

Methoxycarbonylation of styrene to methyl arylpropanoates catalyzed by palladium(II) precursors with 1,1'-bis(diphenylphosphino)metallocenes[☆]

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Abstract

Palladium(II) complexes with 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,1'-bis(diphenylphosphino)octamethylferrocene (dppomf), 1,1'-bis(diphenylphosphino)ruthenocene (dppr) and 1,1'-bis(diphenylphosphino)osmocene (dppo) have been synthesized and used to catalyze the methoxycarbonylation of styrene. Irrespective of the precursor, all the reactions gave methyl phenylpropanoates with prevalence of the linear isomer methyl 3-phenylpropanoate (up to 85% regioselectivity). The highest turnover frequency was obtained with the dppr precursor in the presence of *p*-toluenesulphonic acid co-catalyst (334 mol of styrene converted (mol of catalyst h)⁻¹). A reaction mechanism accounting for both activity and selectivity has been proposed on the basis of operando high-pressure NMR experiments and reactions with model compounds.

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1. Introduction

1,1'-Bis(phosphino)metallocenes constitute a family of potentially chelating tri- and bidentate ligands with many applications in homogeneous catalysis in conjunction with transition metals [1]. The success of these ligands in catalysis is largely due to their unique flexibility that allows one to build up molecular structures with different sandwiched metals and substituents either on the cyclopentadienyl ligands (Cp) or on the phosphorus atoms.

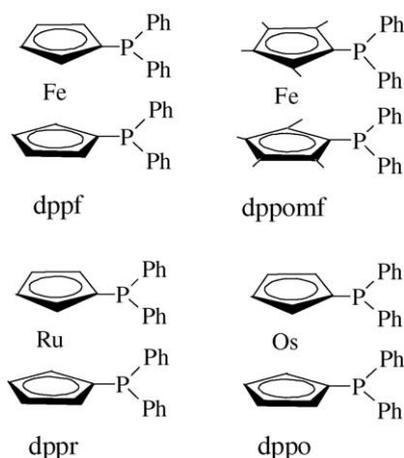
[☆] CCDC-229562 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

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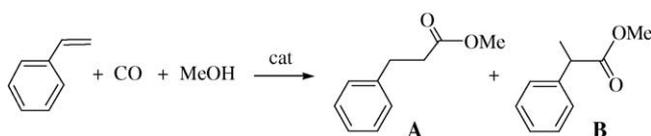
Just to consider the ligands with diphenylphosphino groups, at least four different structural variations (Scheme 1) have been reported as being able to generate catalytically active palladium(II) complexes [1–10].

Most of the research work in catalysis has involved the prototypical ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf). Among the applications of Pd^{II}-dppf complexes in catalysis, carbon–carbon and carbon–nitrogen bond forming reactions are of particular importance. Representative examples include cross-coupling reactions [3], Heck reaction [4], carbonylation of chloroarenes [5], aryl halide amination [6], hydroamination of alkynes [7a], glyoxalate-ene reaction with chiral controllers [8], alternating copolymerization of CO and ethylene [9] and methoxycarbonylation of ethylene [9a,b].

Palladium(II) complexes with 1,1'-bis(diphenylphosphino)octamethylferrocene (dppomf) and 1,1'-bis(diphenylphosphino)osmocene (dppo) have been employed in the



Scheme 1.



Scheme 2.

methoxycarbonylation of ethylene where both precursors proved efficient and selective to give methyl propanoate [9a,b,10].

In this paper, we report a study of the catalytic performance of some known and new palladium(II) complexes with dppf, dppomf, dppr and dppo in the methoxycarbonylation of styrene. Irrespective of the precursor, all the reactions gave methyl phenylpropanoates with prevalence of the linear isomer methyl 3-phenylpropanoate (up to 85% regioselectivity) and quite high turnover frequencies (Scheme 2). However, a significant dependence of the catalytic activity on the 1,1'-bis(diphenylphosphino)metallocene was observed. *Operando* high-pressure NMR experiments (HPNMR), catalytic experiments with classical chelating diphosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) and model reactions with isolated intermediates have contributed to elucidate this *metallocene-effect* as well as gain insight into the overall carbonylation mechanism of styrene.

Preliminary data on the methoxycarbonylation of styrene by dppo-Pd^{II} catalysis have been previously communicated [10].

2. Experimental

2.1. General procedures

All reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk-type techniques. The palladium complexes PdCl(Me)(COD) (COD = cycloocta-1,5-diene) [11], PdCl₂(dppr) [2b], [Pd(H₂O)₂(dppf)](OTs)₂

(1) [9b], [Pd(H₂O)₂(dppomf)](OTs)₂ (2) [9b], [Pd(OTs)(dppo)]OTs (4) [10], [Pd(H₂O)(OTs)(dppe)]OTs (5) [12] and [Pd(H₂O)(OTs)(dppp)]OTs (6) [13] were synthesized according to published procedures. CH₂Cl₂ and diethyl ether were distilled from CaH₂ and LiAlH₄, respectively. All the other reagents and solvents were used as purchased from commercial suppliers. All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Microanalyses were performed in the Laboratory of Microanalysis of the N. Nesmeyanov Institute of Organoelement Compounds. Infrared spectra were recorded on a Specord M-82 spectrophotometer. Conductivities were measured with an Orion model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data [14] were obtained at sample concentrations of ca. 10⁻³ M in nitroethane (ε = 19.7) solutions. Deuterated solvents for routine NMR measurements were dried over molecular sieves. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were obtained on a Bruker ACP 200 spectrometer (200.13, 50.32, and 81.01 MHz, respectively). Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (¹H and ¹³C{¹H} NMR spectra) or 85% H₃PO₄ as an external standard (³¹P{¹H} NMR spectra). The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ICCOM-CNR (Firenze, Italy) [15]. *Caution:* Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes. Carbonylation reactions were performed with a 120 ml stainless steel autoclave, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, a Parr 4842 temperature and pressure controller. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. The GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analysis. The product composition of the catalytic reactions was determined by GC/MS, while the quantification of the products were carried out by GC by using 1,2-dimethoxyethane as the internal standard.

2.2. Catalytic carbonylation of styrene in MeOH

A solution of styrene (4 mmol) in MeOH (20 ml) was introduced by suction into a 120 ml autoclave, previously evacuated by a vacuum pump, containing 0.01 mmol of catalyst precursor along with the desired amounts of TsOH (*p*-toluenesulphonic acid monohydrate) and/or BQ (1,4-benzoquinone). The autoclave was charged with CO to the desired pressure at room temperature and heated to the chosen temperature. As soon as the autoclave reached the desired temperature, the mechanical stirring of the autoclave

was switched on (700 rpm). After the desired time, the reaction was stopped by cooling the autoclave to room temperature by means of an ice-water bath. As the internal temperature of the autoclave reached 0 °C, the unreacted CO was released and 100 μ l of the GC internal standard was added.

2.3. Synthesis of [Pd(H₂O)(OTs)dppr]OTs (**3**)

To a solution of PdCl₂(dppr) (0.51 g, 0.66 mmol) in CH₂Cl₂ (50 ml) was added silver tosylate (0.40 g, 1.43 mmol) at room temperature. After stirring overnight, the mixture was filtered through Celite and the filtrate was concentrated to 4 ml. Addition of diethyl ether (30 ml) led to the precipitation of an orange crystalline product, which was washed with diethyl ether and dried in a stream of nitrogen. Yield 0.60 g (84%). Anal. Calcd. for C₄₈H₄₄O₇P₂PdRuS₂: C, 54.06; H, 4.16. Found: C, 53.66; H, 4.48. Λ_M (nitroethane) = 25 Ω^{-1} cm² mol⁻¹; this value is consistent with a 1:1 electrolyte. ¹H NMR (CD₂Cl₂), δ : 2.32 (s, 6H, Me-OTs), 4.99 (s, 4H, H β -Cp), 5.06 (s, 4H, H α -Cp), 6.09 (s, 2H, H₂O), 6.89 (d, 4H, *J*(HH) = 8.0 Hz, Ar-OTs), 7.31 (d, 4H, *J*(HH) = 8.0 Hz, Ar-OTs), 7.46 (t, 8H, *J*(HH) = 7.4 Hz, *m*-PPh₂), 7.61 (t, 4H, *J*(HH) = 7.4 Hz, *p*-PPh₂), 7.99 (dd, 8H, *J*(HP) = 12.8 Hz, *J*(HH) = 7.4 Hz, *o*-PPh₂). ¹³C{¹H} NMR (CD₂Cl₂), δ : 21.7 (s, Me-OTs), 76.1 (m, |¹*J*(CP) + ²*J*(CP)| = 70.4 Hz, C_{ipso}-Cp), 78.3 (t, *J*(CP) = 4.0 Hz, CH β -Cp), 80.5 (t, *J*(CP) = 6.2 Hz, CH α -Cp), 126.1 (s, CH-OTs), 128.4 (m, |¹*J*(CP) + ²*J*(CP)| = 59.1 Hz, ipso-PPh₂), 129.1 (s, CH-OTs), 129.6 (t, *J*(CP) = 6.1 Hz, *m*-PPh₂), 133.1 (s, *p*-PPh₂), 134.9 (t, *J*(CP) = 6.2 Hz, *o*-PPh₂), 140.8 (s, C_{ipso}-OTs), 142.2 (s, C_{ipso}-OTs). ³¹P{¹H} NMR (CD₂Cl₂), δ : 42.5 (s).

Single crystals of **3** suitable for an X-ray analysis were obtained by slow diffusion of diethyl ether into a CH₂Cl₂ solution of **3** at room temperature.

2.4. Stability study of the catalyst precursors **1–4** in MeOH by NMR spectroscopy

Typically, a sample of the appropriate compound (0.012 mmol) was dissolved in MeOH-*d*₄ (1 ml) at room temperature. The solution was transferred into a 5 mm NMR tube that was then placed into the NMR probe at room temperature. ³¹P{¹H} and ¹H NMR spectra were acquired every 30 min for 6 h. The results of this study are reported in Section 3.2.

Selected ¹H NMR data for the complexes seen by NMR during these experiments. Compound **2**, δ : 1.32 (s, 12H, Me-Cp*), 1.49 (s, 12H, Me-Cp*); compound **3**, δ : 4.85 (br s, H β -Cp), 5.09 (br s, H α -Cp); compound **4**, δ : 4.76 (br s, α H-Cp), 5.84 (br s, H β -Cp); [Pd(dppomf)]₂(OTs)₂ (**7**), δ : 0.51 (br s, 24H, Me-Cp*), 1.86 (br s, 24H, Me-Cp*); [Pd(dppr)]₂(OTs)₂ (**8**), δ : 4.30 (br s, H α -Cp), 5.55 (br s, H β -Cp); [Pd(dppo)]₂(OTs)₂ (**9**), δ : 4.49 (br s, H α -Cp), 5.58 (br s, H β -Cp); [Pd(H₂O)₂(dppo)](OTs)₂ (**10**), δ : 4.98 (br s, H β -Cp), 5.38 (br s, H α -Cp).

2.5. HPNMR study of the carbonylation of styrene catalyzed by **1–4** in TsOH containing MeOH

The reaction was followed by variable-temperature ³¹P{¹H} and ¹H NMR spectroscopy. A 10 mm sapphire HP-NMR tube was charged sequentially with solutions of TsOH (19 mg, 0.10 mmol) in MeOH-*d*₄ (1 ml) and **3** (10.7 mg, 0.01 mmol) (or **1**, **2**, **4**) in MeOH-*d*₄ (1 ml) under nitrogen at room temperature. The tube was placed into a NMR probe at room temperature (³¹P{¹H} NMR singlet at δ : 44.4). Addition of a 100-fold excess of styrene (114 μ l, 1 mmol) caused no change in the ³¹P{¹H} NMR spectrum. In contrast, a dramatic change occurred when the tube was pressurized with 14 bar of CO at room temperature. The results of this study are reported in Section 3.3.

Selected NMR data for [Pd₂(μ -H)(μ -CO)(dppo)₂]OTs (**14**). ³¹P{¹H} NMR (20 °C), δ : 24.4 (s). ³¹P NMR (20 °C), δ : 24.4 (d, *J*(PH) = 42 Hz). ¹H NMR (20 °C), δ : -7.14 (quintet, *J*(HP) = 42.3 Hz, μ -H), 4.71 (br s, H β -Cp), 5.06 (br s, H α -Cp).

2.6. Synthesis of [Pd(dppr)]₂(OTs)₂ (**8**)

A solution of **3** (120 mg, 0.11 mmol) in MeOH (5 ml) was allowed to stand under stirring for 10 h at room temperature. During this time there was a color change from yellow to dark red. The solution was concentrated to dryness and the residue was dissolved in 4 ml of CH₂Cl₂. The formed Pd black was separated by filtration through Celite and the resulting clear filtrate was concentrated to half of its volume. Addition of 4 ml of a 1:1 mixture of diethyl ether and *n*-hexane led to the formation of a dark red powder, which was filtered off and washed with *n*-hexane. Yield: 54 mg (69%). Anal. Calcd. for C₈₂H₇₀O₆P₄S₂Ru₂Pd₂: C, 56.14; H, 4.02. Found: C, 56.30; H, 4.10. ¹H NMR (CD₂Cl₂), δ : 2.30 (s, 6H, Me-OTs), 4.27 (br s, 8H, H α -Cp), 5.73 (br s, 8H, H β -Cp), 6.7–7.8 (m, 48H, Ph + Ar-SO₃). ¹³C{¹H} NMR (CD₂Cl₂), δ : 21.6 (s, Me-OTs), 63.1 (m, C_{ipso}-Cp), 75.6 (br s, CH α -Cp), 82.7 (br s, CH β -Cp), 126.6 (s, CH-OTs), 123.4 (m, ipso-PPh₂), 129.0 (s, CH-OTs), 129.6 (t, *J*(CP) = 6.1 Hz, *m*-PPh₂), 132.7 (s, *p*-PPh₂), 134.2 (t, *J*(CP) = 6.3 Hz, *o*-PPh₂), 140.2 (s, C_{ipso}-OTs), 142.8 (s, C_{ipso}-OTs). ³¹P{¹H} NMR (CD₂Cl₂), δ : 6.3 (s).

2.7. Reaction of **4** with water: synthesis of [Pd(H₂O)₂(dppo)](OTs)₂ (**10**)

Water (500 μ l) was pipetted into a stirred CH₂Cl₂ (5 ml) solution of **4** (114 mg, 0.10 mmol). After 1 h, the solution was concentrated under vacuum to give **10** as a solid residue. Anal. Calcd. for C₄₈H₄₆O₈OsP₂PdS₂: C, 49.12; H, 3.95. Found: C, 49.01; H, 3.92. ¹H NMR (CD₂Cl₂), δ : 2.31 (s, 6H, Me-OTs), 4.32 (s, 4H, H₂O), 5.18 (br s, 4H, H β -Cp), 5.29 (br s, 4H, H α -Cp), 6.9–8.0 (m, 28H, Ph + Ar-SO₃). Λ_M (nitroethane) = 30 Ω^{-1} cm² mol⁻¹; this value is consistent with a 1:1 electrolyte.

2.8. Synthesis of PdCl(Me)(dppr) (**15**)

A solid sample of PdCl(Me)(COD) (66 mg, 0.25 mmol) was added to a stirred solution of dppr (150 mg, 0.25 mmol) in CH₂Cl₂ (20 ml) at room temperature. After 20 min, the solution was concentrated to half of its original volume. Addition of a 1:1 mixture of diethyl ether and *n*-pentane (20 ml) led to the precipitation of **15** as a white microcrystalline solid, which was filtered off and washed with *n*-pentane. Yield 140 mg (74%). Anal. Calcd. for C₃₅H₃₁ClP₂PdRu: C, 55.57; H, 4.13. Found: C, 55.30; H, 3.99. ¹H NMR (CD₂Cl₂), δ: 0.61 (dd, 3H, *J*(HP) = 7.7 Hz, *J*(HP) = 5.0 Hz, Pd-Me), 4.01 (s, 2H, Hβ-Cp), 4.61 (s, 2H, Hβ-Cp), 4.85 (s, 2H, Hα-Cp), 4.93 (s, 2H, Hα-Cp), 7.2–8.0 (m, 20H, Ar). ³¹P{¹H} NMR (CD₂Cl₂), δ: 14.0 (d, ²*J*(PP) = 28.9 Hz), 37.8 (d).

2.9. Synthesis of [PdMe(dppr)]B(Ar')₄ (**16**)

To a stirred solution of the chloride derivative **15** (150 mg, 0.20 mmol) in CH₂Cl₂ (15 ml) was added NaB(Ar')₄ (Ar' = 3,5-(CF₃)₂C₆H₃, 177 mg, 0.20 mmol) at room temperature. After 15 min, the precipitated NaCl was filtered off and the resulting solution was concentrated to dryness. Addition of a 1:10 mixture of diethyl ether/*n*-pentane (15 ml) precipitated pale-yellow crystals of **16**, which were collected by filtration and washed with *n*-pentane. Yield 210 g (66%). Anal. Calcd. for C₆₇H₄₃BF₂₄P₂PdRu: C, 50.79; H, 2.74. Found: C, 50.00; H, 2.66. ¹H NMR (CD₂Cl₂), δ: 2.02 (t, 3H, *J*(HP) = 4.7 Hz, Pd-Me), 3.96 (s, 4H, Hα-Cp), 5.31 (s, 4H, Hβ-Cp), 7.4–7.9 (m, 32H, Ar). ³¹P{¹H} NMR (CD₂Cl₂), δ: –12.4 (s).

2.10. Synthesis of [Pd(COMe)(dppr)]B(Ar')₄ (**17**)

Carbon monoxide was bubbled through a solution of **16** (100 mg, 0.06 mmol) in CH₂Cl₂ (10 ml) for 5 min at room temperature. During this time the color of the solution turned from yellow to red. The solution was then cooled to –20 °C and pumped to dryness to give **17** as a red powder. Yield 90 mg (89%). Anal. Calcd. for C₆₈H₄₃BF₂₄OP₂PdRu: C, 50.29; H, 2.71. Found: C, 50.10; H, 2.56. IR (nujol mull, cm⁻¹): 1707 (CO). ¹H NMR (CD₂Cl₂), δ: 2.75 (t, 3H, *J*(HP) = 1.7 Hz, COMe), 4.24 (s, 4H, Hα-Cp), 5.18 (s, 4H, Hβ-Cp), 7.4–7.8 (m, 32H, Ar). ³¹P{¹H} NMR (CD₂Cl₂), δ: –13.8 (s).

2.11. Reaction of **17** with styrene

A solution of **17** (20 mg, 0.013 mmol) and a 20-fold excess of styrene (30 μl, 0.26 mmol) in CD₂Cl₂ (1 ml) were transferred into a 5 mm NMR tube at room temperature. ³¹P{¹H} and ¹H NMR spectra were acquired at room temperature every hour. No new product was detected in an arch of 24 h.

2.12. Reaction of **17** with MeOH: synthesis of [Pd₂(μ-H)(μ-CO)(dppr)₂]B(Ar')₄ (**13**)

MeOH (200 μl) was syringed into a 10 mm NMR tube containing a solution of **17** (20 mg, 0.013 mmol) in CD₂Cl₂ (1.5 ml) under a stream of CO at room temperature. After 30 min, ¹H and ³¹P{¹H} NMR spectra showed the almost quantitative formation of the binuclear complex **13** and methyl acetate. ¹H NMR (CD₂Cl₂), δ: –7.01 (quintet, ¹H, *J*(HP) = 41.6 Hz, μ-H), 4.43 (s, 8H, Hβ-Cp), 4.72 (s, 8H, Hα-Cp), 7.1–7.8 (m, 52H, Ph + Ar). ³¹P{¹H} NMR (CD₂Cl₂), δ: 19.7 (s). IR (CH₂Cl₂, cm⁻¹): 1851 (CO).

2.13. X-ray data collection and structure determination of **3**

A suitable single crystal of **3** was analyzed with a Bruker Smart 1000 CCD diffractometer. The diffraction data were collected at 120 K. Atomic scattering with anomalous dispersion corrections were taken from Ref. [16]. The structure was solved applying direct methods and refined by full-matrix least squares against *F*² using the SHELXTL-97 package. The data were corrected for Lorentz and polarization effects. All of the non-hydrogen atoms were found through a sequence of *F*₀ Fourier maps and refined initially with isotropic thermal parameters and finally with anisotropic thermal parameters. All of the hydrogen atoms were introduced at calculated positions and refined by applying the riding model.

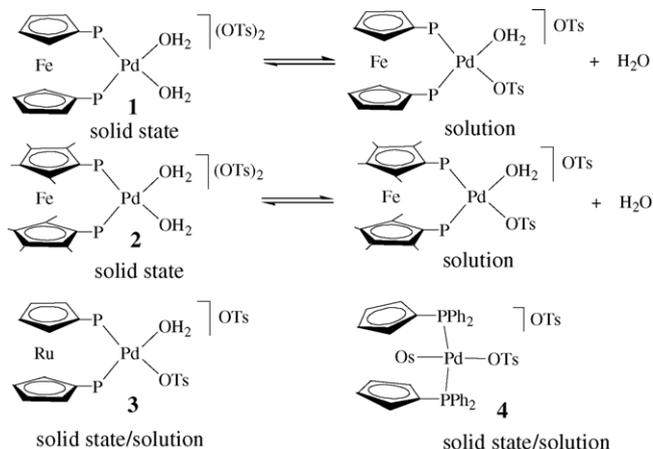
3. Results and discussion

3.1. Synthesis of the catalyst precursors

The palladium(II) complexes [Pd(H₂O)₂(dppf)](OTs)₂ (**1**) [9b], [Pd(H₂O)₂(dppomf)](OTs)₂ (**2**) [9b], [Pd(H₂O)(OTs)(dppr)]OTs (**3**) and [Pd(OTs)(dppo)]OTs (**4**) [10] were obtained by reaction of the corresponding bis-chloride derivative (P–P)PdCl₂ with Ag(OTs) in dichloromethane, followed by ethyl ether addition.

X-ray diffraction analyses reported elsewhere for the triflate analogues of **1** and **2**, **1'** and **2'** showed the cations [Pd(H₂O)₂(P–P)]²⁺ to contain the palladium centers coordinated by two *cis* water molecules taken from adventitious moisture [9b], which reflects the low coordinating ability of sulphonate anions. However, the molar conductivity data of **1** and **2** as well as those of **1'** and **2'** in polar solvents such as nitroethane (ε = 19.7) [9b] are consistent with the formation of monocationic species with one tosylate (or triflate) ion and one water molecule coordinated *trans* to the phosphorus atoms (Scheme 3).

A single-crystal X-ray analysis and conductivity measurements show that the new ruthenocenyl complex **3** contains a *k*²-P,P metallocenyl ligand, one tosylate anion and one water molecule coordinated to the palladium in both the solid state and solution (Scheme 3). An ORTEP drawing of the com-



Scheme 3.

plex cation in **3** [Pd(H₂O)(OTs)(dppr)]⁺ is provided in Fig. 1, while crystallographic data and selected metrical parameters are listed in Tables 1 and 2, respectively. The palladium center is square planarly coordinated with a P(1)–Pd–P(2) crystallographic bite angle of 97.47(4)°, which is slightly smaller than that in the corresponding neutral dichloride precursor (100.02(17) Å) [17]. It is worth noticing that the crystallographic P–Pd–P bite angles in the dppf and dppomf derivatives **1'** and **2'** are 96.37(1)° and 101.3(1)°, respectively [9b].

The distances of ruthenium to the centroids of the Cp rings in **3** are practically identical to each other (1.806(5) and 1.807(5) Å) and match well those in the free ligand (1.803(4) and 1.808(4) Å) [2a]. The Cp rings are planar and tilted towards the palladium atom. The angle between the plane normals related to the Cp rings is 9.0°, while the dihedral angle

Table 1
Crystallographic data for **3**

| | |
|---|--|
| Molecular formula | C ₄₈ H ₄₄ O ₇ P ₂ PdRuS ₂ |
| Formula weight (g mol ⁻¹) | 1066.43 |
| Crystal color, shape | Orange, prism |
| Crystal dimensions (mm) | 0.30 × 0.20 × 0.20 |
| <i>T</i> (K) | 120(1) |
| Crystal system | Orthorhombic |
| Space group | <i>Pbca</i> |
| <i>a</i> (Å) | 20.504(3) |
| <i>b</i> (Å) | 20.372(3) |
| <i>c</i> (Å) | 20.904(3) |
| α (°) | 90.000 |
| β (°) | 90.000 |
| γ (°) | 90.000 |
| <i>V</i> (Å ³) | 8732(2) |
| <i>Z</i> | 8 |
| <i>F</i> (000) | 4320 |
| ρ (calcd.) (g cm ⁻³) | 1.622 |
| λ (Mo Kα) (Å) | 0.71072 |
| μ (mm ⁻¹) | 0.979 |
| θ range (°) | 2.0–30.0 |
| Index ranges | –28 ≤ <i>h</i> ≤ 28 –25 ≤ <i>k</i> ≤ 21 –29 ≤ <i>l</i> ≤ 29 |
| Number of collected reflections | 12189 |
| Number of independent reflections | 7849 |
| <i>R</i> _{int} | 0.0542 |
| Number of data/restraints/parameters | 7849/0/550 |
| Refinement method | Full-matrix least-squares on <i>F</i> ² |
| GOF on <i>F</i> ² | 1.015 |
| Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)] | 0.0573, 0.1215 |
| Final <i>R</i> ₁ , <i>wR</i> ₂ indices (all data) | 0.0887, 0.1304 |
| Peak, hole in final difference map (e Å ⁻³) | 2.03, –0.68 |

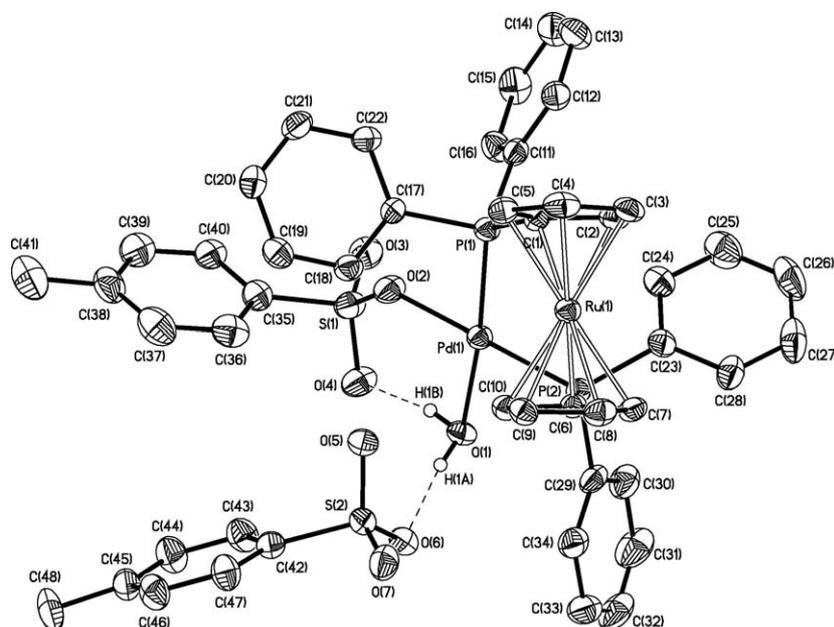
Fig. 1. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 50% probability level.

Table 2
Selected geometrical parameters for **3**

| | |
|---|-------------------|
| Bond lengths (Å) | |
| Ru(1)–Cp(1) ^a | 1.806(5) |
| Ru(2)–Cp(2) ^b | 1.807(5) |
| Ru(1)–C _{Cp} | 2.121(4)–2.223(4) |
| Ru(1)···Pd(1) | 4.215(5) |
| Pd(1)–P(1) | 2.289(1) |
| Pd(1)–P(2) | 2.240(1) |
| Pd(1)–O(1) | 2.102(3) |
| Pd(1)–O(2) | 2.126(3) |
| P–C _{Cp} | 1.799(5)–1.804(4) |
| P–C _{Ph} | 1.809(5)–1.819(5) |
| P1···P2 | 3.404(1) |
| Bond angles (°) | |
| O(1)Pd(1)O(2) | 88.23(11) |
| P(1)Pd(1)P(2) | 97.47(4) |
| P(1)Pd(1)O(1) | 174.00(9) |
| P(2)Pd(1)O(2) | 174.62(10) |
| P(1)Pd(1)O(2) | 86.06(8) |
| P(2)Pd(1)O(1) | 88.36(8) |
| Dihedral and pseudotorsion angles (°) | |
| P(1)Cp(1)Cp(2)P(2) ^{a,b} | 33.8 |
| C(1)Cp(1)Cp(2)C(6) ^{a,b} | 34.1 |
| RuP(1)P(2)/Pd(1)P(1)P(2) | 36.3 |
| α _{Cp} ^c | –9.0 |
| ΔP(1) ^d | 0.048 |
| ΔP(2) ^d | 0.194 |
| Bond lengths and angles (intramolecular hydrogen bond) (Å, °) | |
| H(1B)–O(4) | 1.90 |
| H(1B)–O(1) | 0.77 |
| O(1)···O(4) | 2.622 |
| O(1)H(1B)O(4) | 157 |
| Bond lengths and angles (intermolecular hydrogen bond) (Å, °) | |
| H(1A)–O(6) | 1.78 |
| H(1A)–O(1) | 0.82 |
| O(1)···O(6) | 2.594 |
| O(1)H(1A)O(6) | 172 |

^a Cp(1) denotes the center of the C(1)–C(5) Cp ligand.

^b Cp(2) denotes the center of the C(6)–C(10) Cp ligand.

^c Dihedral angle between the Cp planes. The negative value corresponds to the inclination of the Cp rings toward the Pd atom.

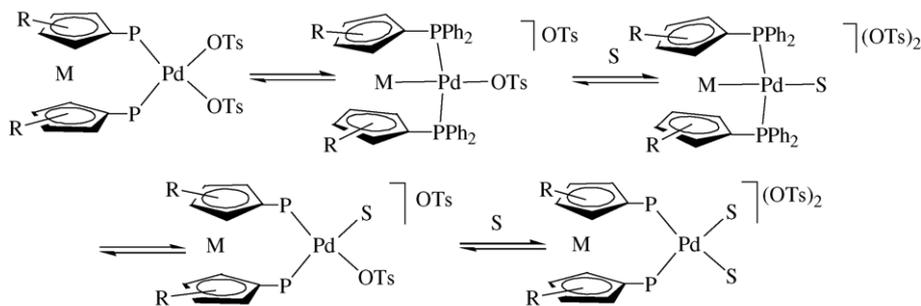
^d Deviations of the P atom from the corresponding Cp ring. The positive value corresponds to the deviation toward the Ru atom.

P(1)–Cp(1)–Cp(2)–P(2) exhibits a value of 33.8°, which is comparable to that found in the corresponding neutral dichloride structure 34.1° [17]. The coordinated water molecule participates in both intra- and intermolecular hydrogen bonds, with O···H distances of 1.90 and 1.78 Å, respectively, with the oxygen atoms of both coordinated and free tosylate anions [13b].

Overall, the coordination geometry of **3** is similar to that of **1'**. Unlike the latter complex, **3** exhibits two rather different Pd–P bond lengths, Pd–P(1) 2.289(1) Å and Pd–P(2) 2.240(1) Å, which may reflect the presence of two different ligands *trans* to phosphorus as well as solid state effects due to the H-bonding network mentioned above.

The osmocenyl complex **4** contains, in both the solid state and solution, a *k*³-P,P,Os osmocenyl ligand with a dative Os–Pd bond and one tosylate group *trans* to Os (Scheme 3) [10]. The major propensity of dppo than dppf or dppr to act as tridentate ligand has been related to the higher electron density of the osmium center, which allows it to compete with both tosylate and water molecules for coordination to palladium (the nucleophilicity of the metallocene metal decreases in the order Os > Ru > (Cp*)Fe > (Cp)Fe in fact [9a,b,10]). On the other hand, it is noteworthy that both strong anionic nucleophiles [10] and even water molecules (*vide infra*), if provided in large excess, can lead to the formation of *k*²-P,P dppo palladium complexes. Indeed, we have found that the addition of water to CH₂Cl₂ solutions of **4** yields the bis-solvento complex [Pd(OH)₂(dppo)](OTs)₂ (**10**). Dppf, dppomf and dppr can bind palladium in the *k*³-P,P,M mode too, yet preferentially in conjunction with a fourth ligand featured by either a large size (e.g., PPh₃: dppf [18], dppomf [9b], dppr [9d], dppo [9d]) or an electron-withdrawing character (e.g., –C(O)OR: dppomf [9a] and –C(O)R: dppomf [9a], dppr [this work], dppo [10]).

In conclusion, the solution structures of **1–3** or **4** depend on a complex web of factors, which include the electronic and steric features of the complementary ligand(s), the nature of the sandwiched metal, the solvent and the water contents in the latter. Scheme 4 provides a picture of the possible equilibria and coordination structures exhibited by **1–4** in reagent grade MeOH.



M = Fe, Ru, Os; R = H, Me; S = solvent

Scheme 4.

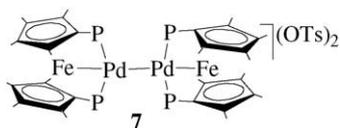
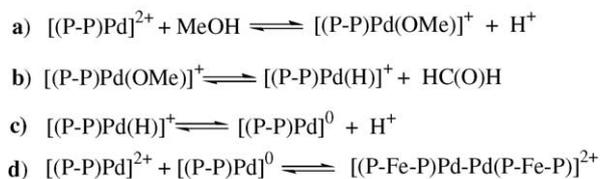
3.2. Stability study of the catalyst precursors 1–4 in MeOH by NMR spectroscopy

Typically, a sample of the appropriate compound was dissolved in MeOH-*d*₄ at room temperature. The solution was transferred into a 5 mm NMR tube that was then placed into the NMR probe at room temperature. ³¹P{¹H} and ¹H NMR spectra were acquired every 30 min for 6 h. The dppf derivative **1** (³¹P{¹H} NMR, δ: 47.9) exhibited no appreciable transformation during the course of the experiment [9a]. In contrast, just the first ³¹P{¹H} NMR spectrum showed the partial conversion (14%) of the dppomf complex **2** (δ: 71.6) into the palladium(I) binuclear complex [Pd(dppomf)]₂(OTs)₂ (**7**, δ: –1.3), which contains a *k*³-P,P,Fe dppomf ligand [9a]. Although the **2/7** ratio did not appreciably vary during the experiment, the intensity of the ³¹P NMR signals of these two compounds decreased at least by half. Palladium metal was observed to settle on the bottom of the NMR tube, however in trace amount, which does not justify the intensity decrease of **2** and **7**. It is therefore likely that other species are formed from either **2** or **7**, each in a too low concentration to be seen by NMR spectroscopy.

The formation of **7**, in analogy with that of structurally similar binuclear Pd^I complexes with chelating diphosphines (P–P) [9a], has been proposed to involve the coupling of (dppomf)Pd^{II} and (dppomf)Pd⁰ moieties, the latter being generated by palladium-promoted oxidation of MeOH to formaldehyde (Scheme 5, steps a–d) [19,20].

A similar behavior was displayed also by the ruthenium analogue **3** (³¹P{¹H} NMR, δ: 44.4). In fact, the binuclear complex [Pd(dppr)]₂(OTs)₂ (**8**) (³¹P{¹H} NMR, δ: 6.8, see below for the independent synthesis and NMR characterization) appeared just in the first spectrum (20%). The stability of the **3/8** system seems to be a little higher than that of the dppomf system as the intensity of the NMR signals of the two dppr compounds decreased by about one-fourth only within the same residence time.

In the case of **4**, the NMR picture was more complex. Indeed, the first ³¹P{¹H} NMR spectrum showed, besides the signals due to the precursor [10] (δ: –17.5, 92%) and to the palladium(I) binuclear complex [Pd(dppo)]₂(OTs)₂ (**9**) (δ: 2.3, 3%), a third signal at δ: 50.4 (5%) due to the bis-



Scheme 5.

aquo complex [Pd(OH₂)₂(dppo)](OTs)₂ (**10**) (see below for its independent synthesis and characterization). With time, the **4/10** ratio remained practically constant, while the concentration of the **4/9/10** system, as a whole, decreased by ca. 60% in 6 h. Complex **10** contains a *k*²-P,P dppo ligand as shown by the small difference between the chemical shifts of the α and β hydrogen atoms of the Cp rings (Δδ(MeOH-*d*₄) = 0.40) [9a,b]. In compounds **4** and **9**, both featured by a *k*³-P,P,Os dppo ligand, the difference is much higher (Δδ(MeOH-*d*₄) = 1.08 and 1.09, respectively) [9a,b,10].

In conclusion, unlike **1**, the metallocene palladium(II) precursors **2–4** tend to decompose spontaneously in MeOH. Roughly, the stability of the precursors decreases in the order **1** > **3** > **4** ≥ **2**. This degradation can be inhibited by adding TsOH. Indeed, as shown by independent NMR experiments, the addition of an excess of TsOH to the mixtures of products obtained by dissolving **2**, **3** or **4** in MeOH-*d*₄ regenerated **2** and **3** and gave a mixture of **4** and **10**. Consistently, no formation of palladium(I) binuclear species was observed by NMR spectroscopy upon dissolution of the palladium(II) precursors **2–4** in MeOH-*d*₄ acidified with TsOH.

3.3. HPNMR study of the carbonylation of styrene catalyzed by 3 in TsOH containing MeOH

Some carbonylation reactions of styrene in the presence of **1–4** were followed by variable-temperature ³¹P{¹H} and ¹H NMR spectroscopy using a 10 mm-OD sapphire HPNMR tube. A sequence of selected ³¹P{¹H} NMR spectra relative to the reaction assisted by **3** is reported in Fig. 2. A tube was charged sequentially with MeOH-*d*₄ solutions of TsOH

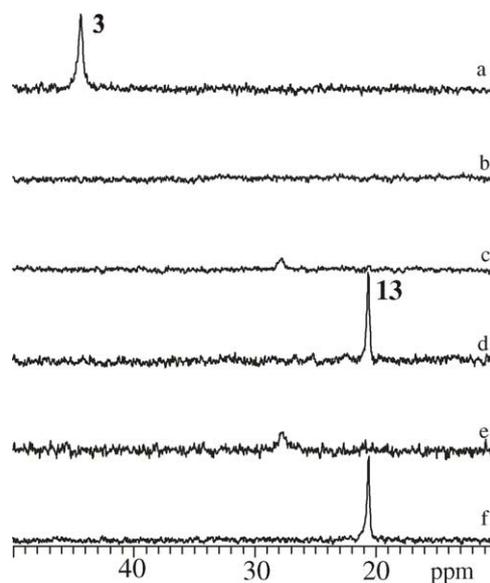


Fig. 2. Variable-temperature ³¹P{¹H} NMR study (sapphire tube, MeOH-*d*₄, 81.01 MHz) of the carbonylation reaction of styrene catalyzed by **3**: (a) **3** in the presence of TsOH (10 equiv) and styrene (100 equiv) under nitrogen at room temperature; (b) after the tube was pressurized with 14 bar of CO at room temperature; (c) at 80 °C; (d) after the tube was cooled to room temperature; (e) at 80 °C; (f) after the tube was cooled to room temperature.

(10 equiv) and **3** under nitrogen at room temperature. The tube was placed into a NMR probe at room temperature (trace a, $^{31}\text{P}\{^1\text{H}\}$ NMR singlet at δ : 44.4). Addition of a 100-fold excess of styrene caused no change in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. In contrast, when the tube was pressurized with 14 bar of CO at room temperature, a highly noisy baseline with no discrete signal appeared immediately (trace b), which suggests the formation of species in fast dynamic exchange.

The temperature was then increased gradually to 50 °C and then to 80 °C. At 50 °C a broad $^{31}\text{P}\{^1\text{H}\}$ NMR signal began to appear at ca. δ : 28, which became more intense at 80 °C (trace c). On cooling to room temperature, the signal transformed into a new one (trace d) at δ : 20.6 due to the μ -hydrido- μ -carbonyl complex $[\text{Pd}_2(\mu\text{-D/H})(\mu\text{-CO})(\text{dppr})_2]\text{OTs}$ (**13**) (see below for its independent synthesis and characterization). The ^1H NMR spectrum showed the formation of both linear and branched esters. To verify the relationship, if any, between **13** and the species responsible for the broad signal at δ : 28, the tube was heated again to 80 °C: the broad signal reformed (trace e). After 15 min, the probe-head was allowed to cool again to room temperature: **13** became the only visible species (trace f). This behavior may be explained by the formation of catalytically active species in fast dynamic exchange with **13** at temperatures higher than 50 °C. Noteworthy, isolated **13** proved to be stereochemically rigid in MeOH- d_4 up to 100 °C. Consistent with the formation of catalytically active species above 50 °C, a comparison between the ^1H NMR spectra recorded at room temperature before and after the last heating to 80 °C showed an increase in the formation of esters. Analysis of the solution by GC confirmed the formation of deuterated samples of both linear and branched esters.

Similar NMR pictures were obtained when the precursors **1**, **2** and **4** were used in the place of **3**: the μ -hydrido- μ -carbonyl complexes **11** (dppf) [9a], **12** (dppomf) [9a], and **14** (dppo) were the only well-defined species detected by NMR spectroscopy at room temperature, while broad humps were observed at high temperature.

3.4. Catalytic studies

3.4.1. Reactions catalyzed by **1–4**

The carbonylation of vinyl aromatics catalyzed by palladium(II) precursors in polar media provides an effective method for both the laboratory and large-scale production of either arylpropionic acids (hydroxycarbonylation) or alkyl arylpropanoates (alkoxycarbonylation) [21]. The use of **1–3** or **4** as catalyst precursors for the methoxycarbonylation of the prototypical vinyl aromatic, styrene led to the formation of mixtures of the saturated monoesters methyl 3-phenylpropanoate (linear ester, **A**) and methyl 2-phenylpropanoate (branched ester, **B**) (Scheme 2) [22].

Experimental details and catalytic data are provided in Table 3. Irrespective of the catalyst precursors and of the experimental conditions, the reactions were featured by the prevalent formation of the linear ester with regioselectivity

values in the range from 77% (with precatalysts **1**, **3**, and **4**) to 84% (with precatalyst **2**). The highest turnover frequency (TOF) of 334 mol of styrene converted (mol of catalyst h) $^{-1}$ was obtained with the dppr derived catalyst. As a whole, these results are of some relevance as they lie in the upper range of activity and regioselectivity for this kind of reactions [22].

A perusal of the data reported in Table 3 shows that only the dppf precursor **1** converts a significant amount of styrene in the absence of acid co-reagents (29.3% in 1 h at 42 bar CO and 100 °C, run 1). Under these conditions, all the other precursors were much less active than **1**, with conversions below 5% (runs 8, 16, 27). For all catalysts, a remarkable increase in productivity, accompanied by a less important increase in regioselectivity (1–2%), was observed by adding an excess of TsOH. Indeed, the addition of 40 equiv of TsOH made **1–4** capable of converting 81.1, 50.6, 85.8 and 65.4% styrene into **A** + **B**, respectively (runs 3, 11, 19, 29). Higher concentrations of acid increased neither the conversion nor the selectivity. Overall, these results reflect the chemical stability of the four precursors in either neutral and acid-containing media as determined by operando NMR spectroscopy (vide infra). Under acidic conditions, the catalysts were still active within 2 h with no apparent change in selectivity (runs 5, 13, 25, 31).

A secondary, undesired, effect caused by the use of TsOH co-catalyst was the formation of the ether PhCH(Me)OMe (**C**), in consequence of the acid-catalyzed addition of MeOH to the olefin double bond of styrene. This drawback is not very important as the yields in **C** never exceeded 3% even with 40 equiv of TsOH at 100 °C. Independent experiments of styrene carbonylation in the absence of palladium catalyst, yet with added TsOH, showed the formation of **C** in 2–3% yield, depending on both acid concentration and temperature. Neither **A** nor **B** were produced by substituting **C** for styrene in the carbonylation reactions, which rules out any role of **C** as intermediate to **A** and **B**.

In an attempt of determining the best experimental conditions for high activity and selectivity as well as rationalizing the reaction mechanism of the carbonylation of styrene catalyzed by **1–4**, a number of reactions were carried out varying some experimental parameters such as pressure of CO, temperature, reaction time and concentration of added oxidant (1,4-benzoquinone, BQ).

In the CO pressure range from 14 to 42 bar, the conversion of styrene increased steadily with no change in selectivity (runs 4, 3/12, 11/23, 19, 21/29, 30). Higher pressures (e.g., 63 bar) did not affect the selectivity, yet a decrease productivity was observed, which may reflect competition of CO with styrene for coordination to palladium.

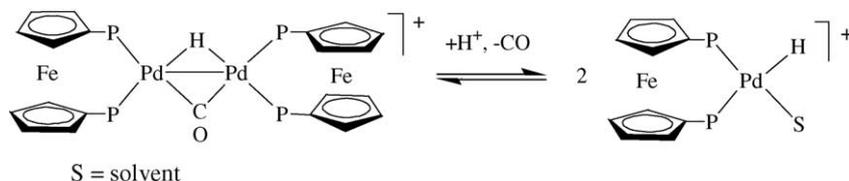
The productivity was found to increase with the temperature for all catalysts. This effect was particularly important for the dppr precursor **3** which, at 100 °C, gave **A** and **B** in more than double yield than at 80 °C (runs 22, 23). Above 100 °C, however, the ether **C** was formed in a too large amount to make the process appealing (run 24); therefore a temperature

Table 3
Methoxycarbonylation of styrene catalyzed by Pd^{II} complexes with dppf, dppomf, dppr, and dppo ligands^a

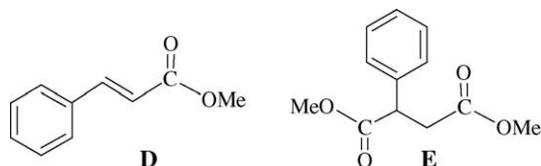
| Run | Catalyst precursor number | BQ (equiv) | HOTs (equiv) | CO (psi) | °C | h | Conversion (%) | Ether C (%) | Ether B (%) | Selectivity of B | Ether A (%) | Selectivity of A | Ether D (%) | Selectivity of D | Ether E (%) | Selectivity of E | CO products (%) | Selectivity of CO products | TOF CO products |
|----------------|---------------------------|------------|--------------|----------|-----|---|----------------|-------------|-------------|------------------|-------------|------------------|-------------|------------------|-------------|------------------|-----------------|----------------------------|-----------------|
| 1 | 1 | 0 | 0 | 42 | 100 | 1 | 29.3 | 0.0 | 7.2 | 24.6 | 22.1 | 75.4 | 0.0 | 0.0 | 0.0 | 0.0 | 29.3 | 100.0 | 117 |
| 2 | 1 | 400 | 0 | 42 | 100 | 1 | 22.3 | 0.0 | 0.8 | 3.6 | 2.3 | 10.3 | 17.4 | 78.0 | 1.8 | 8.1 | 22.3 | 100.0 | 89 |
| 3 | 1 | 0 | 40 | 42 | 100 | 1 | 81.1 | 1.6 | 18.7 | 23.5 | 60.8 | 76.5 | 0.0 | 0.0 | 0.0 | 0.0 | 79.5 | 98.0 | 318 |
| 4 | 1 | 0 | 40 | 14 | 100 | 1 | 46.8 | 2.9 | 10.5 | 23.9 | 33.4 | 76.1 | 0.0 | 0.0 | 0.0 | 0.0 | 43.9 | 93.8 | 176 |
| 5 | 1 | 0 | 40 | 14 | 100 | 2 | 72.3 | 3.8 | 15.9 | 23.2 | 52.6 | 76.8 | 0.0 | 0.0 | 0.0 | 0.0 | 68.5 | 94.7 | 137 |
| 6 | 1 | 20 | 40 | 14 | 100 | 1 | 36.9 | 2.7 | 8.2 | 24.0 | 26.0 | 76.0 | 0.0 | 0.0 | 0.0 | 0.0 | 34.2 | 92.7 | 137 |
| 7 ^b | 1 | 0 | 40 | 14 | 100 | 1 | 27.3 | 0.8 | 5.0 | 18.9 | 21.5 | 81.1 | 0.0 | 0.0 | 0.0 | 0.0 | 26.5 | 97.1 | 106 |
| 8 | 2 | 0 | 0 | 42 | 100 | 1 | 4.9 | 0.0 | 0.8 | 16.3 | 4.1 | 83.7 | 0.0 | 0.0 | 0.0 | 0.0 | 4.9 | 100.0 | 20 |
| 9 | 12 | 0 | 0 | 42 | 100 | 1 | 5.6 | 0.0 | 0.9 | 16.1 | 4.7 | 83.9 | 0.0 | 0.0 | 0.0 | 0.0 | 5.6 | 100.0 | 22 |
| 10 | 2 | 400 | 0 | 42 | 100 | 1 | 2.4 | 0.0 | 0.1 | 4.2 | 0.7 | 29.2 | 1.5 | 62.5 | 0.1 | 4.2 | 2.4 | 100.0 | 10 |
| 11 | 2 | 0 | 40 | 42 | 100 | 1 | 50.6 | 3.1 | 7.3 | 15.4 | 40.2 | 84.6 | 0.0 | 0.0 | 0.0 | 0.0 | 47.5 | 93.9 | 190 |
| 12 | 2 | 0 | 40 | 14 | 100 | 1 | 46.5 | 3.2 | 6.8 | 15.7 | 36.5 | 84.3 | 0.0 | 0.0 | 0.0 | 0.0 | 43.3 | 93.1 | 173 |
| 13 | 2 | 0 | 40 | 14 | 100 | 2 | 73.3 | 3.9 | 10.7 | 15.4 | 58.7 | 84.6 | 0.0 | 0.0 | 0.0 | 0.0 | 69.4 | 94.7 | 139 |
| 14 | 12 | 0 | 40 | 14 | 100 | 1 | 38.1 | 3.4 | 5.3 | 15.3 | 29.4 | 84.7 | 0.0 | 0.0 | 0.0 | 0.0 | 34.7 | 91.1 | 139 |
| 15 | 2 | 20 | 40 | 14 | 100 | 1 | 43.8 | 2.6 | 6.5 | 15.8 | 34.7 | 84.2 | 0.0 | 0.0 | 0.0 | 0.0 | 41.2 | 94.1 | 165 |
| 16 | 3 | 0 | 0 | 42 | 100 | 1 | 2.8 | 0.0 | 0.7 | 25.0 | 2.1 | 75.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.8 | 100.0 | 11 |
| 17 | 3 | 400 | 0 | 42 | 100 | 1 | 1.6 | 0.0 | 0.1 | 6.3 | 0.3 | 18.8 | 1.1 | 68.8 | 0.1 | 6.3 | 1.6 | 100.0 | 6 |
| 18 | 3 | 0 | 20 | 42 | 100 | 1 | 48.2 | 1.3 | 10.8 | 23.0 | 36.1 | 77.0 | 0.0 | 0.0 | 0.0 | 0.0 | 46.9 | 97.3 | 188 |
| 19 | 3 | 0 | 40 | 42 | 100 | 1 | 85.8 | 2.2 | 18.9 | 22.6 | 64.7 | 77.4 | 0.0 | 0.0 | 0.0 | 0.0 | 83.6 | 97.4 | 334 |
| 20 | 3 | 0 | 60 | 42 | 100 | 1 | 85.0 | 3.1 | 18.9 | 23.1 | 63.0 | 76.9 | 0.0 | 0.0 | 0.0 | 0.0 | 81.9 | 96.4 | 328 |
| 21 | 3 | 0 | 40 | 63 | 100 | 1 | 63.1 | 1.4 | 14.8 | 24.0 | 46.9 | 76.0 | 0.0 | 0.0 | 0.0 | 0.0 | 61.7 | 97.8 | 247 |
| 22 | 3 | 0 | 40 | 14 | 80 | 1 | 30.6 | 0.5 | 7.6 | 25.2 | 22.5 | 74.8 | 0.0 | 0.0 | 0.0 | 0.0 | 30.1 | 98.4 | 120 |
| 23 | 3 | 0 | 40 | 14 | 100 | 1 | 73.0 | 2.6 | 15.7 | 22.3 | 54.7 | 77.7 | 0.0 | 0.0 | 0.0 | 0.0 | 70.4 | 96.4 | 282 |
| 24 | 3 | 0 | 40 | 14 | 120 | 1 | 82.1 | 12.7 | 14.1 | 20.3 | 55.3 | 79.7 | 0.0 | 0.0 | 0.0 | 0.0 | 69.4 | 84.5 | 278 |
| 25 | 3 | 0 | 40 | 14 | 100 | 2 | 93.3 | 3.5 | 19.6 | 21.8 | 70.2 | 78.2 | 0.0 | 0.0 | 0.0 | 0.0 | 89.8 | 96.2 | 180 |
| 26 | 3 | 20 | 40 | 14 | 100 | 1 | 53.7 | 2.8 | 11.9 | 23.4 | 39.0 | 76.6 | 0.0 | 0.0 | 0.0 | 0.0 | 50.9 | 94.8 | 204 |
| 27 | 4 | 0 | 0 | 42 | 100 | 1 | 0.8 | 0.0 | 0.2 | 25.0 | 0.6 | 75.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.8 | 100.0 | 3 |
| 28 | 4 | 400 | 0 | 42 | 100 | 1 | 1.0 | 0.0 | 0.1 | 10.0 | 0.3 | 30.0 | 0.5 | 50.0 | 0.1 | 10.0 | 1.0 | 100.0 | 4 |
| 29 | 4 | 0 | 40 | 42 | 100 | 1 | 65.4 | 1.9 | 14.5 | 22.8 | 49.0 | 77.2 | 0.0 | 0.0 | 0.0 | 0.0 | 63.5 | 97.1 | 254 |
| 30 | 4 | 0 | 40 | 14 | 100 | 1 | 45.2 | 2.8 | 9.5 | 22.4 | 32.9 | 77.6 | 0.0 | 0.0 | 0.0 | 0.0 | 42.4 | 93.8 | 170 |
| 31 | 4 | 0 | 40 | 14 | 100 | 2 | 64.2 | 5.0 | 12.9 | 21.8 | 46.3 | 78.2 | 0.0 | 0.0 | 0.0 | 0.0 | 59.2 | 92.2 | 118 |
| 32 | 4 | 20 | 40 | 14 | 100 | 1 | 41.4 | 2.6 | 8.9 | 22.9 | 29.9 | 77.1 | 0.0 | 0.0 | 0.0 | 0.0 | 38.8 | 93.7 | 155 |

^a Catalyst precursor 0.01 mmol; styrene 4 mmol; solvent (MeOH) 20 ml; 700 rpm.

^b Solvent (EtOH) 20 ml.



Scheme 6.



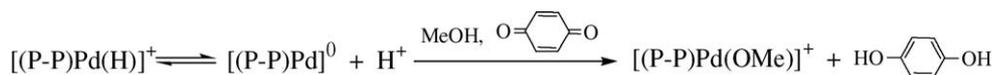
Scheme 7.

of 100 °C represents a limit to conjugate good activity and selectivity.

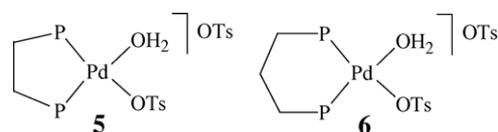
Some catalytic experiments were carried out using the binuclear dppomf complex **12** in the place of the mononuclear precursor **2** (runs 9, 14). Consistent with the HPNMR experiments, the use of **12** led to the conversion of 38.1% styrene with 84.7% selectivity in **A**. Since **2** gave 46.5% conversion and 84.3% selectivity in **A** under identical conditions, the μ -H- μ -CO complexes are likely catalyst resting state that require an induction period to generate catalytically active species; in our case, mononuclear Pd–H complexes. Indeed, previous studies of alternating copolymerization reactions of ethylene with CO in MeOH have proved that μ -H- μ -CO palladium(II) complexes with chelating diphosphines, including dppf, are catalytically active and can re-enter the catalysis cycle as Pd–H through the reaction with the protic acid (Scheme 6) [9a,23].

The addition of BQ to the initial catalytic mixtures caused no beneficial effect either on the yield or on the regioselectivity. On one hand, the contemporaneous presence of 40 equiv of TsOH and 20–100 equiv of BQ gave less esters (10–30%) without improving the selectivity in isomer **A** that was around 77% with **1**, **3** and **4** and around 84% with **2** (runs 6, 15, 26, 32). On the other hand, the use of a large excess of BQ (400 equiv), in the absence of added acid, made the chemoselectivity worse (runs 2, 10, 17, 28). Indeed, besides the saturated esters **A** and **B**, methyl cinnamate (**D**) and dimethyl phenylsuccinate (**E**) were also obtained (Scheme 7). Only the dppf complex showed a significant production (17.4%) of the major product methyl cinnamate (selectivity 78%), in the presence of 400 equiv of BQ (run 2).

The decrease in selectivity caused by the presence of BQ in the reaction mixture has precedent in other carbonylation reactions of alkenes and can be rationalized by considering that BQ is able to convert Pd–H into Pd–OMe in



Scheme 8.



Scheme 9. Proposed reaction schemes for the methoxycarbonylation of styrene with chelating diphosphine-Pd(II) precursors; [Pd] = [(P–P)Pd]²⁺. P–P = dppe, dppp, *k*²-P,P metallocene ligands, [M–Pd] = [(P–M–P)Pd]²⁺, P–M–P = *k*³-P,P,M metallocene ligands. (□) Either a co-ligand or a solvent molecule.

MeOH (Scheme 8) [24]. Indeed, the formation of **D** and **E** requires Pd–OMe initiators [25,26a,b], while the saturated monoesters **A** and **B** are obtained from Pd–H initiators [26a,b,27].

3.4.2. Reactions catalyzed by [Pd(H₂O)(OTs)(dppe)]OTs and [Pd(H₂O)(OTs)(dppp)]OTs

In an attempt of gaining further insight into the role played by the 1,1'-bis(diphenylphosphino)metallocene ligands in governing the methoxycarbonylation of styrene, some reactions were performed with catalyst precursors containing classical diphosphines such as [Pd(H₂O)(OTs)(dppe)]OTs (**5**) [12] and [Pd(H₂O)(OTs)(dppp)]OTs (**6**) [13] (Scheme 9). Similar dppe-Pd^{II} complexes are known to catalyze the oxidative carbonylation of styrene in MeOH to methyl cinnamate and/or dimethyl succinate [25], while **6** and related dppp complexes have been employed to convert styrene into different types of low molecular weight oxygenates (esters, ketones, aldehydes) depending on the reaction parameters [26].

Under the present experimental conditions, both **5** and **6** gave very low conversions of styrene in either neutral or acidic media (Table 4). Previous studies, including in situ and operando HPNMR experiments, indicated the great instability of the [(dppe)PdH]⁺ and [(dppp)PdH]⁺ moieties as the principal factor accounting for the low catalytic activity in MeOH [25,26,28]. Indeed, unlike **1–4**, compounds **5** and **6** undergo rapid and irreversible transformation, under styrene methoxycarbonylation conditions, to give the bis-chelates [(P–P)₂Pd](OTs)₂ via the disruptive reduction of half equivalent of Pd^{II} precursor to Pd⁰ and free diphosphine ligand [25,28a,29].

Table 4
Methoxycarbonylation of styrene catalyzed by Pd^{II} complexes with dppe and dppp ligands^a

| Run | Catalyst precursor number | BQ (equiv) | HOTs (equiv) | CO (psi) | °C | h | Conversion (%) | C (%) | Ether B (%) | Selectivity of B (%) | A (%) | Selectivity of A (%) | D (%) | Selectivity of D (%) | E (%) | Selectivity of E (%) | Others (%) | Selectivity of others (%) | CO products (%) | Selectivity of CO products | TOF CO products |
|-----|---------------------------|------------|--------------|----------|-----|---|----------------|-------|-------------|----------------------|-------|----------------------|-------|----------------------|-------|----------------------|------------|---------------------------|-----------------|----------------------------|-----------------|
| 1 | 5 | 0 | 0 | 43 | 100 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0 |
| 2 | 5 | 400 | 0 | 43 | 100 | 1 | 65.3 | 0.0 | 0.1 | 0.2 | 0.2 | 0.3 | 62.3 | 95.4 | 0.2 | 0.3 | 2.5 | 3.8 | 65.3 | 100.0 | 261 |
| 3 | 5 | 0 | 40 | 43 | 100 | 1 | 6.0 | 2.4 | 0.1 | 2.8 | 0.1 | 2.8 | 0.0 | 0.0 | 0.0 | 0.0 | 3.4 | 94.4 | 3.6 | 60.0 | 14 |
| 4 | 5 | 0 | 40 | 14 | 100 | 1 | 8.8 | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.8 | 100.0 | 3.8 | 43.2 | 15 |
| 5 | 5 | 20 | 40 | 14 | 100 | 1 | 7.5 | 4.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 10.7 | 0.0 | 0.0 | 2.5 | 89.3 | 2.8 | 37.3 | 11 |
| 6 | 6 | 0 | 0 | 43 | 100 | 1 | 2.4 | 0.0 | 0.6 | 25.0 | 1.8 | 75.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.4 | 100.0 | 10 |
| 7 | 6 | 400 | 0 | 43 | 100 | 1 | 69.6 | 0.0 | 0.2 | 0.3 | 1.1 | 1.6 | 67.0 | 96.3 | 1.3 | 1.9 | 0.0 | 0.0 | 69.6 | 100.0 | 278 |
| 8 | 6 | 0 | 40 | 43 | 100 | 1 | 6.7 | 3.5 | 0.9 | 28.1 | 2.3 | 71.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.2 | 47.8 | 13 |
| 9 | 6 | 0 | 40 | 14 | 100 | 1 | 4.9 | 3.7 | 0.3 | 25.0 | 0.9 | 75.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.2 | 24.5 | 5 |
| 10 | 6 | 20 | 40 | 14 | 100 | 1 | 5.0 | 4.3 | 0.2 | 28.6 | 0.5 | 71.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 14.0 | 3 |

^a Catalyst precursor 0.01 mmol; styrene 4 mmol; solvent (MeOH) 20 ml; 700 rpm.

Only in the presence of a large excess of oxidant BQ (400 equiv), which is necessary to oxidize inactive Pd⁰ to active Pd^{II}, the dppe and dppp precursors were able to convert styrene to methyl cinnamate in good yield (65–70% in 1 h) and excellent selectivity (>95%) (Table 4, runs 2, 7) [25]. As said above, the formation of the cinnamate implies Pd–OMe initiators that react with CO to form Pd–CO(O)Me intermediates. These insert styrene exclusively in 2,1-fashion [24b,e,25,26i,30,31]. Therefore, only the cinnamate **D** can form by β -H elimination, provided this reaction is faster than CO insertion. If not, the succinate **E** might be obtained by CO insertion, followed by methanolysis of Pd-acyl (see Scheme 11). Since **D** was selectively produced, the β -H transfer path is apparently favored over CO insertion for the dppe and dppp systems.

3.5. Study of the methoxycarbonylation of styrene catalyzed by model dppr complexes

The methyl complex [PdMe(dppr)]B(Ar')₄ (Ar' = 3,5-(CF₃)₂C₆H₃) (**16**) was straightforwardly prepared by the reaction of PdCl(Me)(dppr) (**15**) with NaB(Ar')₄ in CH₂Cl₂ solution. Under a CO atmosphere (1 bar) at room temperature, **16** converted immediately into the acyl complex [Pd(COMe)(dppr)]B(Ar')₄ (**17**) (Scheme 10).

The different hapticity of dppr in **16** and **17** with respect to **15** was unequivocally put in evidence by comparing the corresponding ³¹P{¹H} and ¹H NMR spectra. Indeed, as previously observed for Pd(II) complexes with dppe-, dppf-, and dppf-related ligands [9a,b,10,18,32], the intramolecular formation of M → Pd bonds causes a remarkable high-field shift of the phosphorus resonance as compared to *k*²-P,P derivatives. As an example, the ³¹P{¹H} NMR spectra of **16** and **17** show singlets at δ : –12.4 and –13.8, respectively, for the two magnetically equivalent phosphorus nuclei that resonate at δ : 33.0 in the dichloride PdCl₂(dppr) [2a,17] and at δ : 14.0 (d, *J*(PP) = 28.9 Hz) and 37.8 (d) in **15**. The presence of Ru–Pd bonds in **16** and **17** can also be inferred by the large chemical shift difference between the α - and β -hydrogen atoms (1.36 and 0.94 ppm in **16** and **17**, respectively) of the cyclopentadienyl rings as compared to *k*²-P,P complexes (0.2–0.5 ppm) [9a,b,10,18,32].

The acyl complex **17** in CD₂Cl₂ underwent fast methanolysis at room temperature under a CO stream yielding the μ -hydride- μ -CO complex **13** and methyl acetate [9a]. In contrast, no reaction occurred when complex **17** was allowed to react with a 20-fold excess of styrene in CD₂Cl₂ at room temperature. The lack of reactivity of the acyl **17** towards styrene and its fast reaction with MeOH are fully consistent with the absence of products containing two styrene units in the final catalytic mixtures.

3.6. Proposed mechanism of the methoxycarbonylation of styrene catalyzed by **1–4**

Scheme 11 reports a sequence of reactions that are generally considered as key steps in the mechanism of the methoxy-

diphosphines bearing bulky phosphorus-substituents [22,35]. The reasons for the linear regioselectivity are still a matter of debate. Steric effects, related to the interaction of the phosphino phenyl groups and the phenyl in the branched alkyl, have been claimed to be determinant in favoring the formation of the linear ester [22c,36]. On the other hand, isotope labeling studies with α -deuterostyrene in MeOH- d_4 have suggested a kinetic control of the regioselectivity caused by the slower insertion of CO into the Pd–C_{branched-alkyl} bond as compared to the Pd–C_{linear-alkyl} bond [26d]. In the case of **1–4**, no appreciable influence of the CO pressure on the regiochemistry was observed from 14 to 42 bar. Therefore, we are inclined to assign a major importance to direct steric effects than to migratory insertion kinetics. Consistent this hypothesis is the fact that the highest regioselectivity in **A** (85%) was obtained with the dpomf complex **2** which exhibits the largest crystallographic P–Pd–P bite angle (101.3(1)° versus 96.37(1)° in **1** and 97.47(4)° in **3**) and hence contains four phenyl rings spatially closer to the alkyl ligand than in the other precursors.

In the presence of a large excess of BQ, without TsOH, **1–4** produced four products, **A**, **B**, **D** and **E**, among which **D** was the major product. However, only the dppf precursor **1** gave a significant conversion of styrene (overall 22.3%). Despite the moderate to scarce overall productivity, the reactions carried out in the presence of 400 equiv of BQ provide interesting information on the mechanism of the oxidative carbonylation of styrene as well as on the factors that differentiate the activity of **1–4**. Therefore, it is worthwhile commenting briefly these reactions.

It is agreed that the formation of the esters **D** and **E** requires a (P–P)Pd^{II}–OMe initiator which can be readily generated by interaction of the Pd^{II} precursor with MeOH as illustrated in step a of Scheme 5. In the course of the catalysis, it is just BQ to provide new Pd–OMe moieties through the oxidation process shown in Scheme 8. The sequence of reactions yielding **D** and **E** are shown in the lower section of Scheme 11. The branched alkyl (step g) is obtained from Pd–OMe by reaction with CO (step e), followed by 2,1-insertion of styrene (step g) [24b,e,25,26i,30,31]. The methyl cinnamate **D** is then released by β -elimination (step h). In consequence of this event, the Pd–H moiety is formed and from this the Pd–OMe one (Scheme 8). The same branched alkyl can also produce the minor diester product **E** through CO insertion (step i), followed by methanolysis (step j). It is important to notice that, even in the presence of a large excess of BQ, some saturated esters **A** and **B** were obtained: this means that: (i) some Pd–H moieties generated in step h enter the catalysis cycle shown in the upper part of Scheme 11; (ii) the protonolysis by MeOH of the branched alkyl, produced in step g, does not occur. Indeed, were the protonolysis possible, only the linear ester **A** would form, which is not experimentally observed in fact.

As said above, only the dppf precursor **1** gave a significant conversion of styrene in the presence of 400 equiv of BQ, while the other catalysts showed yields lower than

3%. In our opinion, this is the indirect consequence of the different propensity of the four 1,1'-bis(diphenylphosphino)metallocene ligands to bind palladium in the k^3 -P,P,M mode. Indeed, in conjunction with electron-withdrawing co-ligands such as the carbomethoxy –C(O)OMe group, dpomf, dppr, and dppe form very robust k^3 -P,P,M palladium(II) complexes which do not react with alkenes [9a]. It cannot be excluded that also dppf forms a complex of the formula [Pd(C(O)OMe)(k^3 -P,P,Fe)]⁺ since the overall conversion of styrene under oxidative conditions is rather low (22.3%). However, some phenyl cinnamate (17.4%) is obtained, which may be explained by the formation of a rather weak Fe–Pd bond. Consistent with the hypothesis that the k^3 -P,P,M bonding mode in carbomethoxy complexes disfavors the insertion of styrene, the precursors **5** and **6**, with diphosphines, that coordinate metal centers exclusively in k^2 -P,P fashion, give rise to selective catalysts for the oxidative carbonylation of styrene to methyl cinnamate (Table 4).

4. Conclusions

1,1'-Bis(diphenylphosphino)metallocene palladium(II) complexes with water and/or tosylate co-ligands are effective and selective catalyst precursors for the methoxycarbonylation of styrene to methyl phenylpropanoates in the presence of TsOH, yielding prevalently the linear regioisomer methyl 3-phenylpropanoate. Varying the metallocene metal between Fe, Ru and Os or substituting Cp* for Cp did not appreciably change either the chemoselectivity or the regioselectivity. In contrast, the nature of the metal and the type of cyclopentadienyl ligand have been found to influence the activity by controlling the chemical stability of the catalytic systems.

The activity exhibited by the 1,1'-bis(diphenylphosphino)metallocene catalysts contrasts that of similar palladium(II) catalysts stabilized by the chelating diphosphine ligands dppe and dppp that, under comparable experimental conditions, were almost inactive due to the very low stability of the Pd–H initiators. The reverse was observed by performing the carbonylation reactions in the presence of a large excess of BQ where Pd–C(O)OMe initiators are formed. In this case, the 1,1'-bis(diphenylphosphino)metallocene catalysts, with the partial exception of the dppf precursor, were almost inactive, while the dppe- and dppp-modified catalysts gave the unsaturated ester methyl cinnamate in good activity and excellent selectivity. The different activity and chemoselectivity exhibited by the catalysts with 1,1'-bis(diphenylphosphino)metallocenes or dppe/dppp has been interpreted in terms of the unique ability of the former to act as tridentate k^3 -P,P,M ligands capable of forming robust intramolecular M–Pd bonds in M–Pd–C(O)OMe intermediates that are not easily disrupted by alkenes. The intermediate behavior of the dppf precursor may reflect its low propensity to form k^3 -P,P,Fe palladium(II) complexes.

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References

- [1] (a) T.J. Colacot, *Platinum Met. Rev.* 45 (2001) 22;
(b) K.S. Gan, T.S.A. Hor, in: A. Togni, T. Hayashi (Eds.), *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH/Wiley, Weinheim, 1995, p. 13, Chapter 1.
- [2] (a) S. Li, B. Wei, P.M.N. Low, H.K. Lee, T.S.A. Hor, F. Xue, T.C.W. Mak, *J. Chem. Soc., Dalton Trans.* (1997) 1289;
(b) J.M. Brown, P.J. Guiry, *Inorg. Chim. Acta* 220 (1994) 149.
- [3] (a) M. Ogasawara, K. Yoshida, T. Hayashi, *Organometallics* 19 (2000) 1567;
(b) B.E. Bosch, I. Brümmer, K. Kunz, G. Erker, R. Frölich, S. Kotila, *Organometallics* 19 (2000) 1255;
(c) Y. Xie, G.K. Tan, Y.K. Yan, J.J. Vittal, S.C. Ng, T.S.A. Hor, *J. Chem. Soc., Dalton Trans.* (1999) 773;
(d) S.W.A. Fong, T.S.A. Hor, *J. Cluster Sci.* 9 (1998) 351;
(e) T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc.* 106 (1984) 158.
- [4] (a) A. Jutand, A.K.-K. Mimi Hii, M. Thornton-Pett, J.M. Brown, *Organometallics* 18 (1999) 5367;
(b) A.L. Boyes, I.R. Butler, S.C. Quayle, *Tetrahedron Lett.* 39 (1998) 7763;
(c) J.M. Brown, K.-K. Mimi Hii, *Angew. Chem. Int. Ed.* 35 (1996) 657.
- [5] W. Mägerlein, A.F. Indolese, M. Beller, *M. Angew. Chem. Int. Ed.* 40 (2001) 2856.
- [6] (a) J.F. Hartwig, *Angew. Chem. Int. Ed.* 37 (1998) 2090;
(b) J.F. Hartwig, *Acc. Chem. Res.* 31 (1998) 852;
(c) M.S. Driver, J.F. Hartwig, *J. Am. Chem. Soc.* 118 (1996) 7217.
- [7] (a) K. Li, P.N. Horton, M.B. Hursthouse, K.-K. Mimi Hii, *J. Organomet. Chem.* 665 (2003) 250;
(b) T.E. Müller, M. Berger, M. Grosche, E. Herdtweck, F.P. Schmidtchen, *Organometallics* 20 (2001) 4384.
- [8] K. Mikami, K. Aikawa, *Org. Lett.* 4 (2002) 99.
- [9] (a) 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, A.M. Kal'sin, *Organometallics* 22 (2003) 2409;
(b) O.V. Gusev, A.M. Kal'sin, M.G. Peterleitner, P.V. Petrovskii, K.A. Lyssenko, N.G. Akhmedov, C. Bianchini, A. Meli, W. Oberhauser, *Organometallics* 21 (2002) 3637;
(c) M.A. Zuideveld, P.C.J. Kamer, P.W.N.M. van Leeuwen, P.A.A. Klusener, H.A. Stil, C.F. Roobeek, *J. Am. Chem. Soc.* 120 (1998) 7977;
(d) O.V. Gusev, private communication.
- [10] O.V. Gusev, A.M. Kal'sin, P.V. Petrovskii, K.A. Lyssenko, Y.F. Oprunenko, C. Bianchini, A. Meli, W. Oberhauser, *Organometallics* 22 (2003) 913.
- [11] (a) D. Drew, J.R. Doyle, *Inorg. Synth.* 13 (1972) 47;
(b) R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, *Inorg. Chem.* 32 (1993) 5769.
- [12] F. Gorla, L.M. Venanzi, *Helv. Chim. Acta* 73 (1990) 690.
- [13] (a) C. Benetolo, R. Bertani, G. Bombieri, L. Toniolo, *Inorg. Chim. Acta* 233 (1995) 5;
(b) P.J. Stang, D.H. Cao, G.T. Poulter, A.M. Arif, *Organometallics* 14 (1995) 1110.
- [14] (a) W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81;
(b) R. Morassi, L. Sacconi, *J. Chem. Soc. A* (1971) 492.
- [15] C. Bianchini, A. Meli, A. Traversi, Italian Patent FI A000025 (1997).
- [16] (a) A.J.C. Wilson, *International Tables for X-ray Crystallography*, Kluwer, Dordrecht, The Netherlands, 1992, p. 219 ;
(b) A.J.C. Wilson, *International Tables for X-ray Crystallography*, Kluwer, Dordrecht, The Netherlands, 1992, p. 500.
- [17] C. Nataro, A.N. Campbell, M.A. Ferguson, C.D. Incarvito, A.L. Rheingold, *J. Organomet. Chem.* 673 (2003) 47.
- [18] M. Sato, H. Shigeta, M. Sekino, S. Akabori, *J. Organomet. Chem.* 458 (1993) 199.
- [19] (a) M. Portnoy, D. Milstein, *Organometallics* 13 (1994) 600;
(b) M. Portnoy, F. Frolow, D. Milstein, *Organometallics* 10 (1991) 3960.
- [20] (a) I. Toth, C.J. Elsevier, *Organometallics* 13 (1994) 2118;
(b) P.H.M. Budzelaar, P.W.N.M. van Leeuwen, C.F. Roobeek, *Organometallics* 11 (1992) 23.
- [21] (a) A. Hohn, in: B. Cornils, W.A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996, p. 138;
(b) M. Beller, A.M. Tafesh, in: B. Cornils, W.A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallics Compounds*, VCH, Weinheim, 1996, p. 187;
(c) E. Drent, P.H.M. Budzelaar, *J. Organomet. Chem.* 593–594 (2000) 211.
- [22] (a) A. Seayad, S. Jayasree, K. Damodaran, L. Toniolo, R.V. Chaudhari, *J. Organomet. Chem.* 601 (2000) 100;
(b) A. Seayad, A.A. Kelkar, L. Toniolo, R.V. Chaudhari, *J. Mol. Catal. A* 151 (2000) 47;
(c) I. Del Rio, N. Ruiz, C. Claver, L.A. van der Veen, P.W.N.M. van Leeuwen, *J. Mol. Catal. A* 161 (2000) 39;
(d) S. Oi, M. Nomura, T. Aiko, Y. Inoue, *J. Mol. Catal. A* 115 (1997) 289.
- [23] (a) P.J. Perez, J.C. Calabrese, E.E. Bunel, *Organometallics* 20 (2001) 337.
- [24] (a) A. Sen, *Acc. Chem. Res.* 26 (1993) 303;
(b) E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663;
(c) E. Drent, J.A.M. van Broekhoven, P.H.M. Budzelaar, in: B. Cornils, W.A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996, p. 333;
(d) A. Sommazzi, F. Garbassi, *Prog. Polym. Sci.* 22 (1997) 1547;
(e) K. Nozaki, T. Hijama, *J. Organomet. Chem.* 576 (1999) 248;
(f) C. Bianchini, A. Meli, *Coord. Chem. Rev.* 225 (2002) 35;
(g) E. Drent, J.A.M. van Broekhoven, P.H.M. Budzelaar, in: B. Cornils, W.A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996, p. 344;
(h) R.A.M. Robertson, D.J.C. Cole-Hamilton, *Coord. Chem. Rev.* 225 (2002) 67;
(i) C. Bianchini, A. Meli, W. Oberhauser, *J. Chem. Soc., Dalton Trans.* (2003) 2627.
- [25] (a) C. Bianchini, G. Mantovani, A. Meli, W. Oberhauser, P. Bruggeller, T. Stampfl, *J. Chem. Soc., Dalton Trans.* (2001) 690.
- [26] (a) M. Sperrle, G. Consiglio, *J. Mol. Catal. A* 143 (1999) 263;
(b) M. Sperrle, G. Consiglio, *Chem. Ber.* 130 (1997) 1557;
(c) M. Sperrle, G. Consiglio, *J. Organomet. Chem.* 506 (1996) 177;
(d) G. Consiglio, S.C.A. Nefkens, C. Pisano, *Inorg. Chim. Acta* 220 (1994) 273;
(e) C. Pisano, G. Consiglio, *Gazz. Chim. Ital.* 124 (1994) 393;
(f) C. Pisano, A. Mezzetti, G. Consiglio, *Organometallics* 11 (1992) 20;
(g) C. Pisano, C.A. Nefkens, G. Consiglio, *Organometallics* 11 (1992) 1975;
(h) C. Pisano, G. Consiglio, A. Sironi, M. Moret, *J. Chem. Soc., Chem. Commun.* (1991) 421;
(i) M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U.W. Suter, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 989.
- [27] R.P. Tooze, K. Whiston, A.P. Molyan, M.J. Taylor, N.W. Wilson, *J. Chem. Soc., Dalton Trans.* (2000) 3441.

- [28] (a) C. Bianchini, A. Meli, G. Müller, W. Oberhauser, E. Passaglia, *Organometallics* 21 (2002) 4965;
(b) C. Bianchini, H.M. Lee, A. Meli, W. Oberhauser, M. Peruzzini, F. Vizza, *Organometallics* 21 (2002) 16;
(c) C. Bianchini, H.M. Lee, A. Meli, S. Moneti, F. Vizza, M. Fontani, P. Zanello, *Macromolecules* 32 (1999) 4183.
- [29] L.M. Engelhardt, J.M. Patrick, C.L. Raston, P. Twiss, A.H. White, *Aust. J. Chem.* 37 (1984) 2193.
- [30] A. Aeby, G. Consiglio, *J. Am. Chem. Soc.* 120 (1998) 11000.
- [31] K. Nozaki, H. Komaki, Y. Kawashima, T. Hiyama, T. Matsubara, *J. Am. Chem. Soc.* 123 (2001) 534.
- [32] (a) M.A. Zuideveld, B.H.G. Swennenhuis, P.C.J. Kamer, P.W.N.M. van Leeuwen, *J. Organomet. Chem.* 637 (2001) 805;
(b) M.A. Zuideveld, B.H.G. Swennenhuis, M.D.K. Boele, Y. Guari Y., G.P.F. van Strijdonck, J.N.H. Reek, P.C.J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, *J. Chem. Soc., Dalton Trans.* (2002) 2308;
(c) P.W.N.M. van Leeuwen, M.A. Zuideveld, B.H.G. Swennenhuis, Z. Freixa, P.C.J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A.L. Spek, *J. Am. Chem. Soc.* 125 (2003) 5523.
- [33] (a) Y. BeCker, J.K. Stille, *J. Am. Chem. Soc.* 100 (1978) 845;
(b) J.S. Roberts, K.J. Klabunde, *J. Am. Chem. Soc.* 99 (1977) 2509.
- [34] G. Cavinato, L. Toniolo, *J. Mol. Catal.* 10 (1981) 161.
- [35] B. Jedlicka, W. Weissensteiner, T. Kegl, L. Kollar, *J. Organomet. Chem.* 563 (1998) 37.
- [36] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, C.F. Roobeek, *J. Organomet. Chem.* 430 (1992) 357.