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Novel diphosphine-modified palladium catalysts for oxidative carbonylation of styrene to methyl cinnamate †

Claudio Bianchini,[a] Giuseppe Mantovani,[a] Andrea Meli,[a] Werner Oberhauser,[a] Peter Brüggeller[b] and Thomas Stampfl[b]

[a] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, ISSECC-CNR, Via J. Nardi 39, 50132 Firenze, Italy*
[b] *Institut fuer Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck, Innrain 52a, Innsbruck, Austria*

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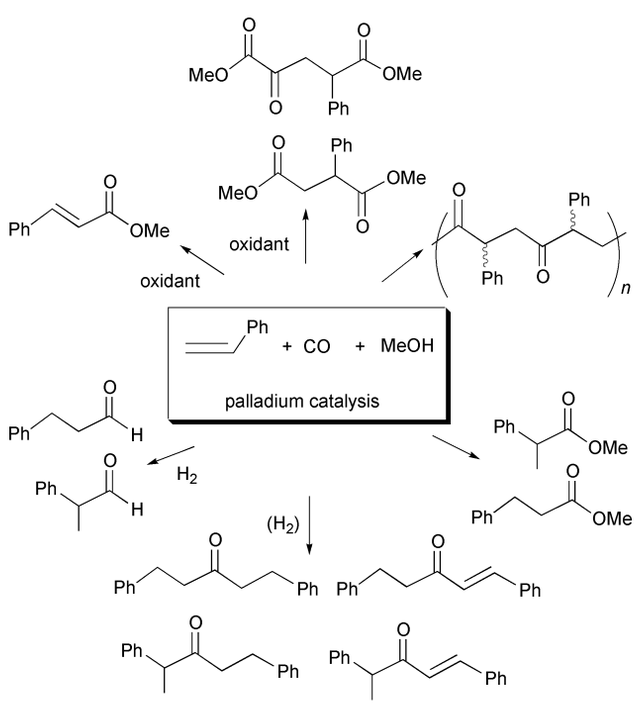
The oxidative carbonylation of styrene has been achieved in MeOH with known and new palladium(II) catalysts of general formulae $[Pd(P–P)(MeCN)_2][PF_6]_2$, $[Pd(P–P)(bipy)][PF_6]_2$, $Pd(P–P)(OAc)_2$, $[Pd_2(cyclo\text{-tetraphos})(MeCN)_4][PF_6]_4$, $[Pd_2(cyclo\text{-tetraphos})(bipy)_2][PF_6]_4$, $Pd_2(cyclo\text{-tetraphos})(OAc)_4$ (P–P = 1,2-bis(diphenylphosphino)ethane, *meso*-2,3-bis(diphenylphosphino)butane or *rac*-2,3-bis(diphenylphosphino)butane; *cyclo*-tetraphos = *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane; bipy = 2,2′-bipyridine; OAc = acetate). The influence of various catalytic parameters on the overall conversion of styrene into carbonylated products and on the product selectivity has been studied by systematically varying the type of palladium initiator, the concentrations of organic oxidant (1,4-benzoquinone) and protic acid (*p*-toluenesulfonic acid), and the CO pressure. This investigation has allowed a partial optimization of the process so as to obtain the largely predominant formation of either methyl cinnamate (highest selectivity 99%) or dimethyl phenylsuccinate (highest selectivity 88%).

The alkoxycarbonylation of olefins belongs to a family of industrially relevant carbonylation reactions that are efficiently catalysed by homogeneous palladium complexes.[1] Despite the simplicity of the reaction and the limited number of starting materials, minor changes in the catalytic system and/or in the reaction conditions may remarkably affect the selectivity leading to the formation of a variety of products. In the case of styrene, carbonylation in methanol in the presence of palladium initiators may yield as many as six different types of products spanning from alternating polyketones, esters, ketones, to aldehydes (Scheme 1).[1,2] The selectivity in the carbonylation of styrene by palladium catalysis is essentially driven by the nature of the supporting ligand: dinitrogen ligands, particularly those with rigid carbon backbones, form selective catalysts for the alternating copolymerization leading to polyketones;[2,3] mono- and di-phosphines contribute to generate effective systems for single, double or triple carbonylation of styrene yielding esters, ketones or aldehydes depending on the co-reagent employed;[4,5] and catalytic systems containing (chiral) ligands with oxygen, sulfur, phosphorus and nitrogen donor atoms may appropriately be tuned so as to give a wealth of products with low to high chemo-, regio- and stereoselectivities.[4,6]

The ability of chelating bidentate ligands with diphenylphosphino donor groups to catalyse, in conjunction with palladium and an oxidant, the alkoxycarbonylation of styrene in MeOH has extensively been investigated by Consiglio and co-workers.[4] Reaction conditions have been developed for which high conversion, chemoselectivity and enantioselectivity to dimethyl phenylsuccinate can be obtained.[4a,b]

Under the conditions employed by Consiglio, methyl cinnamate is often the main by-product,[4a] however, no phosphine-modified palladium system has ever been reported to produce selectively this α,β-unsaturated ester which is an important building block for the production of pharmaceuticals, fragrances, light-sensitive and current-conducting materials, and agrochemicals.[7] To the best of our knowledge, the selective synthesis of methyl cinnamate from styrene, CO and MeOH has been reported previously only with unmodified palladium catalysts based on $PdCl_2$ and complex re-oxidizing systems ($CuCl_2/Cu(OAc)_2/Mn(OAc)_2$ ($OAc^- = OCOCH_3^-$);[8] $CuCl_2/Na(OAc)/MgCl_2$).[9] In contrast, phosphine-modified palladium(II) catalysts have been reported to produce methyl



Scheme 1 Products obtainable by carbonylation of styrene by palladium catalysis in methanol.

† Electronic supplementary information (ESI) available: synthesis of $Pd(L–L)(CN)_2$. See http://www.rsc.org/suppdata/dt/b0/b009635k/

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cinnamate *via* Heck-type methoxycarbonylation of β-bromostyrene.[10]

In this work, we describe new diphosphine-modified palladium systems that are able to catalyse the oxidative carbonylation of styrene in MeOH yielding selectively either methyl cinnamate or dimethyl phenylsuccinate depending on subtle variations in the ligand structure as well as in the reaction conditions. For the first time, diphosphine ligands with two CH_2 spacers between the phosphorus donor atoms have been employed in the alkoxycarbonylation of an α-olefin by palladium catalysis (Chart 1).

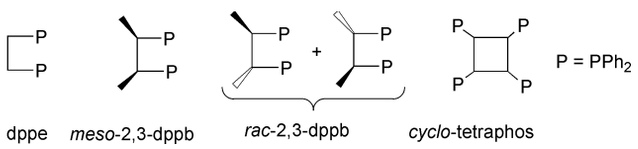

Chart 1

Experimental

General procedure

All reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk-type techniques. The starting palladium complexes Pd(dppe)$(Cl)_2$[11] and Pd(dppe)$(OAc)_2$[12] (**1c**) (dppe = 1,2-bis(diphenylphosphino)ethane), Pd(*meso*-dppb)$(Cl)_2$,[13] Pd(*meso*-dppb)$(OAc)_2$[13] (**2c**), Pd(*rac*-dppb)$(Cl)_2$[13] and Pd(*rac*-dppb)$(OAc)_2$[13] (**3c**) (dppb = 2,3-bis(diphenylphosphino)butane), [Pd_2(*cyclo*-tetraphos)$(NCMe)_4$][PF_6]$_4$[12] (**4a**) and Pd_2(*cyclo*-tetraphos)$(OAc)_4$[12] (**4c**) (*cyclo*-tetraphos = *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane) were prepared according to literature methods. All the isolated metal complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. Styrene was freshly distilled from $LiAlH_4$. All other reagents and solvents were used as purchased from Aldrich, Fluka or Strem. Carbonylation reactions were performed with a 250 cm^3 stainless steel autoclave, constructed at the ISSECC-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. Deuteriated solvents for NMR measurements were dried over molecular sieves. ^1H and ^{31}P-{^1H} NMR spectra were obtained on a Bruker ACP 200 spectrometer (200.13 and 81.01 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H) or 85% H_3PO_4 (^{31}P). The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Firenze, Italy).[14] **CAUTION**: since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. 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 product composition was determined by using acetophenone as the internal standard. Authentic samples of 1,5-diphenyl-3-pentanone and 1,5-diphenyl-1-penten-3-one were prepared as previously described.[4e] GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analysis.

Synthesis of the catalyst precursors

[Pd(P–P)$(NCMe)_2$][PF_6]$_2$ (P–P = dppe, 1a; *meso*-dppb, 2a; or *rac*-dppb, 3a). The appropriate dichloride complex Pd(P–P)Cl_2 (0.3 mmol) and 0.7 mmol of $AgPF_6$ in 20 cm^3 of MeCN were stirred for *ca*. 30 min at room temperature. After this time the reaction mixture was filtered through a Celite column to remove the AgCl precipitate. The filtrate was concentrated to small volume under reduced pressure. Addition of *ca*. 40 cm^3 of *n*-hexane led to precipitation of a brownish solid, which was filtered off, washed several times with *n*-hexane and dried. Yield 70–80%.

1a. Calc. for $C_{30}H_{30}F_{12}N_2P_4Pd$: C, 41.09; H, 3.45; N, 3.20. Found: C, 40.87; H, 3.31; N, 3.11%. ^{31}P-{^1H} NMR (MeCN-d_3): δ 74.9 (s). ^1H NMR (MeCN-d_3): δ 2.31 (s, 6H, NCMe), 2.91 (m, 4H, CH_2) and 7.6–7.9 (m, 20H, Ph). IR: 2320 and 2285 (NCMe); 832 cm^{-1} (PF_6).

2a. Calc. for $C_{32}H_{34}F_{12}N_2P_4Pd$: C, 42.48; H, 3.79; N, 3.10. Found: C, 42.22; H, 3.68; N, 2.98%. ^{31}P-{^1H} NMR (MeCN-d_3): δ 78.0 (s). ^1H NMR (MeCN-d_3): δ 1.15 (dd, ^3J(HP) = 16.0, ^3J(HH) = 7.0 Hz, 6H, CHCH_3), 2.30 (s, 6H, NCMe), 3.49 (m, 2H, CHCH_3) and 7.6–8.1 (m, 20H, Ph). IR: 2324 and 2294 (NCMe); 835 cm^{-1} (PF_6).

3a. Calc. for $C_{32}H_{34}F_{12}N_2P_4Pd$: C, 42.48; H, 3.79; N, 3.10. Found: C, 42.03; H, 3.81; N, 3.02%. ^{31}P-{^1H} NMR (MeCN-d_3): δ 73.8 (s). ^1H NMR (MeCN-d_3): δ 1.12 (m, 6H, CHCH_3), 2.25 (s, 6H, NCMe), 2.95 (br s, 2H, CHCH_3) and 7.6–8.0 (m, 20H, Ph). IR: 2319 and 2289 (NCMe); 831 cm^{-1} (PF_6).

[Pd(P–P)(*N*,*N*′-bipy)][PF_6]$_2$ (P–P = dppe, 1b; *meso*-dppb, 2b; or *rac*-dppb, 3b). To a solution of the appropriate dichloride complex Pd(P–P)Cl_2 (0.35 mmol) in 10 cm^3 of CH_2Cl_2 was added 0.8 mmol of $AgPF_6$. After 5 min of stirring, 2,2′-bipyridine (bipy, 0.35 mmol) was added and stirred for 2 h. After AgCl was removed by filtration on Celite, the filtrate was concentrated to small volume under reduced pressure. Addition of *ca*. 40 cm^3 of *n*-hexane caused the precipitation of a solid (bright yellow, **1b**; pale orange, **2b**; off-white, **3b**), which was filtered off, washed several times with *n*-hexane and dried. Yield 60–70%.

1b. Calc. for $C_{36}H_{32}F_{12}N_2P_4Pd$: C, 45.47; H, 3.39; N, 2.95. Found: C, 45.23; H, 3.28; N, 2.79%. ^{31}P-{^1H} NMR (acetone-d_6): δ 73.0 (s). ^1H NMR (acetone-d_6): δ 3.15 (m, 4H, CH_2), 7.6–8.9 (m, 20H, Ph), 7.55 (t, ^3J(HH) = 6.1, 2H, $H^{5,5'}$), 7.8 (masked, 2H, $H^{6,6'}$), 8.4 (masked, 2H, $H^{4,4'}$) and 8.72 (d, ^3J(HH) = 8.1 Hz, 2H, $H^{3,3'}$).

2b. Calc. for $C_{38}H_{36}F_{12}N_2P_4Pd$: C, 46.62; H, 3.71; N, 2.86. Found: C, 46.59; H, 3.68; N, 2.77%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ 73.7 (s). ^1H NMR (CD_2Cl_2): δ 1.17 (dd, ^3J(HP) = 16.2, ^3J(HH) = 6.8, 6H, CHCH_3), 3.15 (m, 2H, CHCH_3), 7.6–8.2 (m, 20H, Ph), 7.18 (t, ^3J(HH) = 6.1, 2H, $H^{5,5'}$), 7.8 (masked, 2H, $H^{6,6'}$), 8.1 (masked, 2H, $H^{4,4'}$) and 8.37 (d, ^3J(HH) = 8.0 Hz, 2H, $H^{3,3'}$).

3b. Calc. for $C_{38}H_{36}F_{12}N_2P_4Pd$: C, 46.62; H, 3.71; N, 2.86. Found: C, 42.45; H, 3.69; N, 2.78%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ 71.0 (s). ^1H NMR (CD_2Cl_2): δ 1.20 (m, 6H, CHCH_3), 2.71 (br s, 2H, CHCH_3), 7.6–8.2 (m, 20H, Ph), 7.18 (t, ^3J(HH) = 6.1, 2H, $H^{5,5'}$), 7.8 (masked, 2H, $H^{6,6'}$), 8.1 (masked, 2H, $H^{4,4'}$) and 8.29 (d, ^3J(HH) = 8.0 Hz, 2H, $H^{3,3'}$).

[Pd_2(*cyclo*-tetraphos)(*N*,*N*′-bipy)$_2$][PF_6]$_4$ (4b). A solution of complex **4a** (69.8 mg, 0.040 mmol) and bipy (13.8 mg, 0.088 mmol) in MeCN (7 cm^3) was stirred at room temperature. After 15 h the resulting orange solution was concentrated to dryness and the slightly brown solid residue filtered off, washed several times with diethyl ether and then dried. Yield 50%. Calc. for $C_{72}H_{60}F_{24}N_4P_8Pd_2$: C, 45.57; H, 3.19; N, 2.95. Found: C, 45.22; H, 3.04; N, 2.75%. ^{31}P-{^1H} NMR (DMF-d_7): δ 83.2 (s). ^1H NMR (DMF-d_7): δ 3.8 (br s, 4H, CH), 7.2–9.0 (m, 40H, Ph), 7.41 (t, ^3J(HH) = 6.2 Hz, $H^{5,5'}$), 7.8 (masked, 4H, $H^{6,6'}$), 8.48 (t, ^3J(HH) = 7.1 Hz, 4H, $H^{4,4'}$) and 8.96 (d, ^3J(HH) = 8.1 Hz, 4H, $H^{3,3'}$).

***cis*- and *trans*-[Pd(*meso*-dppb)$_2$][PF_6]$_2$.** To a solution of

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Pd(*meso*-dppb)Cl_2 (0.35 mmol) in 10 cm^3 of CH_2Cl_2 was added 0.8 mmol of $AgPF_6$. After 5 min of stirring a solid sample of the ligand *meso*-dppb[13] (0.35 mmol) was added and stirred for 1 h. After AgCl was removed by filtration on Celite, the filtrate was concentrated to small volume under reduced pressure. Addition of *ca.* 40 cm^3 of *n*-hexane caused the precipitation of a mixture of bis(chelated) complexes as an off-white solid, which was filtered off, washed several times with *n*-hexane and dried. Yield 80%. Calc. for $C_{56}H_{56}F_{12}P_6Pd$: C, 53.84; H, 4.52. Found: C, 53.26; H, 4.58%. ^{31}P-{^1H} NMR: two singlets of *ca.* 2:3 intensity at δ 60.7 and 59.1 (CD_2Cl_2); 60.1 and 58.8 (MeOH-d_4). ^1H NMR (CD_2Cl_2): δ 1.06 (m, 12H, $CHCH_3$), 1.20 (m, 12H, *$CHCH_3$), 3.05 (m, 4H, $CHCH_3$), 3.15 (m, 4H, *$CHCH_3$) and 7.0–8.0 (m, 80H, Ph). IR: 835 cm^{-1} (PF_6).

Catalytic carbonylation of styrene

Autoclave experiments. Typically, a 20 cm^3 solution of MeOH containing 0.01 mmol of catalyst precursor, 2 mmol of styrene and the required amounts of 1,4-benzoquinone (BQ) and *p*-toluenesulfonic acid (TsOH) was introduced by suction into a 250 cm^3 autoclave previously evacuated by a vacuum pump. The autoclave was pressurized with CO to 800 psi at room temperature and then heated to 80 °C. As soon as the reaction mixture in the autoclave reached the desired temperature stirring (700 rpm) was applied for the desired time. The reaction was stopped by cooling the autoclave to room temperature with an ice–water bath. The pressure was then released. The product composition was determined by GC using acetophenone as the internal standard. The catalytic results are summarized in Tables 2–6 (see later).

HPNMR experiments. A 10 mm sapphire HPNMR tube was charged with a solution of complex **2a** (18 mg, 0.02 mmol) in MeOH-d_4 (2 cm^3) under nitrogen and then placed into an NMR probe at 20 °C (^{31}P-{^1H} NMR singlet at δ 78.0). Sequential addition of a 10-fold excess of both BQ and styrene, followed by pressurizing with CO to 800 psi at room temperature, caused no change in the ^{31}P-{^1H} NMR spectrum. The reaction was followed by variable-temperature ^{31}P-{^1H} and ^1H NMR spectroscopy. The selective carbonylation of styrene to methyl cinnamate began to occur at 80 °C. Spectra were acquired every 10 min. The results of this investigation are discussed in the following section.

In a similar experiment, complex **2c** was used in the place of **2a**. In contrast, styrene was selectively converted into dimethyl phenylsuccinate as found in the corresponding autoclave experiment.

Results and discussion

Synthesis and characterization of the phosphine-modified palladium(II) precursors

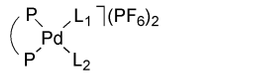
The palladium(II) complexes that have been used in this study as catalyst precursors for the carbonylation of styrene in MeOH are reported in Chart 2. Those containing the acetate co-ligand (**1c**–**4c**) were prepared following known procedures,[12,13] while the complexes with MeCN (**1a**–**4a**) or bipy (**1b**–**3b**) were obtained by treatment of the bis(chloride) derivatives with $AgPF_6$ in the presence of the nitrogen donor. The binuclear bis(chelated) complex [Pd_2(*cyclo*-tetraphos)$_2$(bipy)$_2$][PF_6]$_4$ (**4b**) was prepared by treatment of the MeCN derivative with bipy.

All the complexes have been authenticated by ^{31}P-{^1H} and ^1H NMR spectroscopy, IR spectroscopy and elemental analysis. ^{31}P-{^1H} NMR data are reported in Table 1. The principal spectroscopic characteristics of each compound are rather ordinary and in line with those previously described for related Pd–diphosphine complexes.[11–13] The MeCN derivatives feature two weak IR bands at *ca.* 2300 cm^{-1} and a singlet at δ 2.3–2.5 in the ^1H NMR spectrum; the ^1H NMR spectra of the bipy complexes contain four resonances of equal intensity in the region from δ 7.2 to 9.1 for the $H^{3,3'}$, $H^{4,4'}$, $H^{5,5'}$ and $H^{6,6'}$ protons of the dinitrogen ligand which therefore shows two equivalent halves.

Table 1 ^{31}P-{^1H} NMR chemical shifts (δ) of [Pd(P–P)(L)$_2$]$^{n+}$ complexes

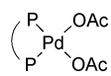
P–P	L = NCMe[a]	L = bipy[b]	L = OAc^-[b]	L = Cl^-[b]	L = CN^-[c]
dppe	74.9	73.0[d]	58.9	67.3	53.8
meso-dppb	78.0	73.7	61.8	69.5	59.4
rac-dppb	73.8	71.0	60.5	66.2	57.6
cyclo-tetraphos	79.3	83.2[c]	67.0	78.0[c]	63.2

[a] In MeCN-d_3. [b] Spectra recorded at 20 °C in CD_2Cl_2 solutions. [c] In DMF-d_7. [d] In acetone-d_6.

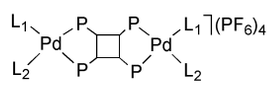


$L_1 = L_2$ = NCMe; P–P = dppe, **1a**; *meso*-2,3-dppb, **2a**; *rac*-2,3-dppb, **3a**

$L_1 + L_2$ = bipy; P–P = dppe, **1b**; *meso*-2,3-dppb, **2b**; *rac*-2,3-dppb, **3b**

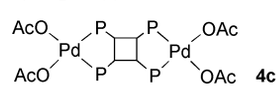


P–P = dppe, **1c**; *meso*-2,3-dppb, **2c**; *rac*-2,3-dppb, **3c**



$L_1 = L_2$ = NCMe, **4a**

$L_1 + L_2$ = bipy, **4b**



4c

Chart 2

It may be worth reporting here that, according to previous studies in solution, the time averaged preferred conformations of the five-membered palladarings in complexes of general formula [Pd(P–P)L_2]$^{n+}$ (L = neutral ligand, $n = 2$; L = monoanionic ligand, $n = 0$) are dictated by the nature of the diphosphine ligand (Chart 3).[12,15] Unlike Pd(dppe) that adopts the energetically equivalent δ and λ chiral conformations (**I** and **II**), the Pd(*rac*-dppb) and Pd(*meso*-dppb) metallarings are fixed into a single twisted (**III**) and envelope (**IV**) conformation, respectively, by the requirement that the methyl groups be equatorially disposed. An envelope conformation with a mirror plane bisecting the PPdP plane (**V**) has been found for the *cyclo*-tetraphos complex.[12,13] Obviously, the metallaring conformation affects, by symmetry, the spatial distributions of the phenyl substituents on the phosphorus donors so that in the *meso*-dppb and *cyclo*-tetraphos palladium(II) complexes the two axial phenyl groups are located on the same side of the PPdP plane, whereas they reside on opposite sides in the chiral *rac*-dppb conformation. In terms of the well known "quadrant effect",[16] this means that the steric crowding provided by the phenyl groups is concentrated on one side of the PPdP plane in the *meso*-dppb and *cyclo*-tetraphos complexes, whereas it is diagonally disposed with respect to the PPdP plane in the dppe and *rac*-dppb derivatives.

Catalytic studies

The oxidative carbonylation of styrene in MeOH has been achieved with catalytic systems comprising palladium(II) stabilized by a chelating diphosphine as catalyst, and BQ as stoichiometric organic oxidant (Tables 2–6). Under the experimental conditions employed in this work, all the complexes feature good stability towards decomposition within 3 hours of reaction time. For longer times the formation of a black

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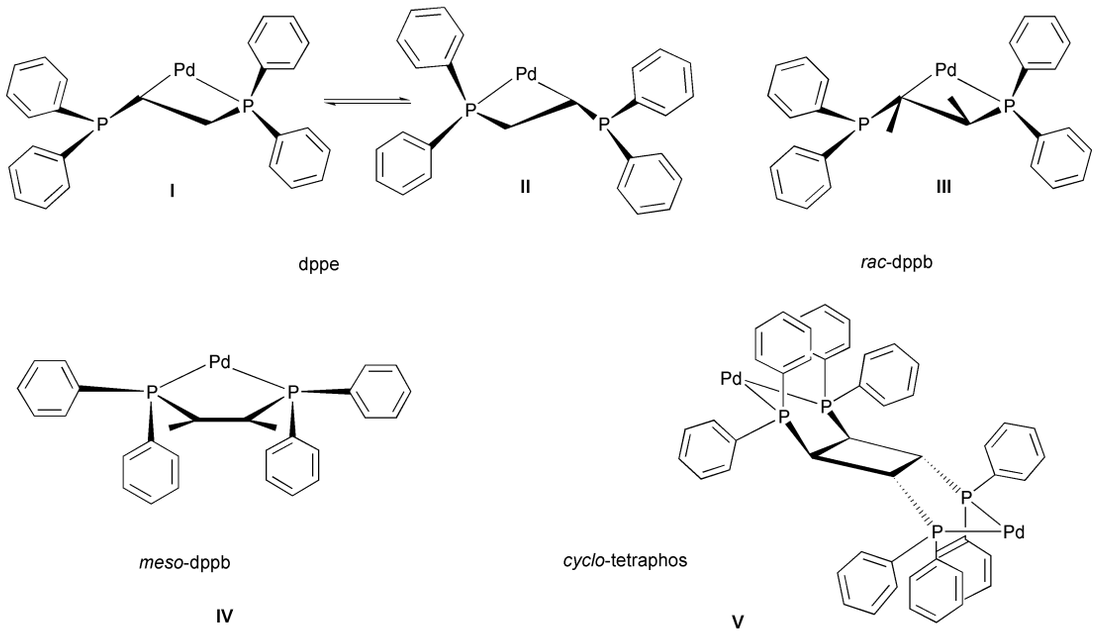

Chart 3

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precipitate of palladium metal was observed in both autoclave and HPNMR experiments with the acetate precursors. A substrate to catalyst ratio of 200 : 1, an initial CO pressure of 800 psi and a 3 h reaction time were initially chosen to evaluate the catalytic performance of the diphosphine-modified palladium(II) complexes. In some reactions TsOH was employed as co-catalyst. Chart 4 shows the reaction products

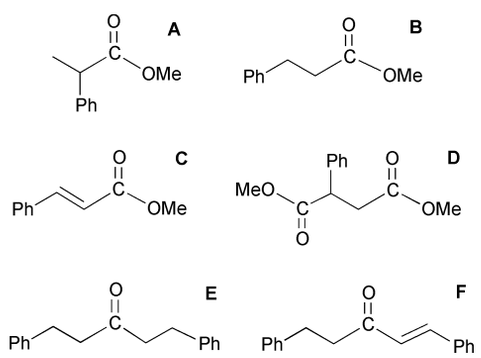

Chart 4

obtained: methyl 2-phenylpropanoate (**A**), methyl 3-phenylpropanoate (**B**), methyl cinnamate (**C**), dimethyl phenylsuccinate (**D**), 1,5-diphenyl-3-pentanone (**E**) and 1,5-diphenyl-1-penten-3-one (**F**).

The influence of some catalytic parameters on the overall conversion of styrene into carbonylated products and on the product selectivity has been determined by systematically varying the type of palladium initiator, the concentrations of the organic oxidant and protic acid, and the CO pressure. This investigation has allowed us to bring about a partial optimization of the process so as to obtain the largely predominant formation of either methyl cinnamate or dimethyl phenylsuccinate.

Oxidative carbonylation of styrene in methanol. *Methyl cinnamate vs. dimethyl phenylsuccinate.* In the absence of protic acid (Table 2), the best results in terms of both conversion and selectivity to methyl cinnamate have been obtained with palladium(II) initiators containing dppe (turnover number TON 136, 95% selectivity) or *meso*-dppb (TON 126, 95% selectivity) as stabilizing ligands and MeCN as co-ligand (runs 1, 2). Independent experiments carried out with methyl cinnamate in place of styrene have demonstrated that the former substrate is not a precursor to dimethyl phenylsuccinate.

From a perusal of Table 2 it is apparent that, independent of the diphosphine ligand, the selectivity to cinnamate is inversely proportional to the binding affinity of the co-ligand for Pd^{II} (MeCN < bipy < OAc^-). Table 2 also shows that, irrespective of the co-ligand, the selectivity to cinnamate decreases in the order dppe ≥ *meso*-dppb > *rac*-dppb > *cyclo*-tetraphos which reflects the backbone rigidity of the diphosphine ligands.[12,15,16]

In general, the best yields are obtained with the MeCN precursors, however the substrate conversion shows a less predictable trend in comparison to selectivity. When the initiator contains the MeCN co-ligand (runs 1–4) the overall conversion of styrene decreases as the backbone rigidity of the diphosphine increases. In contrast, the substrate conversion increases with the ligand rigidity when either bipy or OAc^- is employed as co-ligand (runs 5–8, 9–11). The reaction catalysed by the *cyclo*-tetraphos/OAc derivative **4c** does not follow this trend as it gives the lowest production of cinnamate but also the lowest conversion of styrene (run 12).

These catalytic results are in line with the mechanism of formation of cinnamate which, involving a β-H elimination step in a square-planar palladium(II) intermediate [eqn. (1)], requires both facile creation of a free coordination site at palladium and enough flexibility in the (P–P)Pd ring to lower the energy barrier to metal–β-hydrogen interaction.[17] Consistently, a weak co-ligand and a diphosphine with a flexible backbone would favour a β-H elimination path in the Pd–alkyl intermediate, hence the formation of cinnamate. In a complementary way, retarding the β elimination, using either a less flexible diphosphine or a co-ligand with a good binding affinity for Pd^{II}, would favour coordination of CO to the Pd–alkyl intermediate and hence allow double carbonylation of styrene to compete with β-H elimination. Once the acyl is formed succinate can be obtained *via* a methanolysis reaction [eqn. (2)].

In conclusion, the binding affinity of the co-ligand and the backbone rigidity of the diphosphine appear as the main factors that control the formation of either cinnamate or succinate. In actuality, neither the position of the phenyl substituents on

$$[(P–P)Pd(CO_2Me)L]^+ \overset{PhCH=CH_2}{\rightleftharpoons} [(P–P)Pd\{CH(Ph)CH_2CO_2Me\}L]^+ \xrightarrow{\beta\text{-H elim.}} [(P–P)Pd(H)L]^+ + PhCH=CHCO_2Me \quad (1)$$

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Table 2 Carbonylation of styrene catalysed by (P–P)Pd^{II} complexes. Dependence on both diphosphine and co-ligand[a]

Run	Pre-cursor	P–P	Co-ligand	Styrene (%)	Yield (%)	**A** (%)	**B** (%)	Sel. **A** + **B**	**C** (%)	Sel. **C**	**D** (%)	Sel. **D**	**E** (%)	**F** (%)	Sel. **E** + **F**
1	**1a**	dppe	NCMe	28.0	72.0	0.0	0.3	**0**	68.1	**95**	1.1	**2**	0.4	2.1	**3**
2	**2a**	*meso*-dppb	NCMe	33.4	66.6	0.0	0.5	**1**	63.0	**95**	1.9	**3**	0.2	1.0	**2**
3	**3a**	*rac*-dppb	NCMe	33.8	66.2	0.3	1.2	**2**	55.5	**84**	0.9	**1**	1.2	7.1	**13**
4	**4a**	*cyclo*-tetraphos	NCMe	64.3	35.7	0.0	0.0	**0**	29.2	**82**	6.5	**18**	0.0	0.0	**0**
5	**1b**	dppe	bipy	81.1	18.9	0.2	0.6	**4**	16.1	**85**	2.0	**11**	0.0	0.0	**0**
6	**2b**	*meso*-dppb	bipy	66.2	33.8	0.1	0.6	**2**	28.0	**83**	3.7	**11**	0.0	0.0	**0**
7	**3b**	*rac*-dppb	bipy	68.0	32.0	0.4	1.5	**6**	24.0	**75**	1.7	**5**	0.7	3.7	**14**
8	**4b**	*cyclo*-tetraphos	bipy	44.3	55.7	0.0	0.0	**0**	36.1	**65**	19.6	**35**	0.0	0.0	**0**
9	**1c**	dppe	OAc	81.0	19.0	0.0	0.4	**2**	5.7	**30**	12.9	**68**	0.0	0.0	**0**
10	**2c**	*meso*-dppb	OAc	45.1	54.9	0.0	0.2	**0**	10.5	**19**	44.2	**81**	0.0	0.0	**0**
11	**3c**	*rac*-dppb	OAc	44.7	55.3	0.3	1.2	**3**	8.5	**15**	45.3	**82**	0.0	0.0	**0**
12	**4c**	*cyclo*-tetraphos	OAc	75.6	24.4	0.0	0.0	**0**	2.9	**12**	21.5	**88**	0.0	0.0	**0**

[a] Catalyst (0.01 mmol); styrene (2 mmol); BQ (2 mmol); CO (800 psi); MeOH (20 mL); 80 °C; 3 h; 700 rpm. Sel. = Selectivity.

$$[(P–P)Pd(CO_2Me)L]^+ \overset{PhCH=CH_2}{\rightleftharpoons} [(P–P)Pd\{CH(Ph)CH_2CO_2Me\}L]^+ \overset{CO}{\rightleftharpoons}$$
$$[(P–P)Pd\{C(O)CH(Ph)CH_2CO_2Me\}L]^+ \xrightarrow{\text{methanolysis}} [(P–P)Pd(H)L]^+ + MeO_2CCH(Ph)CH_2CO_2Me \quad (2)$$

the phosphorus donors nor electronic factors associated with the different phosphine ligands seem to affect the rate and selectivity of the carbonylation reactions. Indeed, the ^{31}P-{^1H} chemical shifts of the palladium(II) precursors (Table 1) are quite similar for all the compounds investigated, and, most importantly, no appreciable variation of the ν(CN) stretching frequencies in the homologous series of derivatives Pd(P–P)-$(CN)_2$ was observed, which is consistent with a comparable basicity of the metal centres.[13,18]

Eqn. (2) shows that formation of the succinate occurs *via* the same alkyl intermediate which is necessary for production of cinnamate, *i.e.* by secondary insertion (2,1 mode) of the alkene into the Pd–CO_2Me bond. In principle, however, succinate might also be formed *via* primary insertion (1,2 mode) of styrene, followed by CO insertion to give the acyl [eqn. (3)]. This mechanistic hypothesis can be ruled out in our case as no trace of methyl 1-phenylacrylate $H_2C{=}C(Ph)CO_2Me$, obtainable by β-H elimination of the alkyl ligand in the primary inserted product $[Pd(P–P)\{CH_2CH(Ph)CO_2Me\}]^+$, has been detected over several carbonylation reactions.

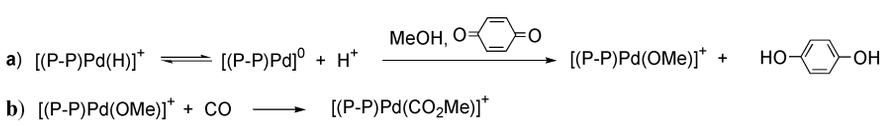
Ketones and monoesters. Besides methyl cinnamate and dimethyl phenylsuccinate, the carbonylation of styrene with the present palladium(II) initiators has also been found to yield small amounts of the saturated esters **A** and **B**, and of the saturated and α,β-unsaturated ketones **E** and **F**, respectively (Table 2, Chart 4). The formation of these by-products is strongly influenced by both the diphosphine and the co-ligand employed. In particular, the ketones are not produced when the diphosphine is *cyclo*-tetraphos (runs 4, 8, 12) and/or when the co-ligand is OAc^- (runs 9–12).

In order to rationalize these results, it is worth recalling that the formation of ketones by either carbonylation or hydrocarbonylation of styrene (Scheme 1) can occur only with metal initiators containing a hydride ligand, in the case at hand $[Pd(P–P)(H)]^+$, and through a reaction sequence involving primary insertion of the olefin into M–H, followed by a secondary insertion into M–acyl [eqn. (4)].[4g,h] Consistently, no trace of 1,4-diphenyl-1-penten-3-one product has been detected by us, which means that the secondary insertion of styrene into Pd–H (Markownikov addition) does not occur as is commonly observed for phosphine-modified palladium catalysts.[4d,e] On the other hand, the higher selectivity to **F** as compared to **E**, due to termination *via* β-H alkyl elimination, is expected for such catalysts.[2,4a–i]

The low selectivity to ketones obtained with our palladium(II) precursors is certainly due to the presence of a large excess of BQ in the catalytic mixtures. It is well known that in olefin alkoxycarbonylation reactions BQ is necessary to oxidize the (P–P)Pd^0 intermediates that may form in the reducing environment of the reaction to active (P–P)Pd^{II} species preventing their decomposition into palladium metal or other catalytically inactive species.[2,4h,19] On the other hand, a recognized role of the oxidant in many Pd–catalysed reactions between CO and olefins in MeOH is that of converting Pd–H into Pd–OMe.[2] In particular, it has been demonstrated that the reaction of $[Pd(P–P)H]^+$ with MeOH and CO to give $[Pd(P–P)(CO_2Me)]^+$ can occur through a series of equilibria involving initial formation of an unstable palladium(0) species [(P–P)Pd]^0 that is then oxidized by BQ [eqns. (5a), (5b)].[2] Intermediate palladium(0) complexes containing an η^4-BQ ligand have been

$$[(P–P)Pd(CO_2Me)L]^+ \overset{PhCH=CH_2}{\rightleftharpoons} [(P–P)Pd\{CH_2CH(Ph)CO_2Me\}L]^+ \overset{CO}{\rightleftharpoons}$$
$$[(P–P)Pd\{C(O)CH_2CH(Ph)CO_2Me\}L]^+ \xrightarrow{\text{methanolysis}} [(P–P)Pd(H)L]^+ + MeO_2CCH_2CH(Ph)CO_2Me \quad (3)$$

$$[(P–P)Pd(H)L]^+ \overset{PhCH=CH_2}{\rightleftharpoons} [(P–P)Pd(CH_2CH_2Ph)L]^+ \overset{CO}{\rightleftharpoons} [(P–P)Pd\{C(O)CH_2CH_2Ph\}L]^+ \overset{PhCH=CH_2}{\rightleftharpoons}$$
$$[(P–P)Pd\{PhCHCH_2C(O)CH_2CH_2Ph\}L]^+ \begin{cases} \xrightarrow{\beta\text{-H elim.}} [(P–P)Pd(H)L]^+ + \mathbf{F} \\ \xrightarrow{\text{protonolysis}} [(P–P)Pd(OMe)L]^+ + \mathbf{E} \end{cases} \quad (4)$$



(5)

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Table 3 Carbonylation of styrene catalysed by Pd(P–P)$(OAc)_2$ complexes. Dependence on both diphosphine and acidity[a]

Run	Pre-cursor	P–P	TsOH (equiv.)	Styrene (%)	Yield (%)	**A** (%)	**B** (%)	Sel. **A** + **B**	**C** (%)	Sel. **C**	**D** (%)	Sel. **D**	**E** (%)	**F** (%)	Sel. **E** + **F**
1	**1a**	dppe	0	65.9	34.1	0.1	0.6	**2**	9.7	**28**	23.7	**70**	0.0	0.0	**0**
2	**2a**	*meso*-dppb	0	34.2	65.8	0.0	0.5	**1**	12.9	**20**	52.4	**80**	0.0	0.0	**0**
3	**3a**	*rac*-dppb	0	28.1	71.9	0.4	1.3	**2**	11.0	**15**	59.2	**82**	0.0	0.0	**0**
4	**4a**	*cyclo*-tetraphos	0	54.0	46.0	0.0	0.0	**0**	7.3	**16**	38.7	**84**	0.0	0.0	**0**
5	**1b**	dppe	2	41.5	58.5	0.2	0.8	**2**	54.7	**94**	1.2	**2**	0.1	1.5	**3**
6	**2b**	*meso*-dppb	2	10.4	89.6	0.1	0.6	**1**	85.9	**96**	2.5	**3**	0.1	0.4	**1**
7	**3b**	*rac*-dppb	2	4.3	95.7	0.3	1.4	**2**	83.4	**87**	4.1	**4**	1.1	5.4	**7**
8	**4b**	*cyclo*-tetraphos	2	16.4	83.6	0.0	0.2	**0**	71.7	**86**	11.7	**14**	0.0	0.0	**0**
9	**1c**	dppe	4	51.8	48.2	0.0	0.3	**1**	46.3	**96**	0.4	**1**	0.2	1.0	**2**
10	**2c**	*meso*-dppb	4	23.5	76.5	0.0	0.1	**0**	75.8	**99**	0.2	**0**	0.1	0.3	**1**
11	**3c**	*rac*-dppb	4	28.1	71.9	0.2	1.0	**2**	63.9	**89**	0.0	**0**	1.1	5.7	**9**
12	**4c**	*cyclo*-tetraphos	4	36.8	62.3	0.1	0.4	**1**	57.4	**91**	5.3	**8**	0.0	0.0	**0**

[a] Conditions as in Table 2.

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detected along proton-assisted oxidation paths of Pd^0 to Pd^{II}.[20]

In view of the reaction sequence shown in eqn. (5a), it is apparent that the nucleophilic character of the co-ligand may remarkably affect the rate of conversion of $[Pd(P–P)H]^+$ into $[Pd(P–P)(OMe)]^+$ and hence promote the production of carbonylated products whose formation requires a Pd–H bond in the initiator. In other words, basic co-ligands like OAc^- would shift to the right the position of the equilibrium in eqn. (5a) and ultimately inhibit the production of ketones [eqn. (6)], which is actually what we have observed (runs 9–12).

$$[(P–P)Pd(H)]^+ + OAc^- \rightleftharpoons [(P–P)Pd(H)(OAc)] \rightleftharpoons [(P–P)Pd]^0 + HOAc \quad (6)$$

The influence of the co-ligands on the stability of hydride metal initiators and hence on product selectivity has previously been reported for Pd–catalysed enantioselective carbonylation reactions of styrene.[4a]

Why *cyclo*-tetraphos does not form an active palladium(II) catalyst to produce ketones, while *rac*-dppb is more efficient than any other ligand investigated, is hard to understand and any answer at this stage would be absolute speculation.

Finally, it may be worthwhile spending a few words on the hydroesterification products **A** and **B**. These saturated esters are produced in very low amounts, the highest selectivity reached being 6% (run 7). In principle, the formation of saturated monoesters from olefin alkoxycarbonylation reactions may involve either Pd–H or Pd–CO_2Me initiators. Recent studies, including the present one, show that the mechanism involving Pd–H is more likely, however.[4a,b,21] We have found, in fact, that saturated esters are generally formed along with ketones whose formation does require a Pd–H initiator. The regioselectivity of styrene insertion into Pd–H cannot be determined as we have no experimental observable to discriminate between the methanolysis and protonolysis termination steps.

Oxidative carbonylation of styrene in methanol with added acid. The selectivity to cinnamate increases remarkably when TsOH, a strong protic acid (pK_a −2.7) with a conjugate base of low binding affinity for Pd^{II}, is added to the catalytic mixture. Table 3 reports the results of some reactions catalysed by the palladium(II) acetate precursors **1c**–**4c** in 6 hours.

For comparative purposes, analogous reactions have been carried out with no acid at all (runs 1–4). The addition of two equivalents of protic acid shifts the selectivity from succinate to cinnamate and also increases the overall yields in carbonylated products (runs 5–8). Peaks of selectivity have been obtained with dppe and *meso*-dppb (94–96%, runs 5, 6), while the highest activity has been observed for the *rac*-dppb-modified catalyst (*ca.* 96%, run 7).

Like in CO/olefin copolymerization reactions with Pd(P–P)$(OAc)_2$ initiators,[2b] the main function of the acid is to create a free site at the metal centre as well as reduce the concentration of acetate ions in solution by shifting to the right the equilibrium $OAc^- + H^+ \rightleftharpoons HOAc$. By doing so, the added acid shifts the selectivity from succinate to cinnamate and also increases the overall conversion of the substrate, speeding up the oxidation of Pd^0 to Pd^{II} by BQ [eqn. (5)].[20]

Doubling the concentration of protic acid (runs 9–12) results in a slight increase in selectivity (99% cinnamate with *meso*-dppb), but also reduces the overall conversion of styrene. For this reason the effect of higher acid concentrations was not investigated.

Dependence of productivity and selectivity on various experimental parameters. In order to gain further insight into the factors that control the productivity and selectivity, the oxidative carbonylation of styrene catalysed by *rac*-dppb-modified catalysts has been investigated by using a single palladium catalyst around which as many as possible experimental parameters have been varied. The choice of *rac*-dppb to carry out this study is motivated by the fact that this diphosphine generally gives rise to mediocre catalysts in terms of both conversion and selectivity. Therefore, the *rac*-dppb-based catalysts, having a good margin of improvement, were considered as appropriate indicators to evaluate the role of the other experimental parameters.

Table 4 summarizes the experiments in either neutral or acidic conditions that have been useful to confirm the relevant role of the co-ligand in determining both the conversion and the selectivity. Some results have already been reported in Tables 2 and 3. In line with the function of the protic acid discussed above, only the catalytic system with the OAc^- co-ligand experiences an increase in cinnamate selectivity by adding TsOH (run 3 *vs.* 8). Interestingly, the addition of two equivalents of sodium acetate to the reaction mixture does not affect the selectivity, while the conversion increases from 55 to 73% (runs 3, 4), most likely due to improved catalyst stability.

Table 5 highlights the dependence of the catalyst activity and selectivity on the concentration of the organic oxidant with or without protic acid. Irrespective of both the palladium(II) initiator and the pH, no carbonylation of styrene occurs in the absence of BQ (runs 4, 8, 10). Moreover, the overall yield in carbonylated products increases as the amount of added BQ is increased from 100 to 300 equivalents with respect to the catalyst, which means that the rate of reduction of active Pd^{II} to inactive Pd^0 is faster than the catalytic rate. Reducing the concentration of BQ has another major but not unexpected effect. As is evident from Table 5, the selectivity to the products that require a Pd–H initiator (*e.g.* the saturated esters A and **B** and the ketones **E** and **F**) increases as the BQ concentration decreases [see eqn. (5)].

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Table 4 Carbonylation of styrene catalysed by (*rac*-dppb)Pd^{II} complexes. Dependence on the co-ligand and acidity[a]

Run	Pre-cursor	Other	Co-ligand	TsOH (equiv.)	Styrene (%)	Yield (%)	**A** (%)	**B** (%)	Sel. **A** + **B**	**C** (%)	Sel. **C**	**D** (%)	Sel. **D**	**E** (%)	**F** (%)	Sel. **E** + **F**
1	**3a**		NCMe	0	33.2	66.8	0.3	1.4	**3**	55.7	**83**	0.9	**1**	1.4	7.1	**13**
2	**3b**		bipy	0	68.0	32.0	0.4	1.5	**6**	24.0	**75**	1.7	**5**	0.7	3.7	**14**
3	**3c**		OAc	0	44.7	55.3	0.3	1.2	**3**	8.5	**15**	45.3	**82**	0.0	0.0	**0**
4	**3c**	2NaOAc	OAc	0	26.9	73.1	0.4	1.5	**3**	10.2	**14**	61.0	**83**	0.0	0.0	**0**
5			Cl	0	98.1	1.9	0.0	0.0	**0**	1.0	**53**	0.9	**47**	0.0	0.0	**0**
6	**3a**		NCMe	2	35.5	64.5	0.1	0.4	**1**	57.5	**89**	0.0	**0**	1.3	5.2	**10**
7	**3b**		bipy	2	88.4	11.6	0.0	0.0	**0**	10.0	**86**	0.0	**0**	0.1	1.5	**14**
8	**3c**		OAc	2	25.8	74.2	0.3	1.5	**2**	62.0	**84**	1.6	**2**	1.8	7.0	**12**
9			Cl	2	100.0	0.5	0.0	0.0	**0**	0.3	**60**	0.0	**0**	0.0	0.2	**40**

[a] Conditions as in Table 2.

Table 5 Carbonylation of styrene catalysed by (*rac*-dppb)Pd^{II} complexes. Dependence on both BQ and acidity[a]

Run	Pre-cursor	Co-ligand	BQ (equiv.)	TsOH (equiv.)	Styrene (%)	Yield (%)	**A** (%)	**B** (%)	Sel. **A** + **B**	**C** (%)	Sel. **C**	**D** (%)	Sel. **D**	**E** (%)	**F** (%)	Sel. **E** + **F**
1	**3c**	OAc	300	2	17.6	82.4	0.0	0.3	**0**	73.5	**89**	0.3	**0**	1.7	6.6	**10**
2	**3c**	OAc	200	2	25.8	74.2	0.3	1.5	**2**	62.0	**84**	1.6	**2**	1.8	7.0	**12**
3	**3c**	OAc	100	2	49.6	50.4	0.3	2.0	**5**	38.2	**76**	1.0	**2**	2.1	6.8	**18**
4	**3c**	OAc	0	2	100.0	0.0	0.0	0.0		0.0		0.0		0.0	0.0	
5	**3c**	OAc	300	0	39.7	60.3	0.3	1.3	**3**	8.9	**15**	49.8	**83**	0.0	0.0	**0**
6	**3c**	OAc	200	0	44.7	55.3	0.3	1.2	**3**	8.5	**15**	45.3	**82**	0.0	0.0	**0**
7	**3c**	OAc	100	0	53.8	46.2	0.6	3.4	**9**	7.0	**15**	35.2	**76**	0.0	0.0	**0**
8	**3c**	OAc	0	0	100.0	0.0	0.0	0.0		0.0		0.0		0.0	0.0	
9	**3a**	NCMe	200	0	33.2	66.8	0.3	1.4	**3**	55.7	**83**	0.9	**1**	1.4	7.1	**13**
10	**3a**	NCMe	0	0	100.0	0.0	0.0	0.0		0.0		0.0		0.0	0.0	

[a] Conditions as in Table 2.

Table 6 Carbonylation of styrene catalysed by (*rac*-dppb)Pd^{II} complexes. Dependence on both co-ligand and CO pressure[a]

Run	Pre-cursor	Co-ligand	*p*CO/ psi	Styrene (%)	Yield (%)	**A** (%)	**B** (%)	Sel. **A** + **B**	**C** (%)	Sel. **C**	**D** (%)	Sel. **D**	**E** (%)	**F** (%)	Sel. **E** + **F**
1	**3c**	OAc	800	44.7	55.3	0.3	1.2	**3**	8.5	**15**	45.3	**82**	0.0	0.0	**0**
2	**3c**	OAc	1500	53.3	46.7	0.3	0.5	**2**	4.9	**10**	41.0	**88**	0.0	0.0	**0**
3	**3a**	NCMe	800	33.2	66.8	0.3	1.4	**3**	55.7	**83**	0.9	**1**	1.4	7.1	**13**
4	**3a**	NCMe	1500	25.8	74.2	0.3	1.4	**2**	61.4	**83**	5.2	**7**	0.7	5.2	**8**

[a] Conditions as in Table 2.

The influence of the CO pressure is reported in Table 6 for reactions that exhibit opposite selectivity. A higher pressure favours production of succinate over cinnamate in the case of the acetate co-ligand (runs 1, 2), and disfavours production of ketones **E** and **F** in the case of MeCN (runs 3, 4). While it is evident why the double carbonylation reaction leading to succinate is favoured by a high pressure of CO (the two processes share the same alkyl intermediate whose kinetic evolution towards β-H elimination or acyl formation will depend on the CO pressure, see eqns. (1) and (2)), the decreased ketone production at higher CO pressure may be ascribed to faster conversion of Pd–H into $Pd–CO_2Me$ according to eqn. (5). A higher concentration of $Pd–CO_2Me$ would actually favour the formation of succinate over ketones [eqn. (4)].

High-pressure NMR study

In an attempt to intercept a catalytic intermediate, the carbonylation of styrene catalysed by either complex **2a** or **2c** was carried out in a high-pressure 10 mm sapphire tube and studied by ^1H and $^{31}P-\{^1H\}$ NMR spectroscopy in MeOH-d_4.[22]

Except for a higher concentration of complex **2a**, all the other reaction parameters were comparable to those of the corresponding autoclave reaction (Table 2, run 2). Methyl cinnamate began to form at 80 °C. In the first 30 min of reaction the $^{31}P-\{^1H\}$ NMR singlet at δ 78.0 of the precursor **2a** was the only resonance to be observed, which may be due to either a shorter lifetime as compared to the NMR timescale or a very low concentration of catalytically active species. After this time when most of the organic oxidant had been consumed two new singlets at δ 60.1 and 58.8 began to appear in the $^{31}P-\{^1H\}$ NMR spectrum. These are due to geometric isomers of the bis(chelated) complex[23] $[Pd(meso\text{-dppb})_2][PF_6]_2$ that have independently been isolated by treatment of $Pd(meso\text{-dppb})Cl_2$ with two equivalents of $AgPF_6$ in the presence of *meso*-dppb. It is noteworthy that substitution of $[Pd(meso\text{-dppb})_2][PF_6]_2$ for **2a** in a catalytic run showed the dimers to be catalytically inactive for the carbonylation of styrene. The concentration of the dimers increased with time and no other species was seen by NMR spectroscopy during the experiment. After 2 h the tube was cooled to room temperature and removed from the spectrometer probe-head. Palladium metal was clearly visible on the tube walls.

A similar experiment was carried out in which complex **2a** was replaced by the neutral acetate **2c**. The overall $^{31}P-\{^1H\}$ NMR data were identical with those observed for the cationic precursor **2a**, whereas ^1H NMR spectroscopy showed selective formation of dimethyl phenylsuccinate as expected for the type of palladium precursor employed (Table 2, run 10).

In conclusion, the HPNMR study shows that an effective deactivation path for the palladium(II) catalysts is the reduction to Pd^0 and "free" ligand. The latter entraps an active $(P–P)Pd^{II}$

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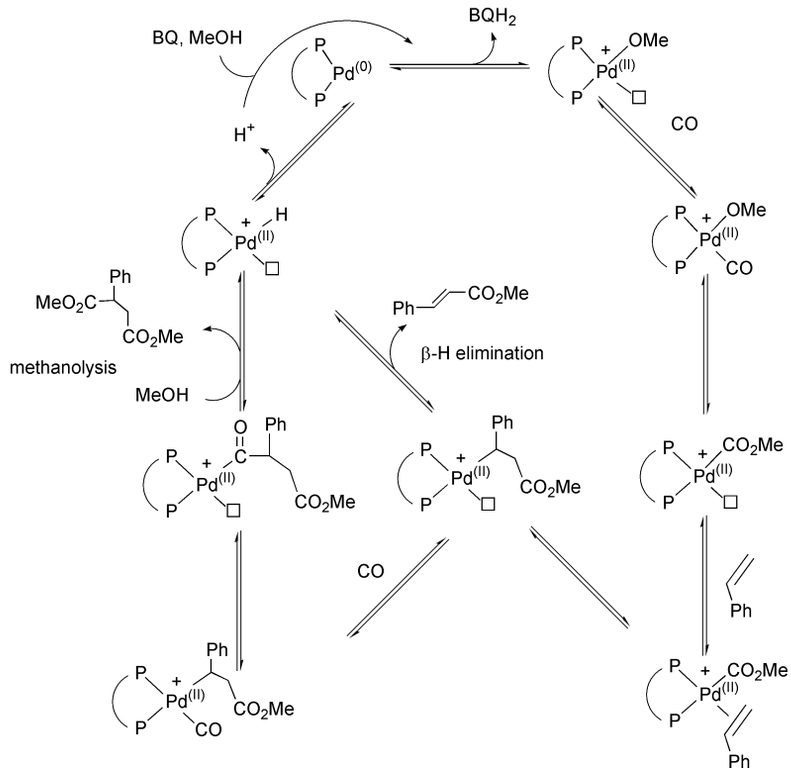

Scheme 2 Proposed mechanism for oxidative carbonylation of styrene with Pd(P–P)L_2 precursors; □ represents either a co-ligand L or a solvent molecule.

yielding inactive bis(chelated) binuclear species, which have been found also in the final catalytic mixtures from the batch experiments.

Proposed mechanism for the oxidative carbonylation of styrene in MeOH

Incorporation of the experimental data obtained with previous reports in the literature leads to the mechanism shown in Scheme 2 for the synthesis of either methyl cinnamate or dimethyl phenylsuccinate catalysed by the present diphosphine-modified palladium(II) precursors under standard experimental conditions.

At the start of the catalysis a palladium methoxide can directly be generated by interaction of the precursor with MeOH. Palladium methoxides with chelating diphosphines are unstable and may spontaneously degrade to palladium hydride and H^+ *via* β-H elimination [eqn. (7)].[2b] However, the presence

$$[(P–P)Pd]^{2+} + MeOH \rightleftharpoons [(P–P)Pd(OMe)]^+ + H^+ \longrightarrow [(P–P)Pd(H)]^+ + HC(O)H + H^+ \quad (7)$$

of BQ ensures an effective stabilization of the palladium methoxide, which rapidly converts into palladium methoxycarbonyl *via* CO migratory insertion [eqn. (5)].[2]

In principle styrene can insert into the Pd–CO_2Me bond in 1,2- or 2,1 fashion. From the observed selectivity to either cinnamate or succinate with no methyl 1-phenylacrylate by-product, we deduce that the secondary insertion prevails over primary insertion, which is in accord with previous reports.[4a,b] From the resulting 2,1-inserted Pd–alkyl intermediate, methyl cinnamate can finally be produced *via* β-H elimination which generates Pd–H. The palladium(II) hydride has a very short lifetime (the production of ketones **E** and **F** is actually almost negligible) but the presence of a high concentration of Pd^{II} in the catalytic systems is ensured by BQ that, in conjunction with MeOH, closes the cycle re-generating Pd–OMe.

As a possible alternative, the 2,1-inserted Pd–alkyl intermediate can coordinate a CO molecule and undergo its migratory insertion to give a palladium acyl. From the latter intermediate, dimethyl phenylsuccinate and Pd–H are finally produced by methanolysis of the Pd–acyl bond.

Conclusion

Palladium(II) catalysts stabilized by diphosphine ligands containing two CH_2 spacers between the PPh_2 groups, and by *N*- or *O*-co-ligands, are effective catalysts for oxidative methoxycarbonylation of styrene to methyl cinnamate or dimethyl phenylsuccinate. The prevalence of either product is determined by a complex web of factors. The β-H elimination required to produce the cinnamate from the 2,1-inserted Pd–alkyl is apparently favoured by diphosphine ligands with flexible carbon backbones and by co-ligands with low binding affinity for Pd^{II}. On the other hand, when the β-H elimination is hampered by an appropriate choice of both the diphosphine ligand and the co-ligand, CO, which has a good binding affinity for Pd^{II},[6e,24] can coordinate the metal centre and then inserts into Pd–alkyl. As a result, succinate can form by the methanolysis mechanism and the selectivity to succinate prevails over that to cinnamate.

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