceptable comonomer solubility. The chain-transfer reaction of CO/ethylene copolymerizations 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 [27].

3.4.3. CO-ethylene copolymerization reactions with the methyl complexes **1c–4c** as catalyst precursors in both CH_2Cl_2 and toluene

A few examples of palladium-catalyzed CO-ethylene copolymerization in aprotic solvents such as dichloromethane, THF or acetone have been reported so far [28]. Herrmann has reported the performance of monocationic palladacycles stabilized by dppe and dppp, while Barron has studied the influence of *tert*-butylaluminum cocatalysts on dppp modified catalysts [29]. Under these conditions, the only effective chain termination mechanism is β -H elimination to give high molecular weight copolymers with vinyl end groups.

The neutral methyl complexes $\text{PdCl}(\text{Me})(\text{P–P})$ **1c–4c** were scrutinized in either CH_2Cl_2 with NaBAR'_4 as activator at 50 °C or in toluene in the presence of MAO at 60 °C. No end-group could be seen by ^1H and ^{13}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_2Cl_2 at higher temperature (85 °C), which is consistent with the formation of Pd–H initiators and β -H transfer as termination path.

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^+ in aprotic solvents. The catalytic data of **1c** and **2c** in CH_2Cl_2 are comparable with those reported by Herrmann [28].

3.5. Operando and in situ HPNMR studies of the CO-ethylene copolymerization 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 HPNMR experiments were carried out in a 1:1 (v:v) mixture of $\text{CD}_2\text{Cl}_2/\text{TFE}$ employing **4b** as catalyst precursor. Selected $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are reported in Fig. 4. Pressurizing the NMR tube with 20 bar CO converted **4b** (δ 19.0 in trace A) into a species featured by a broad signal centered at δ 16.5 (trace B). The line-shape of the latter resonance suggests that the carbonylation of **4b** is accompanied by a fluxional processes. Pressurizing the tube with ethylene to 40 bar led to the formation of polyketone product while the broad signal moved to ca. δ 14 (trace C). Upon heating, first to 50 °C and then to 85 °C, the signal narrowed and shifted to ca. δ 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).

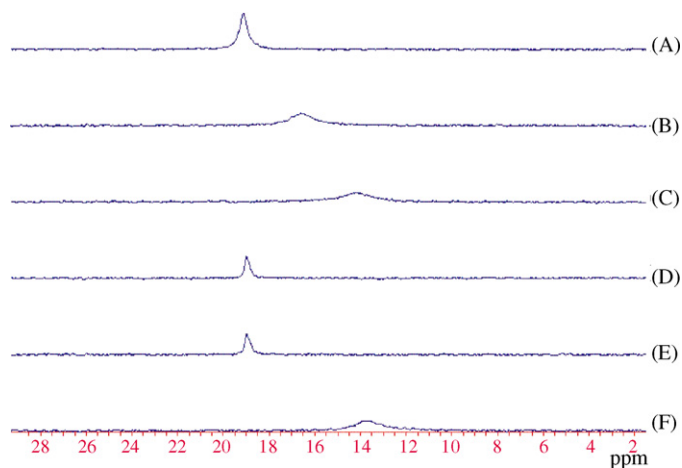


Fig. 4. Operando $^{31}\text{P}\{^1\text{H}\}$ HPNMR study (sapphire tube, 1:1, v:v $\text{CD}_2\text{Cl}_2/\text{TFE}$, 81.01 MHz) of the CO-ethylene copolymerization catalyzed by **4b**: (A) under nitrogen at room temperature; (B) under 20 bar of CO at room temperature; (C) under 40 bar of 1:1 CO/ethylene at room temperature; (D) at 50 °C; (E) at 85 °C; (F) after the sapphire tube was cooled to room temperature.

In line with previously reported studies of CO-ethylene copolymerization by palladium complexes stabilized by dppp-like diphosphines, the resonances shown in traces C–F are attributed to a catalyst resting state containing “Pd(P–P) $^{2+}$ ” moieties stabilized by OTs $^-$ ligands, eventually in rapid exchange with solvent molecules and/or monomers [1,19a]. In analogous operando HPNMR experiments carried either in $\text{CD}_2\text{Cl}_2/\text{TFE}$ with the catalyst precursor **2b** or in $\text{MeOH-}d_4$ 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 Fig. 4 forms only when the reaction is performed in TFE and the catalyst is modified with a diphosphine ligand containing OMe-aryl substituents.

In an attempt of elucidating the structure of the species formed by carbonylation of **4b** (trace B in Fig. 4), 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}C labeled CO. A selected sequence of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra is presented in Fig. 5. Traces A (singlet at δ 19.0) and B (broad resonance at ca. δ 3.0) are consistent with **4b** being in axial/equatorial aryl conformational exchange (see the NMR study in Section 3.3). 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 centered at δ 16.5 at 20 °C, analogous to that reported in trace B of Fig. 4, which resolved at –40 °C into at least three broad resonances at ca. δ 7, –16, and –20 (trace C). A quite similar NMR picture was observed at –40 °C when the tube was pressurized with 20 bar ethylene (trace D).

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the latter reaction mixture were acquired at different temperatures. At room temperature, a rather broad resonance centered at ca. δ 186 was observed, which resolved at low temperature into several resonances between δ 187 and 185. The spectrum at –80 °C is shown in Fig. 6. Apart from the sharp signal at δ 186.7 of free CO, no clear cut assignment of the other resonances was possible due to the broadness of

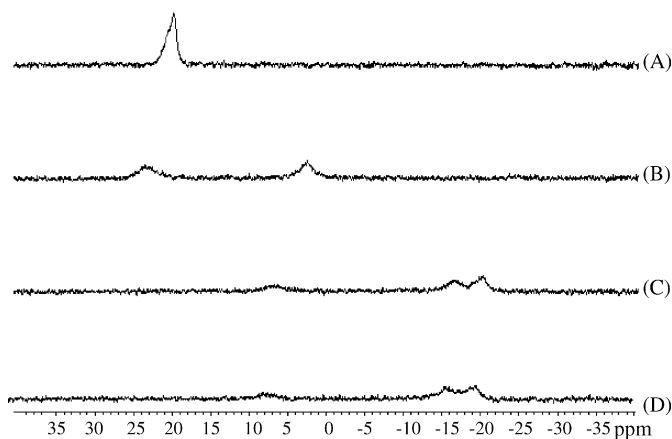


Fig. 5. *In situ* $^{31}\text{P}\{^1\text{H}\}$ NMR study (sapphire tube, 1:1, v:v $\text{CD}_2\text{Cl}_2/\text{TFE}$, 81.01 MHz) of the CO/ethylene copolymerization catalyzed by **4b**: (A) under nitrogen at room temperature; (B) under nitrogen at -40°C ; (C) under 20 bar of 1:19 $^{13}\text{C}/^{12}\text{C}$ at -40°C ; (D) under 20 bar of 1:19 $^{13}\text{C}/^{12}\text{C}$ and 20 bar of ethylene at -40°C .

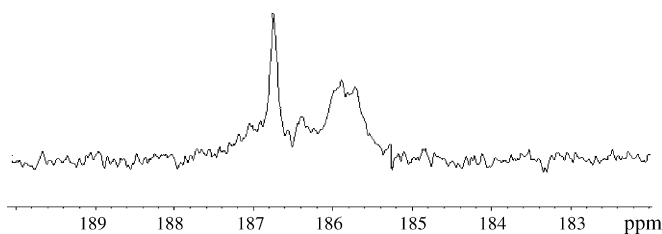


Fig. 6. High-pressure $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4b** under 20 bar of 1:19 $^{13}\text{C}/^{12}\text{C}$ at -80°C .

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 alkoxy-carbonyl ligands. 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 [25a] with the dppp-modified catalysts, which is consistent with its much higher activity.

4. Conclusions

The results obtained in this work confirm that, irrespective of the reaction medium, the palladium(II) catalysts based on dppp-like chelating diphosphines give higher productivities as well as higher molecular weight polyketones as compared to the dppe-like counterparts (i.e., $\text{dppp} > \text{dppe}$ and $o\text{-MeO-dppp} > o\text{-MeO-dppe}$). Except for the reactions performed in TFE, the *ortho*-methoxy modified catalysts are by far more productive than their unmodified catalysts ($o\text{-MeO-dppp} > o\text{-MeO-dppe} > \text{dppp} > \text{dppe}$) 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 CH_2Cl_2 and toluene promote the formation of very high molecular weight materials, yet in unsatisfactory yields.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.10.035.

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