Synthesis and characterization of palladium(II) complexes with new diphosphonium-diphosphine and diphosphine ligands. Production of low molecular weight alternating polyketones *via* catalytic CO/ethene copolymerisation

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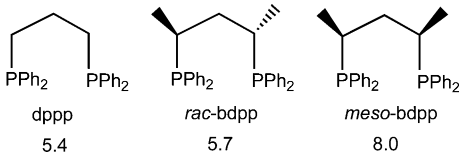
The bis-cationic diphosphonium-diphosphine 6,7-di(di-2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphoniumbicyclo[3.1.1]heptane-bis(PF_6) ((*o*-MeO-PCP)$(PF_6)_2$) and the diphosphine *rac*-2,4-bis((di-2-methoxyphenyl)phosphino)pentane (*rac*-*o*-MeO-bdpp) have been synthesized. Both ligands have been employed to coordinate $PdCl_2$ and $Pd(OAc)_2$ to give [$PdCl_2$(*o*-MeO-PCP)]$(PF_6)_2$ (**1a**), $PdCl_2$(*rac*-*o*-MeO-bdpp) (**1b**), [$Pd(OAc)_2$(*o*-MeO-PCP)]$(PF_6)_2$ (**2a**) and $Pd(OAc)_2$(*rac*-*o*-MeO-bdpp) (**2b**). The ligands and complexes have been fully characterized in solution by multinuclear NMR spectroscopy. In addition, **1a** and **1b** have been authenticated by single crystal X-ray structure analyses. The Pd^{II} complexes **1a** and **1b** have been employed as catalyst precursors for the CO/ethene copolymerisation in water–acetic acid mixtures, while **2a** and **2b** have been tested in methanol in the presence of *p*-toluenesulfonic acid. Irrespective of the reaction media, perfectly alternating polyketones were obtained in excellent yields and with number-average molecular weights ranging from 7.1–13.9 kg mol^{-1} with the diphosphonium-diphosphine catalysts and from 37.2–48.2 kg mol^{-1} with the diphosphine catalysts.

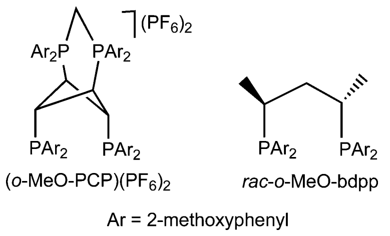
Introduction

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



Scheme 1

In this work, we report the synthesis of the new stereochemically rigid, C_3-bridged, bis-cationic diphosphonium-diphosphine 6,7-di(di-2-methoxyphenyl)phosphino-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphonium bicyclo[3.1.1]heptane that has been isolated as a PF_6^- salt ((*o*-MeO-PCP)$(PF_6)_2$, Scheme 2).



Scheme 2

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Bis-cationic complexes of (*o*-MeO-PCP)(PF_6)$_2$ with $PdCl_2$ and Pd(OAc)$_2$ (OAc = acetate), namely [$PdCl_2$(*o*-MeO-PCP)](PF_6)$_2$ (**1a**) and [Pd(OAc)$_2$(*o*-MeO-PCP)](PF_6)$_2$ (**2b**), have been synthesized and fully characterized. As a comparison to a neutral and less strained C_3-bridged diphosphine, we have also prepared the new diphosphine *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac-o*-MeO-bdpp) as well as its $PdCl_2$ and Pd(OAc)$_2$ complexes $PdCl_2$(*rac-o*-MeO-bdpp) (**1b**) and Pd(OAc)$_2$(*rac-o*-MeO-bdpp) (**2b**). All these Pd^{II} complexes have been tested as catalyst precursors for the copolymerisation of CO and ethene in different solvents, showing high activity and a remarkable control on the molecular weight of the alternating polyketone products.

Experimental

Materials and physical measurements

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deoxygenated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. $PdCl_2$(COD) (COD = 1,5-cyclooctadiene),[7] bis(*o*-methoxyphenyl)phosphine[8] and *meso*/*rac*-2,4-pentanediol dimesylate[9] were prepared according to literature methods. The synthesis of *trans*,*trans*,*trans*-tetrakis((di-2-methoxyphenyl)phosphino)cyclobutane (*o*-MeO-dppcb) will be described elsewhere.[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. Copolymerisation reactions were performed with a 250 mL stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column (30 m, 0.25 mm id, 0.25 μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}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 (δ) with reference to either TMS as an internal standard (^{1}H and ^{13}C NMR) or 85% H_3PO_4 as an external standard (^{31}P NMR). High pressure NMR (HPNMR) experiments were carried out on the Bruker ACP 200 spectrometer, using a 10 mm HPNMR tube (Saphikon sapphire tube; titanium high pressure charging head constructed at the ICCOM-CNR).[11] 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). 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] Polyketone products were analysed by IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The NMR measurements were performed in a solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2–C_6H_6-d_6 (5 : 1, v/v) showing a perfectly alternating structure with ketone or ketone/ester end groups. ^{13}C{^{1}H} NMR (HFIP–C_6H_6-d_6, 100.62 MHz, ppm): δ 6.80 (CH_2CH_3), 27.90 ($CH_3OC(O)CH_2$), 52.50 ($C(O)OCH_3$), 176.10 ($CH_3O(O)C$), 212 ($CH_2CH_2C(O)$), 217 ($CH_3CH_2C(O)$).[2] The number-average molecular weight (M_n) of the copolymers was determined by ^{1}H NMR spectroscopy.

Preparations

(*o*-MeO-PCP)(PF_6)$_2$. The tetraphosphine *o*-MeO-dppcb (0.62 g, 0.60 mmol) was stirred in CH_2Cl_2 (30 mL) for 7 d at room temperature. The resultant yellow solution was concentrated to 5 mL and diethyl ether (150 mL) was added to complete the precipitation of a yellow product, which was then filtered off, dried under vacuum and dissolved in water (120 mL). The water solution was filtered through a column of Celite to remove any trace of suspended material. The addition of solid $NaPF_6$ (2.00 g, 12.00 mmol) to the resultant clear solution caused the precipitation of an off-white powder, which was filtered off, washed three times with water (20 mL) and then dried under vacuum. Yield 90.5% (0.72 g, 0.54 mmol). $C_{61}H_{62}F_{12}O_8P_6$ (1336.29): calc. C 54.83, H 4.64; found C 54.91, H 4.71%. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, ppm): δ 3.38 (s, 12H, OCH_3), 3.52 (s, 12H, OCH_3), 4.25 (t, ^3J(HP) 18.0 Hz, 2H, P–CH), 4.37 (t, ^3J(HP) 9.6 Hz, 2H, P–CH), 4.59 (t, ^2J(HP) 15.3 Hz, 2H, P–CH_2), 6.87–7.70 (m, 32H, Ar-*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.62 MHz, ppm): δ 8.02 (t, ^1J(CP) 50.0 Hz, P-CH_2), 32.00 (m, P-*C*H), 32.31 (m, P-*C*H), 55.78 (s, O-CH_3), 56.51 (s, O-CH_3), 104.70 (d, ^1J(CP) 90.6 Hz, P-*C*(*ipso*)), 112.83 (s, Ar-*C*), 113.50 (s, Ar-*C*), 121.20 (s, Ar-*C*), 121.85 (s, Ar-*C*), 122.80 (s, Ar-*C*), 132.72 (s, Ar-*C*), 133.25 (s, Ar-*C*), 135.08 (s, Ar-*C*), 138.53(s, Ar-*C*), 161.64 (s, O-*C*(Ar)), 162.02 (s, O-*C*(Ar)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.98 MHz, ppm) δ 25.08 (t, ^3J(PP) 16.0 Hz), −17.16 (br. t).

***meso*/*rac*-2,4-Dibromopentane.** This mixture of stereoisomers was synthesized using a modified version of the synthetic protocol reported by Wiberg and Lowry.[13] LiBr (7.33 g, 84.4 mmol) was added to an acetone solution of *meso*/*rac*-2,4-pentanediol dimesylate (5.50 g, 21.1 mmol). The mixture was refluxed for 20 h, then it was cooled to room temperature. The solvent was removed by distillation and the crude residue was suspended in a solvent mixture of water–Et_2O–*n*-pentane (60 mL) (30 : 15 : 15, v/v/v). The organic layer was separated and the solvent was removed under reduced pressure to give a yellow liquid residue. Yield 65.7% (26 : 74) (*meso* : *rac*) (3.19 g, 13.862 mmol). $C_5H_{10}Br_2$ (229.85): calc. C 26.13, H 4.35; found C 26.40, H 4.55%. ^{1}H NMR ($CDCl_3$, 200.13 MHz, ppm) δ 1.73 (d, ^3J(HH) 6.72 Hz, 6H, CH_3), 1.77 (d, ^3J(HH) 6.60 Hz 6H, CH_3), 2.15 (m, 3H, *meso*-*C*HH, *rac*-CH_2), 2.47 (dt, ^2J(HH) 14.2 Hz, ^3J(HH) 8.0 Hz, 1H, *meso*-CH*H*), 4.21 (m, 2H, Br–C*H*), 4.38(m, 2H, Br–C*H*).

***rac-o*-MeO-bdpp.** *n*-BuLi (6.80 mL, 10.8 mmol) was slowly added to bis(*o*-methoxyphenyl)phosphine (2.00 g, 8.13 mmol) dissolved in anhydrous and degassed THF (150 mL) at 0° C. After the yellow Li salt precipitated, the suspension was stirred for 1 h at room temperature. A 26 : 74 mixture of *meso*/*rac*-2,4-dibromopentane (0.92 g, 4.02 mmol) was added dropwise to this suspension at room temperature, then the yellow solution was stirred overnight. Afterwards, the reaction was quenched with water (3 mL), concentrated to dryness, and washed with water and ethanol. Yield of *meso*/*rac*-*o*-MeO-bdpp 71.0% (1.62 g, 2.89 mmol). Recrystallisation of the mixture from CH_2Cl_2/EtOH led to the precipitation of a pure sample of *rac*-*o*-MeO-bdpp as an off-white powder. Yield 36.0% (0.82 g, 1.46 mmol). $C_{33}H_{38}O_4P_2$ (560.26): calc. C 70.70, H 6.83; found C 70.65, H 6.85%. ^{1}H NMR ($CDCl_3$, 200.13 MHz, ppm) δ 1.06 (dd, ^3J(HP) 15.8 Hz, ^3J(HH) 6.8 Hz, 6H, CH_3), 1.53 (m, 2H, CH_2), 2.75 (m, 2H, P–C*H*), 3.63 (s, 6H, OCH_3), 3.69 (s, 6H, OCH_3), 6.72–7.83 (m, 16H, Ar-*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz, ppm) δ −23.8 (s). All attempts to isolate the *meso* ligand in a pure form were unsuccessful.

[PdCl$_2$(*o*-MeO-PCP)](PF$_6$)$_2$ (1a). $PdCl_2$(COD) (0.03 g, 0.10 mmol) was added to a degassed solution of (*o*-MeO-PCP)(PF_6)$_2$ (0.13 g, 0.10 mmol) in CH_2Cl_2 (10 mL). The resultant mixture was stirred under nitrogen for 2 h, then *n*-hexane (50 mL) was added slowly to complete the precipitation of **1a** as an off-white solid, which was filtered off, washed with *n*-hexane (5 mL) and dried under vacuum. Yield 85.2% (0.13 g, 0.08 mmol). $C_{61}H_{62}Cl_2F_{12}O_8P_6Pd$ (1513.61): calc. C 48.40, H 4.09; found C 48.55, H 4.21%. ^{1}H NMR (DMSO-d_6, 400.13 MHz, ppm) δ 3.64 (s, 12H, OCH_3), 3.70 (s, 12H, OCH_3), 3.90 (m, 2H, P–C*H*), 4.09 (td, ^3J(HP) 15.6 Hz, ^2J(HP) 8.8 Hz, 2H, P–C*H*), 4.79 (br. t, ^2J(HP) 15.0 Hz, 2H, P–CH_2), 6.35–8.85 (m, 32H, Ar-*H*). ^{31}P{^{1}H} NMR (DMSO-d_6, 161.98 MHz, ppm) δ 30.60 (t, ^3J(PP) 24.9 Hz), 24.20 (br. t).

Crystals of **1a**·2CH_3COCH_3 suitable for X-ray analysis were obtained by slow evaporation of an acetone solution of **1a**.

[Pd(OAc)$_2$(*o*-MeO-PCP)](PF$_6$)$_2$ (2a). Pd(OAc)$_2$ (0.02 g, 0.10 mmol) was added to a degassed solution of (*o*-MeO-PCP)(PF_6)$_2$ (0.13 g, 0.10 mmol) in CH_2Cl_2 (10 mL). The resultant mixture was stirred at room temperature for 12 h, then it was concentrated to a smaller volume (3 mL). The addition of *n*-hexane (50 mL) caused the precipitation of **2a** as an orange red powder, which was filtered off, washed with *n*-hexane (5 mL) and dried under vacuum. Yield 82.6% (0.13 g, 0.08 mmol). $C_{65}H_{68}F_{12}O_{12}P_6Pd$ (1560.71): calc. C 50.02, H 4.36; found C 50.22, H 4.44%. ^{1}H NMR (DMSO-d_6, 400.13 MHz, ppm) δ 1.15 (s, 6H, OAc–CH_3), 3.20–3.50 (m, 24H, OCH_3), 3.88 (br. t, ^3J(HP) 15.0 Hz, 2H, P–C*H*), 3.99 (td, ^3J(HP) 15.3 Hz, ^2J(HP) 8.2 Hz, 2H, P–C*H*), 4.78 (br. t, ^2J(HP) 15.0 Hz, 2H, P–CH_2), 6.60–8.00 (m, 32H, Ar-*H*). ^{31}P{^{1}H} NMR (DMSO-d_6, 161.98 MHz, ppm) δ 32.50 (br. s), 24.45 (br. s).

PdCl$_2$(*rac*-*o*-MeO-bdpp) (1b). *rac*-*o*-MeO-bdpp (0.11 g, 0.20 mmol) was dissolved in degassed CH_2Cl_2 (20 mL) under nitrogen. To this colourless solution was added $PdCl_2$(COD) (0.06 g, 0.20 mmol). The resultant suspension was stirred for 1 h, then it was concentrated to half the volume. The addition of a 1 : 1 (v/v) mixture of *n*-pentane and diethyl ether (20 mL) completed the precipitation of **1b** as an off-white microcrystalline solid, which was filtered off and dried in a stream of nitrogen. Yield 69.8% (0.10 g, 0.14 mmol). $C_{33}H_{38}Cl_2O_4P_2Pd$ (737.58): calc. C 53.71, H 5.19; found C 53.69, H 5.20%. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, ppm) δ 0.86 (dd, ^3J(HP) 15.9 Hz, ^3J(HH) 6.7 Hz, 6H, CH_3), 1.82 (m, 2H, CH_2), 3.24 (m, 2H, P–C*H*), 3.72 (s, 6H, OCH_3), 3.90 (s, 6H, OCH_3), 6.80–7.70 (m, 16H, Ar-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.98 MHz, ppm) δ 34.50(s).

Crystals of **1b** suitable for X-ray analysis were obtained by slow diffusion of toluene into a saturated CH_2Cl_2 solution at room temperature.

Pd(OAc)$_2$(*rac*-*o*-MeO-bdpp) (2b). Compound **1b** (0.26 g, 0.35 mmol) was dissolved in degassed CH_2Cl_2 (30 mL) under nitrogen. To this solution was added Ag(OAc) (0.13 g, 0.77 mmol) and the resultant suspension was stirred for 30 min. The precipitated AgCl was removed by filtration through a column of Celite and the clear solution was concentrated to *ca.* 5 mL. The addition of a 1 : 1 (v/v) mixture of *n*-hexane and diethyl ether (20 mL) completed the precipitation of **2b** as yellow microcrystals which were filtered off, and dried in a stream of nitrogen. Yield 60% (0.16 g, 0.21 mmol). $C_{37}H_{44}O_8P_2Pd$ (784.69): calc. C 56.60, H 5.65; found C 56.63, H 5.66%. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, ppm) δ 1.01 (dd, ^3J(HP) 16.0 Hz, ^3J(HH) 6.9 Hz, 6H, CH_3), 1.10 (s, 6H, OAc–CH_3), 1.88 (m, 2H, CH_2), 3.12 (m, 2H, P–C*H*), 3.68 (s, 6H, OCH_3), 3.93 (s, 6H, OCH_3), 6.95–7.68 (m, 16H, Ar-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.98 MHz, ppm) δ 31.78 (s).

Catalytic copolymerisation of CO and ethene

HPNMR experiment in water–AcOH with 1b as catalyst precursor. A 10 mm sapphire HPNMR tube was charged with a suspension of **1b** (0.01 g, 0.02 mmol) in a mixture of D_2O and AcOH (0.4 mL and 1.6 mL, respectively) under nitrogen and then placed into the NMR probe maintained at 20 °C. After a ^{31}P{^{1}H} NMR spectrum was acquired, the sapphire tube was removed from the NMR probe and pressurized with a 1 : 1 mixture of CO–C_2H_4 to a total pressure of 40 bar at room temperature. A ^{31}P{^{1}H} NMR spectrum was recorded at 20 °C and then the probe-head was heated to 85 °C. This temperature was maintained for 1 h, during which time ^{31}P{^{1}H} NMR spectra were acquired every 20 min. The tube was then allowed to cool to 20 °C and a final ^{31}P{^{1}H} NMR spectrum was acquired. The formation of copolymer was observed.

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

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

Table 1 Crystallographic data for **1a**·$2CH_3COCH_3$ and (*S*,*S*)-**1b**

	1a·$2CH_3COCH_3$	(*S*,*S*)-**1b**
Empirical formula	$C_{67}H_{74}Cl_2F_{12}O_{10}P_6Pd$	$C_{33}H_{38}Cl_2O_4P_2Pd$
Formula weight	1630.41	737.87
T/K	243(2)	293(2)
λ/Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$
a/Å	14.3205(2)	10.6259(7)
b/Å	20.4675(3)	13.6492(11)
c/Å	24.5985(3)	11.9265(9)
α/°	90.0	90.0
β/°	91.8346(9)	107.937(7)
γ/°	90.0	90.0
V/Å^3	7206.2(2)	1645.7(2)
Z	4	2
D_c/Mg m^{-3}	1.503	1.489
μ/mm^{-1}	0.552	0.859
F(000)	3336	756
Crystal size/mm	0.25 × 0.15 × 0.10	0.40 × 0.20 × 0.10
Absorption correction	MULTI-SCAN	SADABS
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameter	13017/0/895	10051/1/391
Goodness-of-fit on F^2	1.017	0.855
Final R indices	$[I > 3\sigma(I)]$ $R1 = 0.0477$, w$R2 = 0.1497$	$[I > 2\sigma(I)]$ $R1 = 0.0451$, w$R2 = 0.0808$
R indices (all data)	$R1 = 0.1017$, w$R2 = 0.1685$	$R1 = 0.1015$, w$R2 = 0.0949$
Largest diff. peak, hole/e Å^3	0.630, −0.451	1.122, −0.375

X-Ray crystallographic data collection and refinement of the structures

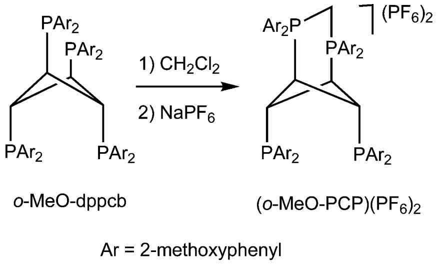
The crystallographic data for **1a**·$2CH_3COCH_3$ and (*S*,*S*)-**1b** are summarized in Table 1. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used. The data collection was performed on a Nonius Kappa CCD diffractometer using ϕ-ω-scans and on an Oxford Diffraction CCD diffractometer using ω-scans for **1a**·$2CH_3COCH_3$ and (*S*,*S*)-**1b**, respectively. Cell refinement, data reduction and empirical absorption correction were carried out with the Denzo and Scalepack programs[14a] for **1a**·$2CH_3COCH_3$ and with the Oxford diffraction software and SADABS[14b] for (*S*,*S*)-**1b**. All structure determination calculations for **1a**·$2CH_3COCH_3$ were performed with SHELXTL NT 5.10 including SHELXS-97 and SHELXL-97,[14c] while the WINGX package[14d] with SIR-97,[14e] SHELXL-97 and ORTEP-3 programs[14f] were used for (*S*,*S*)-**1b**. Final refinements on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were included using a riding model with isotropic U values depending on the U_{eq} of the adjacent carbon atoms.

CCDC reference numbers: 293490 and 293489 for **1a**·$2CH_3COCH_3$ and (*S*,*S*)-**1b**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601154c

Results and discussion

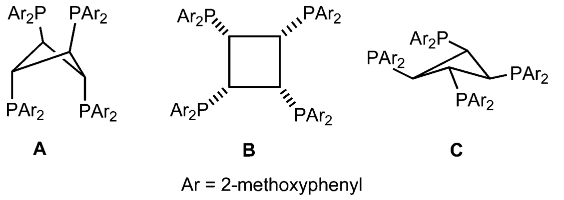
Synthesis of the ligands

The diphosphonium-diphosphine ligand (*o*-MeO-PCP)$(PF_6)_2$ has been obtained by regioselective bis-alkylation of the tetraphosphine *o*-MeO-dppcb[10] with neat CH_2Cl_2, followed by exchange of the chloride counteranions with PF_6^- in water. This procedure gave (*o*-MeO-PCP)$(PF_6)_2$ in analytically pure form and 90% yield (Scheme 3).



Scheme 3

The contemporaneous alkylation of two phosphorus atoms of *o*-MeO-dppcb is quite surprising as dichloromethane is a weak alkylating agent. A driving force to the observed reaction may be the formation of a six-membered diphosphonium ring which stabilizes the all-axial positions of the phosphorus donor atoms in *o*-MeO-dppcb. The latter ligand can in fact adopt three distinct conformations in solutions (Scheme 4).[10]



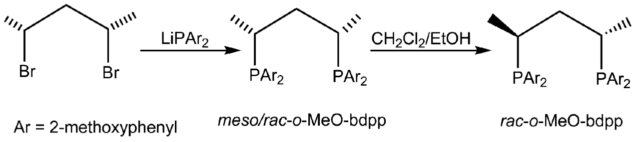
Scheme 4

The bis-cationic diphosphonium-diphosphine (*o*-MeO-PCP)$(PF_6)_2$ is stable in both protic and aprotic solvents and no trace of ylide formation was observed even for long residence times in solution.

The $^{31}P\{^1H\}$ NMR spectrum of (*o*-MeO-PCP)$(PF_6)_2$ consists of a broad triplet in the phosphine region at −17.16 ppm and of a narrow triplet in the phosphonium region at 25.08 ppm.[15a]

The ^{3}J(PP) coupling constant of 16 Hz is rather small compared to other cyclic phosphonium-phosphine ligands.[15] This finding may be due to the conformational flexibility of the six-membered diphosphonium heterocycle, which, affecting the dihedral angle between the phosphine and phosphonium units, would average the PP coupling constant. The presence of a CH_2 bridge in between the phosphonium units is put in evidence by a triplet at 4.59 ppm with a ^{2}J(HP) value of 15.3 Hz in the ^{1}H NMR spectrum and by a triplet in the ^{13}C{^{1}H}NMR spectrum at 8.02 ppm with a ^{1}J(CP) value of 50.0 Hz. The coupling constant values are comparable to those reported for similar $Ar_2P^+CH_2P^+Ar_2$ fragments in six-membered diphosphonium heterocycles.[16]

The less strained diphosphine *rac*-*o*-MeO-bdpp was synthesized by the reaction of $LiPAr_2$ (Ar = 2-methoxyphenyl)[9] with a 26 : 74 *meso* : *rac* mixture of 2,4-dibromopentane in THF (Scheme 5).

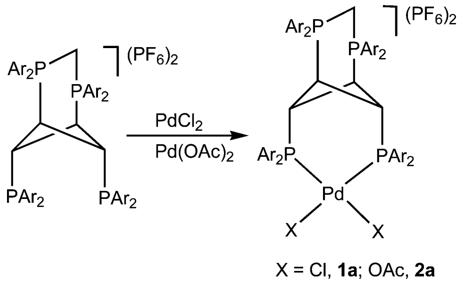


Scheme 5

Only the *rac* isomer of *o*-MeO-bdpp could be isolated in a pure form (36% yield) as an off-white solid by recrystallisation of the stereoisomeric mixture from CH_2Cl_2–ethanol.

Synthesis and characterization of the catalytic precursors

The reaction of (*o*-MeO-PCP)$(PF_6)_2$ with $PdCl_2$(COD) or $Pd(OAc)_2$ in CH_2Cl_2 gave the bis-cationic Pd^{II} complexes $[Pd(Cl)_2$(*o*-MeO-PCP)]$(PF_6)_2$ (**1a**) and $[Pd(OAc)_2$(*o*-MeO-PCP)]$(PF_6)_2$ (**2a**), respectively, as air stable compounds in 85 and 83% yield, respectively (Scheme 6).



Scheme 6

Compounds **1a** and **2a** are slightly soluble in water at room temperature and very soluble in DMF and DMSO. They have been characterized in solution by multinuclear NMR spectroscopy. Both compounds exhibit a ^{31}P{^{1}H} NMR spectrum containing two signals in a 1 : 1 ratio that are assigned to the phosphonium atoms (*ca.* 24.3 ppm) and the coordinated phosphine atoms (30.60 ppm for **1a** and 32.50 ppm for **2a**, respectively). In the case of **1a** the two ^{31}P{^{1}H} NMR signals appear as triplets with a ^{3}J(PP) value of 24.9 Hz, while **2a** exhibits two broad singlets. The ^{1}H NMR spectra of **1a** and **2a** show a broad triplet at *ca.* 4.8 ppm with a ^{2}J(HP) coupling constant of 15.0 Hz due to the phosphonium bridging CH_2 group.

The presence of a strained 6–4–6 ring system in **1a** was confirmed by a single crystal X-ray structure analysis. A selected ORTEP drawing of the cation $[PdCl_2$(*o*-MeO-PCP)$]^{2+}$ ($\mathbf{1a}^{2+}$) in **1a**·$2CH_3COCH_3$ is presented in Fig. 1.

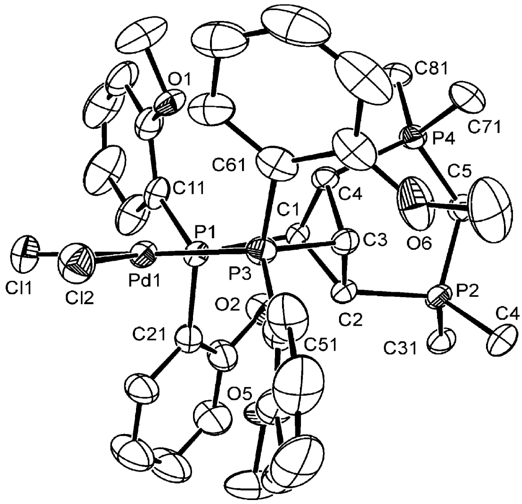


Fig. 1 ORTEP diagram of **1a**·$2CH_3COCH_3$ with 30% probability ellipsoids. The two PF_6^- counterions and the two acetone molecules are omitted for clarity. Only the *ipso* carbon atoms of the 2-methoxyphenyl units are presented on P(2) and P(4).

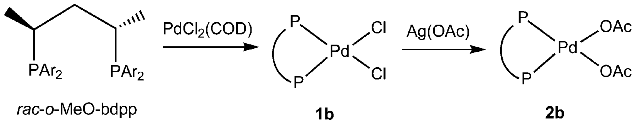
Besides $\mathbf{1a}^{2+}$ cations and PF_6^- anions, the crystal structure shows the presence of two molecules of acetone in the asymmetric unit. Crystallographic data and selected bond distances and angles for the complex cation $\mathbf{1a}^{2+}$ are reported in Tables 1 and 2, respectively. The Pd atom shows a square-planar coordination with a deviation from the coordination plane, defined by the atoms P(1), P(3), Cl(1) and Cl(2), of 0.1867(8) Å in the direction of C(11). The rather short Pd(1)–P(1) and Pd(1)–P(3) bond distances of 2.2546(13) and 2.2403(13) Å, respectively, lead to the formation of a P(1)–Pd(1)–P(3) bite angle of 95.05(4)°, which is *ca.* 5° higher than that reported for other six-membered Pd^{II} complexes with chelating diphosphines.[17] The six-membered ring system containing the

Table 2 Selected bond distances (Å) and angles (°) for **1a**·$2CH_3COCH_3$ and (*S*,*S*)-**1b**

	1a·$2CH_3COCH_3$	(*S*,*S*)-**1b**
Pd(1)–P(1)	2.2546(13)	2.2671(11)
Pd(1)–P(2)		2.2757(11)
Pd(1)–P(3)	2.2403(13)	
Pd(1)–Cl(1)	2.3288(14)	2.3620(11)
Pd(1)–Cl(2)	2.3436(14)	2.3608(10)
P(1)–Pd(1)–P(2)		90.11(4)
P(1)–Pd(1)–P(3)	95.05(4)	
Cl(1)–Pd(1)–Cl(2)	91.42(5)	91.53(4)
Cl(1)–Pd(1)–P(2)		177.98(4)
Cl(1)–Pd(1)–P(3)	177.76(5)	
Cl(2)–Pd(1)–P(1)	175.82(5)	179.62(5)
Intramolecular distances/Å		
Pd(1)–O(1)	3.2949(33)	3.5077(36)
Pd(1)–O(2)	5.2054(37)	5.1814(31)
Pd(1)–O(3)		5.1989(31)
Pd(1)–O(4)		3.4846(35)
Pd(1)–O(5)	3.5361(39)	
Pd(1)–O(6)	5.1555(40)	

metal centre is connected to a folded cyclobutane ring and to a further six-membered heterocyclic ring, which contains two phosphonium units in the 1,3 positions with respect to the cyclobutane ring, which exhibits a folding angle of 27.94(37)°. The two six-membered ring systems are almost perpendicular to each other, which is shown by an interplanar angle of 86.43(10)° between the two planes defined by P(1), C(1), C(3), P(3) and P(2), C(2), C(4), P(4). A folding along the coordinating phosphorus atoms P(1) and P(3) is apparently hindered by the steric crowding created by the eight *ortho*-methoxyphenyl groups.[4b] Evidence for ring strain in the six-membered palladacycle is provided by the bond angles Pd(1)–P(1)–C(1), Pd(1)–P(3)–C(3), P(3)–C(3)–C(2) of 114.97(14), 113.45(14) and 118.5(3)°, respectively. These deviate significantly from known unstrained cases that show values of *ca.* 109°. The *ortho*-methoxyphenyl rings on the phosphorus donor atoms P(1) and P(3) deviate significantly from an ideal diagonal disposition with respect to the coordination plane of palladium. This is shown by the deviation of the four *ipso*-carbon atoms C(11), C(21), C(51) and C(61) of 1.199(5), −1.521(5), −0.711(6) and 2.117(5) Å from the coordination plane defined by the atoms P(1), P(3), Cl(1) and Cl(2), due to the interplanar angle of 11.47(24)° between the planes defined by Pd(1), P(1), C(1) and Pd(1), P(3), C(3). The two H atoms attached to the bridging carbon atom C(5) have been located by difference Fourier maps. Both the P(4)–C(5) and P(2)–C(5) bond lengths of 1.806(4) and 1.803(4) Å, respectively, and the bond angle P(4)–C(5)–P(2) of 117.9(2)° match well the values reported for cyclic CH_2 bridged diphosphonium units.[16a,18] The intramolecular distances between Pd(1) and the four *o*-methoxy oxygen atoms O(1), O(2), O(5) and O(6), in the range from 3.2949(33)–5.2054(37) Å, are not bonding interactions. Like those observed in Ni^{II}(*o*-MeO-dppp) complexes (*o*-MeO-dppp = 1,3-bis((di-2-*o*-methoxyphenyl)phosphino)propane), the diagonally disposed oxygen atoms O(1) and O(5) are close to pseudo-apical positions of a distorted octahedron.[19] The two acetone molecules in the crystal lattice build up a web of short intermolecular distances. Within these short contacts the most important are: O(11)···H(1A) 2.421, O(11)···H(5A) 2.301, O(11)···H(27A) 2.698, O(10)···H(16A) 2.590 and H(6A)···C(25) 2.745 Å.

The reaction of *rac*-*o*-MeO-bdpp with $PdCl_2(COD)$ in CH_2Cl_2 gave $PdCl_2$(*rac*-*o*-MeO-bdpp) (**1b**), while the analogous reaction with $Pd(OAc)_2$ yielded $Pd(OAc)_2$(*rac*-*o*-MeO-bdpp (**2b**) as an impure product. However, the reaction of **1b** with Ag(OAc) in CH_2Cl_2 gave **2b** in a pure form. **1b** and **2b** were obtained in 70 and 60% yield, respectively (Scheme 7). The diphosphine *rac*-*o*-MeO-bdpp is just the *o*-methoxy derivative of the well-known ligand skewphos ligand.[20]



Scheme 7

The crystal structure of **1b** shows the *S*,*S* stereoisomer (*S*,*S*-**1b**), which crystallizes in the chiral space group $P2_1$. A selected ORTEP plot of *S*,*S*-**1b** is reported in Fig. 2.

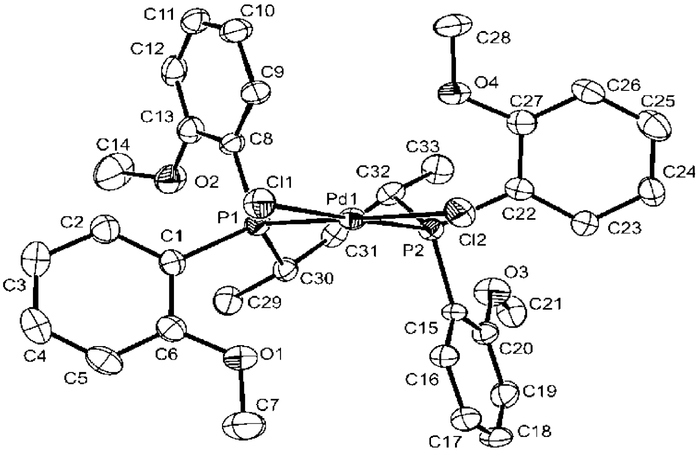


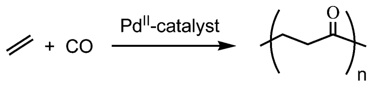
Fig. 2 ORTEP diagram of (*S*,*S*)-**1b** with 30% probability ellipsoids.

Crystallographic data and selected bond distances and angles for (*S*,*S*)-**1b** are reported in Tables 1 and 2, respectively. The Pd centre is square-planarly coordinated by two phosphorus and two chloride atoms. The deviation of the metal centre from the coordination plane, defined by the atoms P(1), P(2), Cl(1) and Cl(2), is 0.0192(7) Å in the direction of C(1). Unlike **1a**$^{2+}$, (*S*,*S*)-**1b** exhibits a typical P(1)–Pd(1)–P(2) bite angle of 90.11(4)°, which is comparable to that of many other six-membered palladium diphosphine complexes.[18] The Pd(1)–P(1) and Pd(1)–P(2) bond lengths of 2.2671(11) and 2.2757(11) Å, respectively, are significantly longer in (*S*,*S*)-**1b** than in **1a**$^{2+}$ (2.2546(13) and 2.2403(13) Å, respectively). This effect may be accounted for the higher ring strain of the palladacycle in **1a**$^{2+}$ as compared to (*S*,*S*)-**1b**, which would trigger a higher s-character of the phosphorus orbitals in the former complex.[21]

Like in other *S*,*S*-skewphos metal complexes, the carbon backbone of the ligand in (*S*,*S*)-**1b** exhibits a diagonal disposition with respect to the coordination plane, which is the most common conformation for skewphos metal complexes.[20] Strictly related to the diagonal disposition of the C5 carbon backbone, the four 2-methoxyphenyl groups are disposed diagonally with respect to the Pd coordination plane, which is shown by the deviation of the four *ipso* carbon atoms from the coordination plane (C(1) 0.9327(51), C(8) −1,7077(45), C(15) 1.6957(43) and C(22) −0.8764 Å). Furthermore, two *o*-methoxy oxygen atoms, namely O(1) and O(4), show shorter intramolecular distances to Pd(1) (3.5077(36) and 3.4846(35) Å, respectively), while O(2) and O(3) show by far a higher intramolecular distance to Pd(1) of 5.1814(31) and 5.1989(31) Å, respectively.

Catalytic copolymerisation of CO and ethene

The solvent of choice of most CO/C_2H_4 copolymerisation reactions by PdX_2(diphosphine) catalysis (Scheme 8) is either MeOH or water. This implies the use of weakly coordinating co-ligands ($X = TsO^-$, $CF_3CO_2^-$) to allow for the activation of either solvent to give Pd–H, Pd–OMe or Pd–OH initiators.[2] Recently, however, Toniolo *et al.* have shown that the bis-chloride and bis-acetate complexes PdX_2(diphosphine) (diphosphine = dppe, dppp,



Scheme 8

Table 3 Alternating copolymerisation of CO with ethene catalysed by **1a** and **1b** in water–AcOH[a]

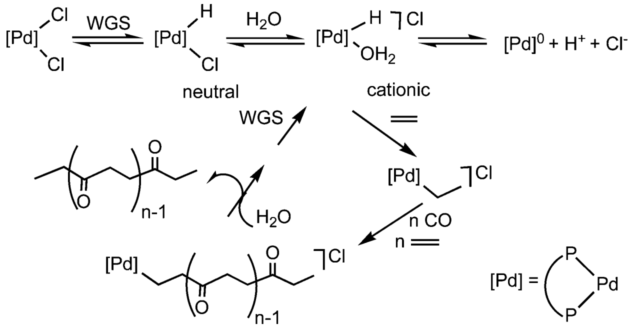
Entry	Precatalyst	Water/mol%	Time/h	Polymer/g	Productivity[b]	M_n/kg mol^{-1}
1	**1a**	55	1	3.10	5.83	
2	**1a**	65	1	3.70	6.95	7.3
3	**1a**	65	2	6.46	6.07	
4	**1a**	75	1	3.18	5.98	7.1
5	**1a**	85	1	2.19	4.11	
6	**1b**	55	1	4.12	7.74	
7	**1b**	65	1	4.75	8.93	37.4
8	**1b**	75	1	5.28	9.92	37.2
9	**1b**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

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

dppb) (X = Cl^-, OAc^-) can generate very active catalysts in water–AcOH mixtures.[22] Therefore, the bis-chloride complexes **1a** and **1b** were tested in different mixtures of water–AcOH under standard experimental conditions (40 bar 1 : 1 CO : ethene, 85 °C). The results obtained are reported in Table 3. Irrespective of catalyst and solvent composition, perfectly alternating polyketone products were obtained with exclusively ketone end-groups.

A maximum catalytic activity for **1a** was observed with the use of a 65 and 35 mol% mixture of water–AcOH (entry 2), while a mixture containing 75 mol% water was the optimum value for **1b** (entry 8). In reactions lasting 1 and 2 h, **1b** was slightly more active than **1a** but appreciably less stable with time (entries 2 and 3 *vs* 8 and 9). However, the most striking catalytic difference between **1a** and **1b** was the M_n of the polyketone products: around 7 kg mol^{-1} with **1a** and 37 kg mol^{-1} with **1b** (Table 3). These results indicate that the chain-transfer rate is significantly faster in the reactions catalysed by **1a** than for the reactions catalysed by **1b**.

The mechanism of the CO/C_2H_4 copolymerisation by Pd^{II}–diphosphine catalysis has been intensely studied over recent years and most of the elementary steps involved, especially chain-transfer and propagation, have been clarified.[2] Scheme 9 provides a brief summary of the mechanism proposed for CO/ethene copolymerisations catalysed by $PdCl_2$(diphosphine) complexes in acidic aqueous media.[23]



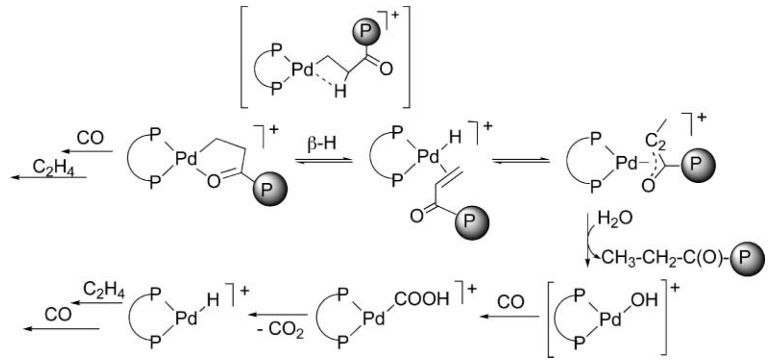
Scheme 9

It is agreed that the neutral Pd^{II}–H complexes are generated from the bis-chloride precursors by a water gas shift reaction (WGS),[23] and then converted into the catalytically active cationic Pd^{II}–H species by a water-controlled solvolysis process.[23a] Toniolo *et al.*[22] and Zudin *et al.*[23] have also demonstrated 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, too large a proportion of water has been found to have a detrimental effect on the solubility of CO and C_2H_4.[22] This may account for the significant decrease in productivity (from 6.95 to 4.11 kg (g(Pd) × h)$^{-1}$) by increasing the water proportion from 65 to 85 mol% (Table 3, entries 2,4,5).

The chain-transfer reaction of CO/ethene copolymerisations performed in acidic aqueous media has been demonstrated to occur exclusively *via* protonolysis by water with formation of a Pd–OH unit that regenerates a Pd–H initiator by WGS.[24] In these conditions, the intimate mechanism of chain transfer involves a β-hydride elimination in a β-keto alkyl chelate, followed by hydride migration to give an enolate whose regioselective protonation terminates the chain growth (Scheme 10).[25] The rate of the β-H elimination determines the overall chain transfer rate, hence it controls the molecular weight of the polyketone produced.[2]

β-H elimination reactions in organometallics are steered by both electronic and steric factors.[26] In particular, it is agreed that the agostic interaction between the metal and β-hydrogen (the precursor to hydrogen transfer to the metal) is favoured by a low electron density at the metal centre. In complexes of the same metal ion, the electron density at the metal depends on the electronic and steric characteristics of the supporting ligand(s) as well as on the overall charge of the complex. In the present case, a lower electron-donating ability of (*o*-MeO-PCP)(PF_6)$_2$ as compared to *rac*-*o*-MeO-bdpp is indicated by the significantly shorter Pd–P bond distances in **1a** as compared to **1b** (2.2546(13) and 2.2403(13) Å *vs*. 2.2671(11) and 2.2757(11) Å). As mentioned previously, due to the ring strain of the six-membered palladacycle, the phosphorus donor atoms in **1a** exhibit a higher s-character, and hence have shorter van der Waals radii, than in **1b**.[27] As a further, indirect proof of the lower metal basicity of complexes with (*o*-MeO-PCP)(PF_6)$_2$ *vs*. complexes with *rac*-*o*-MeO-bdpp, we have found that the IR spectrum of the bis-carbonyl complex *cis*-[Rh(CO)$_2$(*o*-MeO-PCP)](PF_6)$_3$ shows, in CH_2Cl_2, *ν*(CO) bands at 2097 and 2052 cm^{-1}, while *cis*-[Rh(CO)$_2$(*rac*-*o*-MeO-bdpp)](PF_6) exhibits red shifted bands at 2086 and 2036 cm^{-1}.[10]

Besides metal basicity, the β-H elimination rate in the propagating Pd–alkyl (Scheme 10), might be influenced by the interaction of the metal centre with the oxygen atoms from the *ortho*-methoxy



Scheme 10

substituents. Indeed, evidence has been reported in the literature for the coordinative interaction of these oxygen to metal centres.[28] In the eventuality of an analogous interaction in the propagating alkyls generated by **1a** and **1b**, the oxygen atoms would compete with the β-hydrogens for coordination, with a retarding effect on the β-H elimination rate. In this mechanistic picture, the stereochemical rigidity of (*o*-MeO-PCP)(PF$_6$)$_2$ would disfavour the interaction of the *o*-methoxy units with the palladium centre, whereas a simple twisting of the C$_5$ backbone of *rac*-*o*-MeO-bdpp would allow for an axial interaction between the *o*-methoxy groups and the metal centre.

In an attempt to gain further information on the present copolymerisation reactions in water–AcOH, a catalytic run was performed in a HPNMR tube containing D$_2$O–AcOH (45 mol% D$_2$O) and catalyst precursor **1b**. A selected sequence of ^{31}P{^{1}H} HPNMR spectra is presented in Fig. 3.

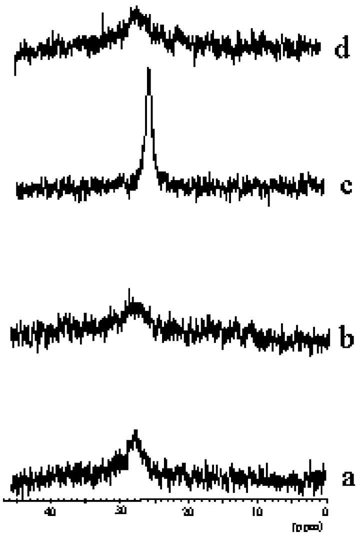


Fig. 3 Selected ^{31}P{^{1}H} HPNMR spectra (sapphire tube, D$_2$O–AcOH, 20–85 °C, 81.01 MHz) recorded during a CO/C$_2$H$_4$ copolymerisation reaction catalysed by **1b**: (a) **1b** suspended in D$_2$O–AcOH (45 mol% D$_2$O) at 20 °C; (b) after pressurisation of the tube with a 1 : 1 mixture of CO and C$_2$H$_4$ (40 bar total pressure) at 20 °C; (c) spectrum taken after 1 h at 85° C); (d) after cooling to 20 °C.

A 10 mm sapphire tube was charged with **1b** (0.02 mmol) in a solvent mixture D$_2$O–AcOH (45 mol% D$_2$O) (2 mL). A ^{31}P{^{1}H} NMR spectrum acquired at 20 °C showed a broad resonance centred at 28.00 ppm (trace a).[29] The HPNMR tube was then pressurized with a 1 : 1 mixture of CO and C$_2$H$_4$ to a total pressure of 40 bar and a ^{31}P{^{1}H} NMR spectrum was acquired at 20 °C (trace b), which showed no substantial change. The probe-head was heated to 85 °C for 1 h during which time ^{31}P{^{1}H} NMR spectra were acquired every 20 min. Since the first spectrum, a quite sharp singlet appeared at 25.5 ppm. The ^{31}P{^{1}H} spectrum acquired after 1 h at 85 °C is reported in Fig. 3 as trace c. When the probe-head was cooled to 20 °C, the ^{31}P{^{1}H} NMR spectrum showed the same broad hump as in the initial spectrum (trace d). The tube was removed from the NMR probe showing formation of the copolymer as an off-white powder. A very similar sequence of ^{31}P{^{1}H} HPNMR spectra has been observed for the CO/ethene copolymerisation catalysed by Pd(CF$_3$CO$_2$)$_2$(NaDPPPDS) in water.[24b] It was suggested, and the same can be said for the present case, that most of the palladium remains incorporated into the precursor from which a small and undetectable aliquot is delivered into the catalysis cycle.

The catalytic activity of the neutral bis-acetate complexes **2a** and **2b** was tested in MeOH in the presence of 2 or 20 equiv. of TsOH, which serves both as a scavenger of the acetate ion and as an oxidizing agent for Pd^0 species eventually formed by Pd^{II} reduction (Scheme 9).[2] The results of this study are reported in Table 4.

With either catalyst precursor, the copolymer contained keto and ester end-groups in a 1 : 1 ratio. As observed in the water–AcOH solvent, the (*o*-MeO-PCP)(PF$_6$)$_2$ precursor, **2a**, gave lower molecular weight products (7.7–13.9 kg mol^{-1}) compared to the *rac*-*o*-MeO-bdpp precursor (47.0–48.2 kg mol^{-1}). However, with either catalyst the copolymers exhibited larger M_n values compared to the products obtained in water–AcOH, which is consistent with a slower chain transfer rate in MeOH than in water–AcOH.

Increasing the concentration of TsOH had a beneficial effect on the productivity of **2a** (entries 1 *vs.* 3 and 2 *vs.* 4) and a detrimental effect on that of **2b** (entries 5 *vs.* 7 and 6 *vs.* 8).

The lower activity in the presence of 2 equiv. of TsOH and the much higher M_n of the polyketones obtained with 20 equiv. of acid in the reactions with **2a** suggest that the acid concentration is important not only for decreasing the extent of Pd^{II} reduction but also for stabilising the overall metal–ligand assembly, likely by inhibiting the deprotonation of the diphosphonium-diphosphine ligand with formation of ylide species.

Table 4 Alternating copolymerisation of CO with ethene catalysed by **2a** and **2b** in MeOH in the presence of TsOH[a]

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

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

The reverse dependence of the productivity on the acid concentration for the reactions catalysed by the *rac*-*o*-MeO-bdpp precursor **2b** (entries 5–8) is quite surprising as the opposite trend is generally observed for CO/ethene copolymerisations in MeOH by Pd^{II}–diphosphine catalysis.[2] In our opinion, this effect is a direct consequence of the presence of the *o*-methoxy substituents on the phenyl rings. Indeed, a large excess of TsOH, containing one water molecule of crystallization, would promote the creation of a web of hydrogen bonding interactions around the metal centre, involving not only the coordinated solvent molecules but also the four oxygen atoms of the *o*-methoxyphenyl groups. As a result, the Pd^{II} centre would become less accessible to the incoming monomers,[30,31] and contemporaneously the beneficial effect of the *o*-methoxy groups on the propagation rate would be diminished and even lost.[2d,28,32] Support to the hydrogen bonding interactions around the palladium centre in *rac*-*o*-MeO-bdpp catalysis intermediates is provided by several molecular structures of Pd^{II}–aquo complexes with TsO$^-$ anions, which show the presence of hydrogen bonds between the coordinated water molecules and the oxygen atoms of both tosylate ligands and counteranions.[5c,30] Moreover, DFT calculations performed on cationic [$L_3Pd(H_2O)$]$^+$ compounds have confirmed that the stability of such compounds is due to an efficient interaction of the counteranions with the coordinated water molecule.[33]

Conclusions

The pool of available chelating diphosphine ligands has been enriched by two new members. The bis-cationic diphosphonium-diphosphine (*o*-MeO-PCP)(PF_6)$_2$ has been synthesized by a kinetically controlled regioselective bis-alkylation of *o*-MeO-dppcb, using CH_2Cl_2 as an alkylating agent, while a standard procedure has been employed to prepare *rac*-*o*-MeO-bdpp. Both ligands have been used to coordinate $PdCl_2$ and Pd(OAc)$_2$ yielding square-planar complexes that generate active catalysts for the copolymerisation of CO and ethene in either water–AcOH mixtures or MeOH–TsOH. The perfectly alternating polyketones bear either exclusively ketone or 1 : 1 ketone ester end groups depending on the reaction solvent. The polyketone products produced with the diphosphonium-diphosphine catalysts show number-average molecular weights up to five times smaller than those obtained with the phosphine catalysts. These results have been interpreted in terms of faster chain-transfer rate due to the electronic and steric properties of the diphosphonium-diphosphine ligand.

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References

1 (*a*) J. C. Hierso, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier and P. Kalck, *Coord. Chem. Rev.*, 2003, **236**, 143; (*b*) J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Organometallic Chemistry of Transition Metals: Principles and Use*, University Science Books, Mill Valley, CA, 1987; (*c*) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley & Sons, New York, 3rd edn, 2001; (*d*) Z. Freixa and P. W. N. M. van Leeuwen, *Dalton Trans.*, 2003, 1890; (*e*) C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney and D. R. Powell, *J. Am. Chem. Soc.*, 1992, **114**, 5535; (*f*) R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345; (*g*) K. L. Arthur, Q. L. Wang, D. M. Bregel, N. A. Smythe, B. A. O'Neil, K. I. Goldberg and K. G. Moloy, *Organometallics*, 2005, **24**, 4624.

2 (*a*) E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663; (*b*) C. Bianchini and A. Meli, *Coord. Chem. Rev.*, 2002, **225**, 35; (*c*) C. Bianchini, A. Meli and W. Oberhauser, *Dalton Trans.*, 2003, 2627.

3 C. Bianchini, H. M. Lee, A. Meli, W. Oberhauser, F. Vizza, P. Brüggeller, R. Haid and C. Langes, *Chem. Commun.*, 2000, 777.

4 (*a*) R. D. Jackson, S. James, A. G. Orpen and P. G. Pringle, *J. Organomet. Chem.*, 1993, **458**, C3; (*b*) S. L. James, A. G. Orpen and P. G. Pringle, *J. Organomet. Chem.*, 1996, **525**, 299; (*c*) A. Karacar, M. Freytag, P. G. Jones, R. Bartsch and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1571; (*d*) A. Karacar, M. Freytag, P. G. Jones, R. Bartsch and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 2002, **628**, 533; (*e*) L. J. Higham, A. J. Middleton, K. Heslop, P. G. Pringle, A. Barber and A. G. Orpen, *J. Organomet. Chem.*, 2004, **689**, 2963; (*f*) M. Straditto, C. M. Kozak and M. J. McGlinchey, *J. Organomet. Chem.*, 1998, **564**, 101; (*g*) W. Kwok Wong, F. lung Chow, H. Chen and T. C. W. Mak, *J. Organomet. Chem.*, 1989, **377**, C65; (*h*) T. Gutmann, E. Dombrowski, N. Burzlaff and W. A. Schenk, *J. Organomet. Chem.*, 1998, **552**, 91.

5 (*a*) R. C. J. Atkinson, V. C. Gibson and N. J. Long, *Chem. Soc. Rev.*, 2004, **33**, 313; (*b*) C. Bianchini, A. Meli, W. Oberhauser, P. W. N. M. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev and A. M. Kal'sin, *Organometallics*, 2003, **22**, 2409; (*c*) C. Bianchini, A. Meli, W. Oberhauser, S. Parisel, E. Passaglia, F. Ciardelli, O. V. Gusev, A. M. Kal'sin and N. V. Vologdin, *Organometallics*, 2005, **24**, 1018; (*d*) M. A. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek and P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, 2002, 2308.

6 (*a*) T. Sturm, W. Weissensteiner, F. Spindler, K. Mereiter, A. M. López-Agenjo, B. R. Manzano and F. A. Jalón, *Organometallics*, 2002, **21**, 1766; (*b*) P. Liptau, T. Seki, G. Kehr, A. Abele, R. Fröhlich, G. Erker and

S. Grimme, *Organometallics*, 2003, **22**, 2226; (*c*) P. Liptau, L. Tebben, G. Kehr, R. Fröhlich, G. Erker, F. Hollmann and B. Rieger, *Eur. J. Org. Chem.*, 2005, 1909.

7 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52.

8 C. Bianchini, G. Lenoble, W. Oberhauser, S. Parisel and F. Zanobini, *Eur. J. Inorg. Chem.*, 2005, 4794.

9 C. Bianchini, H. M. Lee, A. Meli, S. Moneti, F. Vizza, M. Fontani and P. Zanello, *Organometallics*, 1999, **32**, 4183.

10 P. Brüggeller, G. Czermak and W. Oberhauser, unpublished results.

11 C. Bianchini, A. Meli and A. Traversi, Ital. Patent FI A000025, 1997.

12 (*a*) W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81; (*b*) R. Morassi and L. Sacconi, *J. Chem. Soc. A*, 1971, 492.

13 K. B. Wiberg and B. R. Lowry, *J. Am. Chem. Soc.*, 1963, **85**, 3188.

14 (*a*) Z. Otwinowski and W. Minor, in *Methods in Enzymology, Macromolecular Crystallography, Part A*, ed. C. W. Carter Jr. and R. M. Sweet, Academic Press, New York, 1997, vol. 276, pp. 307–326; (*b*) G. M. Sheldrick, *SADABS, Program for Empirical Absorption Corrections*, University of Göttingen, Göttingen, Germany, 1986; (*c*) G. M. Sheldrick, *SHELXL 97, A Computer Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1997; (*d*) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 83; (*e*) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Gagliardi, A. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115; (*f*) M. N. Burnett and C. K. Johnson, *ORTEP-3, Report ORNL-6895*, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.

15 (*a*) J. G. Verkade and L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, Organic and Metal Complexes*, VCH, 1987; (*b*) L. D. Quin and K. A. Mesch, *J. Chem. Soc., Chem. Commun.*, 1980, 959.

16 (*a*) M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Chem. Soc., Dalton Trans.*, 2001, 355; (*b*) H. Schmidbaur and T. Costa, *Chem. Ber.*, 1981, **114**, 3063; (*c*) H. Schmidbaur, S. Gamper, C. Paschalidis, O. Steigelmann and G. Müller, *Chem. Ber.*, 1991, **124**, 1525; (*d*) H. Schmidbaur and U. Deschler, *Chem. Ber.*, 1981, **114**, 2491.

17 (*a*) G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc.*, 1975, **97**, 1059; (*b*) W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.

18 P. J. Carroll and D. D. Titus, *J. Chem. Soc., Dalton Trans.*, 1977, 824.

19 I. M. Angulo, E. Bouwman, S. M. Lok, M. Lutz, W. P. Mul and A. L. Spek, *Eur. J. Inorg. Chem.*, 2001, 1465.

20 (*a*) J. Bakos, I. Tóth, G. Szalontai, V. Flp and B. Heil, *J. Organomet. Chem.*, 1989, **371**, 101; (*b*) J. Bakos, I. Tóth, B. Heil, G. Szalontai, L. Párkányi and V. Flp, *J. Organomet. Chem.*, 1989, **370**, 263; (*c*) J. L. Portscheller, S. E. Lilley and H. C. Malinakova, *Organometallics*, 2003, **22**, 2961; (*d*) E. Farkas, L. Kollár, M. Moret and A. Sironi, *Organometallics*, 1996, **15**, 1345; (*e*) P. A. MacNeil, N. K. Roberts and B. Bosnich, *J. Am. Chem. Soc.*, 1981, **103**, 2273.

21 P. B. Hitchcock, B. Jacobsen and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2043.

22 (*a*) A. Vavasori, L. Toniolo and G. Cabinato, *J. Mol. Catal. A: Chem.*, 2004, **215**, 63; (*b*) A. Vavasori, L. Toniolo, G. Cabinato and F. Visentin, *J. Mol. Catal. A: Chem.*, 2003, **204–205**, 295.

23 (*a*) V. N. Zudin, V. D. Chinakov, V. M. Nekipelov, V. A. Likholobov and Y. I. Yermakov, *J. Organomet. Chem.*, 1985, **289**, 425; (*b*) V. N. Zudin, G. N. Ll'inich, V. A. Likholobov and Y. I. Yermakov, *J. Chem. Soc., Chem. Commun.*, 1984, 545.

24 (*a*) G. Verspui, G. Papadogianakis and R. A. Sheldon, *Chem. Commun.*, 1998, 401; (*b*) C. Bianchini, H. M. Lee, A. Meli, S. Moneti, V. Patinec, G. Petrucci and F. Vizza, *Macromolecules*, 1999, **32**, 3859.

25 M. A. Zuideveld, P. C. J. Kamer, P. W. N. M. van Leeuwen, P. A. A. Klusener, H. A. Stil and C. F. Roobeek, *J. Am. Chem. Soc.*, 1998, **120**, 7977.

26 (*a*) S. Strömberg, K. Zetterberger and P. E. M. Siegbahn, *J. Chem. Soc., Dalton Trans.*, 1997, 4147; (*b*) L. Fan, A. Krzywicki, A. Somogyvari and T. Ziegler, *Inorg. Chem.*, 1996, **35**, 4003; (*c*) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley and Sons, New York, 1988, p. 38.

27 P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2043.

28 (*a*) K. R. Dunbar and J.-S. Sun, *J. Chem. Soc., Chem. Commun.*, 1994, 2387; (*b*) J.-S. Sun, C. E. Uzelmeier, D. L. Ward and K. R. Dunbar, *Polyhedron*, 1998, **17**, 2049; (*c*) J.-F. Ma, Y. Kojima and Y. Yamamoto, *J. Organomet. Chem.*, 2000, **616**, 149; (*d*) C. Bianchini, W. Oberhauser, manuscript in preparation.

29 To prove that **1b** does not convert into **2b** on dissolution in D_2O–AcOH, a sample of **2b** was independently dissolved in D_2O–AcOH (45 mol% D_2O) in a 5 mm NMR tube. The addition of 2 mol of KCl gave the complete conversion of **2b** into **1b** ($^{31}P\{^1H\}$NMR evidence).

30 J. Vicente and A. Arcas, *Coord. Chem. Rev.*, 2005, **249**, 1135.

31 J. Vicente, A. Arcas, M. A. Blasco, J. Lozano and M. C. Ramírez de Arellano, *Organometallics*, 1998, **17**, 5374.

32 (*a*) T. M. Shryne and H. V. Holler, US Pat. 3984388, 1976; (*b*) E. Drent and M. C. T. De Kock, US Pat. 5688909, 1997; (*c*) E. Drent, US Pat. 4835250, 1989; (*d*) E. Drent and L. Wife, Eur. Pat. Appl. B222454, 1987.

33 J. Van den Broeke, J. J. H. Heeringa, A. V. Chuchuryukin, H. Kooijman, A. M. Mills, A. L. Spek, J. H. van Lente, P. J. A. Ruttino, B. J. Deelman and G. van Koten, *Organometallics*, 2004, **23**, 2287.