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Ethene hydromethoxycarbonylation catalyzed by *cis*-$[Pd(SO_4)(PPh_3)_2]/H_2SO_4/PPh_3$

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ABSTRACT

The neutral precursor *cis*-$[Pd(SO_4)(PPh_3)_2]$ turns into an active catalyst for the hydromethoxycarbonylation of ethene when used in combination with H_2SO_4 and PPh_3. The influence of the following operating conditions on the catalytic activity have been studied: (i) H_2SO_4/Pd ratio; (ii) PPh_3/Pd ratio; (iii) total pressure with CO/ethene = 1/1; (iv) pressure of one gas at constant pressure of the other; (v) H_2O concentration; (vi) temperature. At 100 °C a TOF = 2168 h^{-1} has been achieved when the catalytic system is used in the ratios Pd/H_2SO_4/P = 1/107/18 (mol/mol), under 6 bar (CO/E = 1/1), H_2O concentration 0.16% in MeOH by weight. After catalysis and upon addition of LiCl, *trans*-$[Pd(COEt)Cl(PPh_3)_2]$, which is related to the "Pd–H" catalytic cycle, has been isolated. *Cis*-$[Pd(SO_4)(PPh_3)_2]$ in CD_2Cl_2/MeOH reacts with CO to give a PdCOOMe complex (related to the "carbomethoxy mechanism"), which neither inserts ethene, nor gives methyl propanoate (MP). In the presence of H_2O and H_2SO_4 the carbomethoxy complex is unstable giving a Pd–H complex, which yields catalysis to MP in the presence of CO and ethene. The "Pd–H" and "Pd–COOMe" catalytic cycles are discussed on the basis of the influence of the operating conditions on the TOF and of NMR evidences.

1. Introduction

The recent discovery of a highly active and selective cationic catalyst, [PdH(MeOH)(dtbpx)](TfO) (dtbpx = 1,2-bis[(di-*t*-butyl) phosphinomethyl]benzene; TfO = trifluoromethansulphonate), for the hydromethoxycarbonylation of ethene (E) to methyl propanoate (MP) (TOF 50,000 h^{-1}, selectivity 99.98%, 80 °C, 10 bar, CO/E = 1/1) [1,2] has opened the way to a new convenient environmentally preferred route for the commercial production of methyl methacrylate [3–5].

Other cationic Pd(II)–diphosphine systems have been reported to be highly active and selective, for example the one based on 1,3-bis(di-*t*-butylphosphino)propane (TOF = 25,000 h^{-1}, 97.4% selectivity at 120 °C and 40 bar, CO/E = 2/1) [6,7].

For the catalyst [PdH(MeOH)(dtbpx)](TfO), it has been demonstrated that catalysis initiates through the insertion of the olefin into the Pd–H bond with formation of a Pd-ethyl intermediate, followed by the insertion of CO leading to a Pd-acyl species, which undergoes methanolysis with formation of the product and of the Pd–H species that initiates another catalytic cycle [8–10]. It has been proposed that the steric bulkness of the diphosphino ligand favours the methanolysis step [11] and impedes further insertions of E and CO [11,12], which would produce an alternating CO–E copolymer, as normally is the case when less hindered disphophine ligands are used [12–15].

The use of Pd(II)-monophosphine catalysts for the hydromethoxycarbonylation of olefins has been known for a longer time [16–18]. Though less active, they are of interest because they allow the isolation of Pd(II)-acyl and Pd(II)-carbomethoxy [19–27], which are related to the so called "hydride" mechanism, outlined above, and to the so called "carbomethoxy" mechanism. This initiates through the insertion of CO into a Pd-methoxy bond, which gives a carbomethoxy intermediate, followed by the insertion of the olefin with formation of an ethylcarbomethoxy-β-chelate, which, through the intermediacy of its enolate isomer, undergoes protonolysis by MeOH yielding the ester and the Pd-methoxy species back to the catalytic cycle.

Compared to above reported diphosphine-based catalysts, the cationic catalytic system $[Pd(TsO)_2(PPh_3)_2]/PPh_3$ is moderately active in the presence of a hydride source such as hydrogen, water or *p*-toluensulphonic acid (TOF 1800 h^{-1} at 100 °C, 40 bar, CO/E = 1/1, Pd/TsOH/P = 1/8/10, H_2O 800 ppm in MeOH [24]).

Here, we report an investigation on the hydromethoxycarbonylation of E using the neutral complex *cis*-$[Pd(SO_4)(PPh_3)_2]$, which turns into an active catalyst even under relatively low pressure when used in combination with H_2SO_4.

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2. Experimental

2.1. Materials

Carbon monoxide and ethene (purity higher then 99%) were supplied by SIAD Spa (Italy). MeOH, NEt_3, PPh_3, H_2SO_4 (96%) and CD_2Cl_2 were purchased from Aldrich Chemicals. $Pd(OAc)_2$ was purchased from Chimet (Italy). NEt_3 and the solvents were of commercial grade and used without further purification. *Cis*-$[Pd(SO_4)(PPh_3)_2]$ [28], *trans*-$[PdCl_2(PPh_3)_2]$ [29], *trans*-$[Pd(COEt)Cl(PPh_3)_2]$ [22], *cis*-$[Pd(H_2O)_2(PPh_3)_2](TsO)_2{\cdot}2H_2O$ [22], *cis*-$[Pd(TsO)_2(PPh_3)_2]$ [22] and *trans*-$[Pd(COEt)(TsO)(PPh_3)_2]$ [26] were prepared according to methods reported in the literature.

2.2. General procedure

The IR spectra were recorded in nujol mull on a Nicolet FTIR instruments mod. Nexus. ^1H and $^{31}P\{^1H\}$ NMR spectra of the complexes dissolved in CD_2Cl_2 (typically 10^{-2} mol L^{-1}) were recorded on a Bruker AMX 300 spectrometer equipped with a BB multinuclear probe operating in the FT mode at 300 and 121.5 MHz for ^1H and $^{31}P\{^1H\}$, respectively. ^1H and $^{31}P\{^1H\}$ chemical shifts are reported in ppm downfield of the deuterated solvent used as internal standard or of externally referenced to 85% H_3PO_4, respectively. GC analysis was performed using a GC Agilent 7890A instrument, equipped with a column HP-5 30 m × 0.320 mm, 0.25 μm, conditions: oven 40 °C (10 min) to 180 °C (30 min) at 25 °C/min, *T*(inj) = 250 °C, *T*(det) = 250 °C, flow = 2.2 mL/min, N_2. Conductivity measurements were carried out using an instrument Radiometer Copenhagen CDM 83.

2.3. Hydromethoxycarbonylation of E

The catalytic reactions were carried out using a stainless steel autoclave of *ca.* 250 mL provided with a four-blade self-aspirating turbine. In order to avoid contamination by metallic species due to the corrosion of the internal surface of the autoclave, the solvent and the catalytic system were contained in a *ca.* 150 mL Pyrex bottle placed inside the autoclave.

In a typical experiment 10 mg of *cis*-$[Pd(SO_4)(PPh_3)_2]$ (1.38×10^{-2} mmol), 58 mg of PPh_3 (0.22 mmol) were added to 80 mL MeOH containing 151 mg H_2SO_4 (96%) in the Pyrex bottle placed into the autoclave. The autoclave was purged by pressurizing it with a mixture of CO and E (1/1, *ca.* 3 bar) and depressurizing it to atmospheric pressure (this cycle was repeated 5 times at room temperature). Then the autoclave was heated rapidly up to 100 °C and then charged first with E and then with CO to the desired pressure. The pressure was maintained constant throughout the batch time (1 h) by continuously feeding CO and E in the ratio 1/1 from a reservoir connected to the autoclave through a constant pressure regulator. Then the autoclave was rapidly cooled to 5–10 °C and the gas was carefully released. The liquid was analyzed by GC. The H_2O content in the reaction medium was measured before and after the reaction by the Karl–Fischer method.

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments were carried out under 60 bar of total pressure with CO/E = 1/1, at 100 °C. Above this temperature partial decomposition of the catalyst occurs as evidenced by the formation of Pd metal. The catalytic activity of the $[Pd(SO_4)(PPh_3)_2]/H_2SO_4/PPh_3$ system in the hydrocarbomethoxylation of E (reaction (1)) is strongly influenced by the H_2SO_4/Pd ratio as shown in Fig. 1. It rises quickly from 103 h^{-1}, when no H_2SO_4 is added, up to a maximum of 1700 h^{-1} when the H_2SO_4/Pd ratio is 107/1.

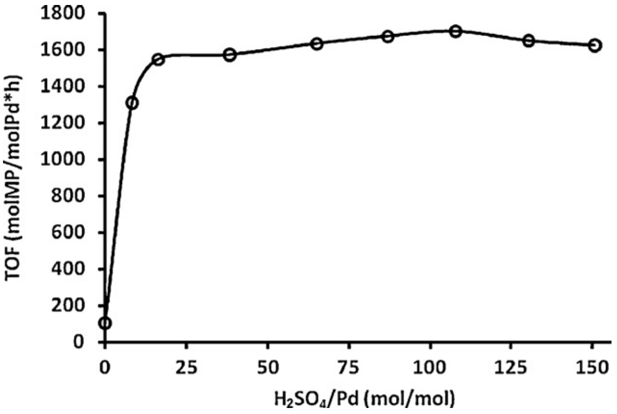

Fig. 1. Influence of the H_2SO_4/Pd ratio on the TOF. *Run conditions*: $[Pd(SO_4)(PPh_3)_2]$, 1.38×10^{-2} mmol; PPh_3, 0.22 mmol; solvent MeOH, 80 mL; $p_{CO} = p_E = 30$ bar; temperature, 100 °C; reaction time, 1 h.

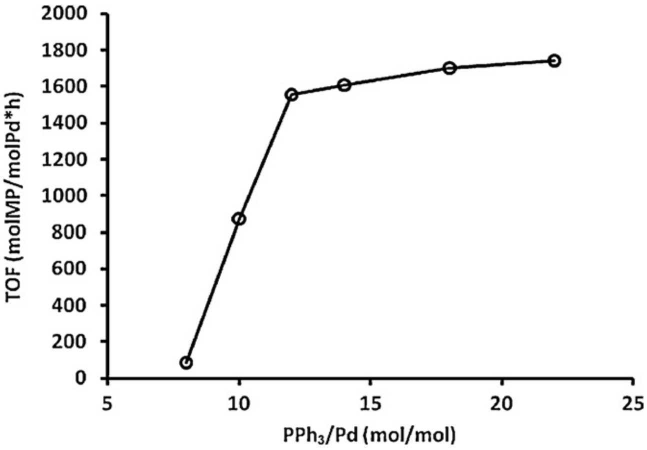

Fig. 2. Influence of added PPh_3/Pd ratio on the TOF. *Run conditions*: $[Pd(SO_4)(PPh_3)_2]$, 1.38×10^{-2} mmol; H_2SO_4, 96% 151 mg, 1.48 mmol H_2SO_4; solvent MeOH, 80 mL; $p_{CO} = p_E = 30$ bar; temperature, 100 °C; reaction time, 1 h.

(1)

Fig. 2 shows the influence of the P/Pd ratio on the catalytic activity. Some decomposition to Pd metal occurs when the ratio is <10/1. The catalytic activity is not inhibited even when using a relatively large excess of PPh_3. As a matter of fact, it increases of *ca.* 15% when the P/Pd ratio is increased from 12 to 22. Under comparable reaction conditions (Pd/P/acid = 1/10/10–30) the sulphate system is *ca.* 30% more active that the tosylate system [24].

The promoting effects of the acid and of PPh_3 will be discussed later (see the proposed catalytic cycle).

3.2. Influence of the pressure

The results shown in Figs. 1 and 2 induced us to study the influence of the pressure of CO and of E using the catalytic system in the ratios Pd/P/H_2SO_4 = 1/18/100.

Fig. 3 shows the influence of total pressure of CO and E (CO/E = 1/1). Upon increasing the pressure up to 6 bar the TOF increases rapidly up to a maximum of 2168 h^{-1} and then it decreases gently down to 1540 h^{-1} under 100 bar.

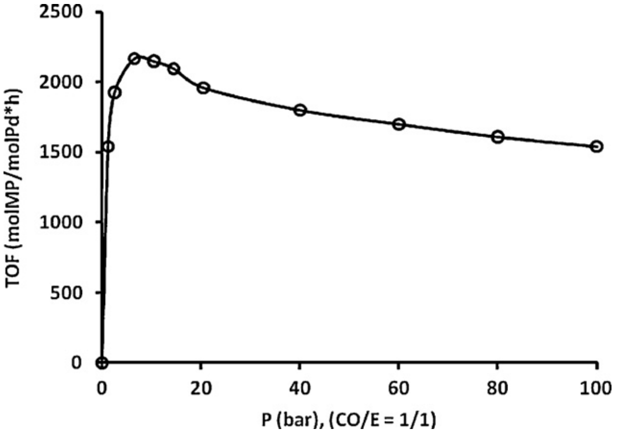

Fig. 3. Influence of the total pressure (CO/E = 1/1) on the TOF. *Run conditions*: [Pd(SO_4)(PPh_3)$_2$], 1.38 × 10^{-2} mmol; PPh_3, 0.22 mmol; H_2SO_4, 96% 151 mg, 1.48 mmol H_2SO_4; solvent MeOH, 80 mL; temperature, 100 °C; reaction time, 1 h.

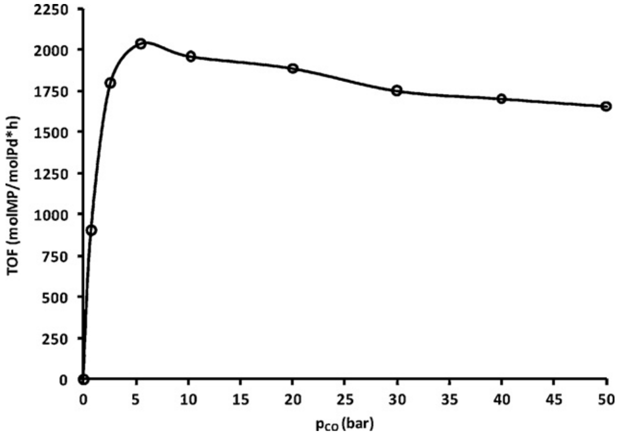

Fig. 4. Influence of CO partial pressure at constant E pressure. *Run conditions*: [Pd(SO_4)(PPh_3)$_2$], 1.38 × 10^{-2} mmol; PPh_3, 0.22 mmol; H_2SO_4, 96% 151 mg, 1.48 mmol H_2SO_4; solvent MeOH, 80 mL; p_E, 10 bar; temperature, 100 °C; reaction time, 1 h.

Figs. 4 and 5 show the influence of the pressure of CO or of E keeping the pressure of the other gas at a constant value of 10 bar. Again, the catalytic activity increases rapidly to reach a maximum TOF = 2040 h^{-1} or 1960 h^{-1} upon increasing the pressure of CO or E up to 5.5 or up to 10 bar, respectively. And again, under higher pressure the TOF decreases gently (1656 h^{-1} or 1380 h^{-1} under 50 bar of CO or E, respectively). These results suggest that CO and E are only slightly competitive for coordination to the metal centre.

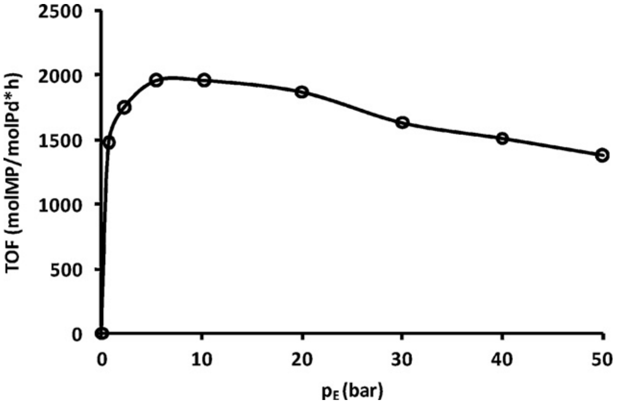

Fig. 5. Influence of E partial pressure at constant CO pressure. *Run conditions*: [Pd(SO_4)(PPh_3)$_2$], 1.38 × 10^{-2} mmol; PPh_3, 0.22 mmol; H_2SO_4, 96%, 151 mg, 1.48 mmol H_2SO_4; solvent MeOH 80 mL; p_{CO}, 10 bar; temperature, 100 °C; reaction time, 1 h.

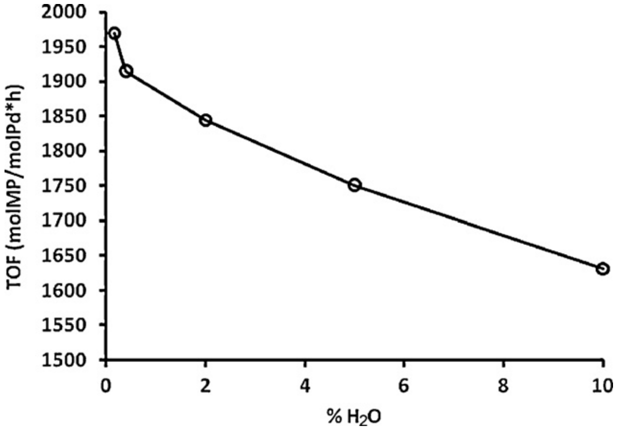

Fig. 6. Influence of concentration of H_2O on the TOF. Run conditions: [Pd(SO_4)(PPh_3)$_2$], 1.38 × 10^{-2} mmol; PPh_3, 0.22 mmol; H_2SO_4 96% 151 mg, 1.48 mmol H_2SO_4; solvent (MeOH + H_2O) 80 mL; p_{CO} = p_E 10 bar; temperature, 100 °C; reaction time 1 h.

3.3. *Influence of the water concentration*

The initial concentration of H_2O in the MeOH we used was 400 ppm. After catalysis under the conditions of Figs. 1–5 the concentration of H_2O is higher (2500 ppm when the precursor and the acid are used in the ratio Pd/H_2SO_4 = 1/150). Analogously, the H_2O concentration increases up to 2000 ppm under the conditions of Fig. 2 when Pd/H_2SO_4/P = 1/110/18. The increasing of H_2O concentration is likely to be due to esterification of MeOH with H_2SO_4. These observations prompted us to investigate the effect of H_2O added to the solvent. Under the conditions of Fig. 6, the TOF decreases to 1700 h^{-1} when MeOH with 10% of H_2O is used. This fact suggests that H_2O competes with the reacting molecules for coordination to the metal centre.

3.4. *Influence of the temperature*

The catalytic activity falls rapidly below 70 °C (Table 1). The data fit satisfactorily the Arrhenius plot only in the range 70–100 °C (Fig. 7). In this range the activation energy is 22.6 kcal mol^{-1}. At 60 °C the catalytic activity is significantly lower than that expected from the Arrhenius plot. This fact suggests that at this temperature the interaction of free PPh_3 and the metal centre is such as to inhibit the coordination of the molecules that lead to the formation of MP.

3.5. *On [Pd(SO$_4$)(PPh$_3$)$_2$]*

The IR spectrum of *cis*-[Pd(SO_4)(PPh_3)$_2$] has been already reported. The sulphato ligand acts as bidentate in the expected four

Table 1
Influence of temperature on the TOF.

Experiment	Temperature (K)	TOF (h^{-1})
1	373	2168
2	363	1200
3	353	513
4	343	149
5	333	8.4

Run conditions: [Pd(SO_4)(PPh_3)$_2$], 1.38 × 10^{-2} mmol; PPh_3, 0.22 mmol; H_2SO_4, 96%, 151 mg, 1.48 mmol H_2SO_4; solvent MeOH, 80 mL; p_{CO} = p_E = 3 bar at the working temperature; reaction time, 1 h.

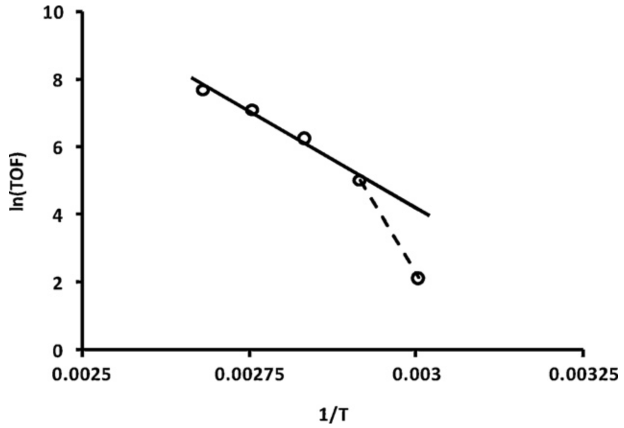

Fig. 7. Arrhenius plot ln TOF *versus* 1/*T* relevant to the data on the Table 1.

co-ordination of Pd(II) [30], so that the complex has a *cis*-geometry. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 shows a singlet at 35.56 ppm, well above 30 ppm. It has been suggested that this is an indication for a *cis*-geometry [31]. Therefore, the complex has a *cis*-geometry also in solution.

In nitromethane solution the complex is not ionic ($\Lambda_M < 2\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$, which is the same as the solvent), in contrast with the analogous tosylate complexes *cis*-$[Pd(TsO)_2(PPh_3)_2]$ and *cis*-$[Pd(H_2O)_2(PPh_3)_2](TsO)_2{\cdot}2(H_2O)$ (Λ_M 51.1 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ and 41.8 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$, respectively, at 25 °C, concentration $10^{-3}\,\text{mol}\,\text{L}^{-1}$). The fact that *cis*-$[Pd(TsO)_2(PPh_3)_2]$ presents a conductivity close to that of the cationic complex *cis*-$[Pd(H_2O)_2(PPh_3)_2](TsO)_2{\cdot}2(H_2O)$ suggests that in the first complex the solvent displaces the TsO anion which is weakly coordinating.

It has been reported that *cis*-$[Pd(TsO)_2(PPh_3)_2]$ reacts with CO (1 bar) in CD_2Cl_2/MeOH even at −78 °C to give *trans*-$[Pd(COOMe)(TsO)(PPh_3)_2]$ [31]. This fact also suggests that the TsO anion is weakly coordinating. In contrast, the sulphate complex is rather inert. After 1 h at room conditions the $^{31}P\{^1H\}$ and ^1H NMR spectra show, in addition to the signals of the starting sulphate, a new signal at 18.86 ppm and at 2.51 ppm, respectively. The intensities of the $^{31}P\{^1H\}$ and ^1H signals of the unreacted sulphate and of the new complex are in the ratio 3/1 and 30/1, respectively, which indicates that the sulphate complex is 25% converted. Under 4 bar of CO the conversion is 100% in *ca.* 30 min. The new signals at 18.86 ppm and at 2.51 ppm are close to those of the carbomethoxy complexes *trans*-$[Pd(COOMe)(X)(PPh_3)_2]$ (X = Cl, TsO) and *trans*-$[Pd(COOMe)(H_2O)(PPh_3)_2](TsO)$ [23,27,31], which suggests that the new complex is likely to be an analogous carbomethoxy complex having a *trans*-geometry. Though it has not been isolated, the new complex may be reasonably formulated as *trans*-$[Pd(COOMe)(SO_4H)(PPh_3)_2]$. Its formation may be depicted by reaction (2), in which the proton released from MeOH is captured by the sulphate ligand.

$$\begin{aligned} &cis\text{-}[Pd(SO_4)(PPh_3)_2] \\ &\quad + CO + MeOH \rightleftharpoons trans\text{-}[Pd(COOMe)(HSO_4)(PPh_3)_2] \end{aligned} \tag{2}$$

The conductivity measurements and the reactivity with CO and MeOH suggest that the sulphate ligand is not so labile as the tosylate one. It is well known that the tosylate anion possesses a weakly coordinating ability, so that the metal centre presents easily available coordination sites, which is a factor of paramount importance in promoting the catalytic activity [11–13,18,32]. And yet, the catalytic activity of the neutral sulphate complex is higher than that of the cationic tosylate one. The fact that *cis*-$[Pd(SO_4)(PPh_3)_2]$ is highly active when used in combination with H_2SO_4 suggests that the sulphate ligand may be easily removed from the coordination sphere of Pd(II). That the acid may interacts with the sulphate complex has been proved by the fact that when the sulphate is treated with H_2SO_4 ($Pd/H_2SO_4 = 1/10$) at room temperature the $^{31}P\{^1H\}$ signal shifts immediately from 35.56 ppm to 40.38 ppm. This interaction is likely to occur through hydrogen bridges between the sulphate ligand and H_2SO_4. Thus, though the precursor is taken in a neutral form, under the action of H_2SO_4 it transforms into a cationic species and the catalytic cycle performs *via* cationic intermediates. The acid has also another important function that will be discussed later together with the proposed catalytic cycle.

3.6. *On the catalytic cycle*

The generally accepted catalytic cycles are shown in the Scheme 1. They have been briefly outlined in Section 1. Hereafter, we discuss the evidences that are in their favour.

When, after the formation of the carbomethoxy complex through reaction (2), CO is replaced by E (4 bar) or by a mixture of CO and E (1/1, 4 bar) no change is observed in the NMR spectra even at 50 °C for *ca.* 30 min, which indicates that the complex is rather stable and that the Pd–COOMe moiety is reluctant to insert the olefin. It is worth noting that in the presence of E there are all the ingredients necessary for the formation of MP, which however does not occur.

Instead, when the carbomethoxy complex is treated with H_2SO_4 ($Pd/H_2SO_4 = 1/5$) at room temperature it slowly decomposes. The intensity of the ^1H NMR of the Pd–COOMe moiety lowers and at the same time a broad signal appears in the Pd–H region (*ca.* −6 ppm). The intensity of the $^{31}P\{^1H\}$ signal at 18.86 ppm of the carbomethoxy complex also lowers (in 15 min is reduced of *ca.* 40%) and a new signal appears at 24.00 ppm, which is close to that of the dinuclear complex $[(PPh_3)_2Pd(\mu\text{-}H)(\mu\text{-}CO)Pd(PPh_3)_2](CF_3COO)$ [33] (see later). The instability of the carbomethoxy complex and the formation of the hydride is presumily due to adventitious H_2O in the solvent and to that introduced with the acid (reaction a on the Scheme 1). The fact that in the absence of the acid the carbomethoxy is stable (see above) suggests that the acid promotes reaction a. If some H_2O is added ($Pd/H_2SO_4/H_2O = 1/5/5$) the Pd–COOMe moiety is destroyed in a short time and does not reform even under 4 atm. of CO. Again, there is formation of a Pd–H species which is revealed by the broad signal at *ca.* −6 ppm, which turns into a quintet centred at −6.27 ppm ($J_{H\text{-}P}$ 40 Hz) when the temperature is lowered to −30 °C. Upon adding 3 equiv. of PPh_3 at room temperature the quintet is replaced by a not well resolved doublet of triplets (−6.78 ppm, $J_{H\text{-}P}$ 177 Hz) (see later for the nature of these hydrides and Refs. [33,34]). Therefore, if during catalysis there might be the formation of a Pd–COOMe species, this would likely be transformed into a Pd–H species by the action of H_2O. All these evidences are not in favour of the "Pd–COOMe" cycle.

The other cycle starts from a Pd–H species. The NMR spectrum of the sulphate complex in CD_2Cl_2/MeOH (6/1, v/v), either in the presence of H_2SO_4 ($Pd/H_2SO_4 = 1/5$) or in its absence, does not show any signal in the hydride region. Therefore, MeOH is not the source of a hydride, although it can be even in the presence of an acid [7]. Neither H_2O is the source, because when it is added to the NMR tube no hydride signal appears. In contrast, when CO is admitted (4 bar, $Pd/H_2SO_4/H_2O = 1/5/5$) the quintet at −6.27 ppm[1] is detected. Therefore, H_2O in combination with CO is the source of the hydride, which may form through a reaction closely related to the well known water gas shift reaction (WGSR) [34,35]. When

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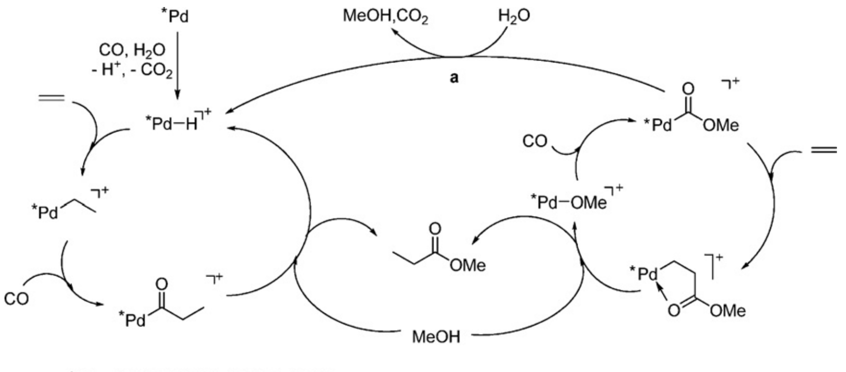
[1] In the presence of 3 equiv. of PPh_3, the doublet of triplets reported above is detected.



$^*Pd = [Pd(SO_4)(PPh_3)_2]/PPh_3/H_2SO_4$

Scheme 1. “Pd–H” and “Pd–COOMe” catalytic cycles for the hydromethoxycarbonylation of ethene.

E is admitted (E/CO = 1/1, total pressure 4 bar) formation of MP is observed (300% in the presence of 3 equiv. of PPh_3 after 1 h at 40 °C).

Attempts to isolate cationic acyl or carbomethoxy complexes, after catalysis had occurred in the autoclave, did not give satisfactory results. Instead, upon adding a LiCl solution in MeOH a white precipitate was formed. Its IR spectrum shows a band at 1684 cm^{-1}. The $^{31}P\{1H\}$ and the ^1H NMR spectra in CD_2Cl_2 show a signal at 20.55 ppm and at −0.11 (t, CH_3, 3H, CH_2CH_3, *J* 6.82 Hz) and at 1.89 ppm (q, CH_2, 2H, CH_2CH_3, *J* 6.82 Hz). These data are identical to those of *trans*-$[Pd(COEt)Cl(PPh_3)_2]$ synthesized from *trans*-$[Pd(COEt)(TsO)(PPh_3)_2]$ and LiCl in MeOH [26] or by pressurizing *trans*-$[PdCl_2(PPh_3)_2]$ with CO in MeOH [22]. Therefore the complex isolated after addition of LiCl is *trans*-$[Pd(COEt)Cl(PPh_3)_2]$, which is related to the “Pd–H” cycle. All these observations are in favour of this mechanism. The results of a detailed NMR investigation on the mechanism of the catalytic hydrocarbomethoxylation of E will be the object of a forthcoming article.

As far as the nature of the hydrides above mentioned is concerned, we report here some results on the reactivity of $[Pd(CF_3COO)_2(PPh_3)_2]$ with CO in aqueous trifluoroacetic acid solution. This system catalyzes the WGSR through the intermediacy of $[PdH(PPh_3)_3](CF_3COO)$, which shows a doublet of triplets at −7.0 ppm ($J_{H\text{–}Ptrans}$ 177 Hz, $J_{H\text{–}Pcis}$ 13.5 Hz) [33,34] in the ^1H NMR spectrum. This hydride reacts with CO, giving the binuclear palladium carbonyl hydride complex $[(PPh_3)_2Pd(\mu\text{-}H)(\mu\text{-}CO)Pd(PPh_3)_2](CF_3COO)$ (^1H hydride signal at −6.3(q), $J_{H\text{–}P}$ 40 Hz [33]), which gives $[PdH(PPh_3)_3]^+$ when is treated with an excess of PPh_3. Therefore, these are the hydrides generated in the present study.

It has been proposed that the formation of the dinuclear species occurs through partial deprotonation of the mononuclear hydride with formation of a Pd(0) complex, which reacts with the remaining undeprotonate Pd(II)–hydride complex to give the formally Pd(I) dinuclear complex (reaction (3)) [33].

$$[P_3PdH]^+ \overset{-H^+}{\rightleftharpoons} P_3Pd^0 \overset{CO,-P}{\rightleftharpoons} P_2Pd^0(CO) \overset{[P_3PdH]^+,-P}{\rightleftharpoons} [P_2Pd(\mu\text{-}H)(\mu\text{-}CO)PdP_2]^+ \qquad (3)$$

Equilibria (3) help us to give a sound explanation on the promoting effect of H_2SO_4 and on the role of PPh_3 (*cf.* Figs. 1 and 2). Though a fraction of added PPh_3 may be subtracted from the reaction medium because of the reaction with H_2SO_4 (equilibrium (4)) [36], it remains enough free PPh_3 to stabilize the catalytic system, because the phosphonium salt is a PPh_3 buffer, which releases it when necessary [36]. Thus, the combined action of PPh_3 and H_2SO_4 may prevent the formation of dinuclear complexes as well as further degradation to inactive Pd(0).

$$PPh_3 + H_2SO_4 \rightleftharpoons [HPPh_3]^+HSO_4^- \qquad (4)$$

In addition to easy the displacement of the sulphate anion mentioned above, the acid stabilizes $[PdH(PPh_3)_3]^+$ against deprotonation thus providing a higher concentration of the hydride, which leads to higher TOFs. Moreover, the fact that higher TOFs are achieved in the presence of a relatively high excess of PPh_3 suggests that this ligand does not impede access of the reacting molecules to the coordination sites of Pd(II). In addition, PPh_3 may promote rearrangements in the catalytic intermediates in such a way as to bring together the moieties involved in the insertion and in the product-forming steps.

Thus the promoting effect of the acid is also more in favour of the Pd–H cycle. In addition, it should be pointed out that in no case there was any formation of dimethyl succinate, either under relatively high pressure with the monomers in the ratio 1/1 (Fig. 3) or with a significant excess of CO (CO/E = 5/1) (Fig. 4). Formation of this diester would occur through insertion of E into a Pd–COOMe. Therefore, this is another reason why catalysis to MP through the “carbomethoxy” cycle is unlikely.

In spite of these experimental evidences the “Pd–COOMe” mechanism cannot be excluded to occur. Indeed, it has been found that the hydromethoxycarbonylation of E using the diphosphine precursor $[Pd(H_2O)_2(dppf)](TsO)_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) yields MP and oligoketoesters as well as diesters such as dimethyl succinate and higher ketodiesters even when the precursor is used in combination with a relatively large amount of TsOH (Pd/TsOH = 1/160) and with CO and E in the ratio 1/1 [37]. Therefore, MP may form through both mechanisms. The simultaneous occurrence of the two cycles has been demonstrated in the hydromethoxycarbonylation of E using a Pd(II)-$[1,3\text{-}(iBu_2P)_2C_3H_6]$ cationic precursor [38]. However, it should be pointed out that these complexes possess a *cis*-geometry, which favours the insertion reactions.

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