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An NMR study on the mechanism of ethene hydromethoxycarbonylation catalyzed by cationic Pd(II)–PPh₃ complexes

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ABSTRACT

The reactivity of cis-[Pd(H₂O)₂(PPh₃)₂](TsO)₂.2(H₂O) (I,H₂O), trans-[Pd(COEt)(TsO)(PPh₃)₂] (II) and trans- $[Pd(COOMe)(TsO)(PPh_3)_2]$ (III) has been studied by ¹H and ³¹P{¹H} NMR spectroscopy under conditions that mime the catalytic ethene hydromethoxycarbonylation (EHMC), *i.e.* in the presence of PPh₃, H₂O and TsOH. (I_{H_2O}), in the presence of two equivalents of PPh₃, reacts with MeOH and CO (0.3 MPa) at 193 K to give [Pd(COOMe)(TsO)(PPh₃)₃] (III'), which reacts with H₂O in the presence of TsOH at 293 K to generate [PdH(PPh₃)₃](TsO) (IV) quantitatively. This hydride inserts ethene (0.3 MPa, 293 K) to give trans- $[Pd(Et)(TsO)(PPh_3)_2]$ (V), which reacts with CO (0.3 MPa, 223 K) giving $[Pd(COEt)(PPh_3)_3](TsO)$ (II)[/] and initiates the catalytic EHMC at 293 K. II, in combination with PPh3 and TsOH, reacts at 293 K with MeOH with quantitative formation of methyl propanoate (MP) and IV and promotes the catalysis starting from this temperature, under 0.6 MPa of CO/ethene (1/1) when the ratio PPh₃/TsOH/II is 2/6/1; upon increasing the PPh₃/II ratio, the catalytic activity passes through a maximum when the ratio is 4/1, even though it initiates at a higher temperature. In the absence of added ligand, MP is formed in a stoichiometric amount, catalysis is not observed and decomposition to Pd metal occurs. Therefore, PPh₃ is essential in order to stabilize hydride IV, though an excess of ligand is detrimental. III does not insert ethene even at 343 K, a temperature well above that at which catalysis is observed. All these experimental evidences support the Pd-H cycle.

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1. Introduction

Pd(II)—phosphine complexes are efficient catalysts for the carbonylation of ethene which yields a wide spectrum of products, ranging from monocarbonylated ones to perfectly alternating CO— ethene high molecular weight polyketones (PKs) [1–3]. In MeOH as a solvent, catalysis may start from a Pd—H initiator and/or a Pd— OMe one. In the case of the copolymerization, catalysis undergoes through both initiators, as proved by end-group analysis of the copolymer [4]. The crossover between the hydride and the other mechanism has been proven by a multinuclear NMR study [5].

When the copolymerization process is interrupted just after the incorporation of only one molecule of each monomer, methyl propanoate (MP) is formed. In this case, several studies have shown that the "hydride" cycle plays a major role, if not the only one [6–11]. This is rather surprisingly being the two reactions closely related. In the hydride cycle, the olefin inserts into a Pd–H bond giving a Pd–alkyl intermediate, which inserts CO generating a Pd-acyl intermediate, which undergoes methanolysis with production of the ester and regeneration of the starting hydride. This route has gained wide acceptance also using other olefins [12–15]. The other mechanism is initiated by the formation of a Pd–OMe species. Successive insertion of CO and of the olefin, followed by protonolysis with MeOH of the resulting intermediate, yields the product and regenerates the Pd–OMe initiator [16–18].

Using the system $[Pd(TsO)_2(PPh_3)_2](I)/PPh_3$ for the EHMC, the catalytic activity is significantly higher in the presence of a hydride source such as H₂O, H₂ and TsOH [19]. After catalysis, the propionyl complex *trans*-[Pd(COEt)(TsO)(PPh_3)_2] (II), related to the hydride







Abbreviations: EHMC, ethene hydromethoxycarbonylation; PK, polyketone; MP, methyl propanoate.

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mechanism, was isolated [20]. **II** reacts with MeOH to give the expected MP in an almost stoichiometric amount and is active in the EHMC and in the HMC of other olefins. These facts prove that, though it is sufficiently stable to be isolated, is also reactive enough to enter the catalytic cycle [20].

The activity of the carbomethoxy complex trans-[Pd(COO-Me)(TsO)(PPh₃)₂] (III), related to the other cycle, has also been studied [21,22]. Significant catalytic activity occurs only in the presence PPh₃, TsOH and of H₂O. MP is formed together with light CO-ethene co-oligomers having only keto- and ester-ending groups and no dimethyl succinate (DMS) or higher diesters are formed. These results are also in favour of the hydride route. In addition, (III) and the corresponding carbomethoxy complexes with HSO_4^- in place of TsO⁻, are rather reluctant to insert ethene into the Pd-COOMe bond [22,23]. Nevertheless, it has been found that $[Pd(COOMe)X_2(PPh_3)_2]$ (X = coordinating or non-coordinating anion) catalyze the oxidative carbonylation of ethene in MeOH using benzoquinone as a stoichiometric oxidant, yielding DMS and dimethyl oxalate, together with minor amounts of MP and dimethyl carbonate. The formation of DMS unambiguously proves that ethene inserts into a Pd-COOMe bond [24].

Direct evidences that a Pd–H species is an effective initiator for the catalytic EHMC were briefly reported using the $[Pd(SO_4)(PPh_3)]/H_2SO_4/PPh_3$ catalytic system [23]. Taking advantage that **I**, **II** and **III** can be prepared as solid complexes, to handle, we undertook a detailed NMR investigation on their reactivity, under conditions that mime those used in the catalytic EHMC, *i.e.* in the presence of PPh₃, H₂O and TsOH. The results are hereafter discussed.

2. Experimental section

2.1. Reagents

Carbon monoxide and ethene (purity higher than 99%) were supplied by SIAD Spa (Italy). MeOH, PPh₃, TsOH.H₂O, CD₂Cl₂ were purchased from Aldrich Chemicals. Pd(AcO)₂ and PdCl₂ were purchased from Chimet SpA (Italy). MeOH, and CD₂Cl₂ were stored together with molecular sieves and under argon. The other chemicals were used as received. *cis*-[Pd(H₂O)₂(PPh₃)₂](TsO)₂.2(H₂O) (**I**,H₂O) [25], *trans*-[Pd(COEt)(TsO)(PPh₃)₂] (**II**) [20] and *trans*-[Pd(COOMe)(TsO)(PPh₃)₂] (**III**) [23] were prepared according to literature procedures.

2.2. Instrumentation

GC analysis was performed using a GC Agilent 7890A instrument, equipped with a column HP-5 30 m \times 0.320 mm, 0.25 micron, conditions: oven 313 K (10 min) to 453 K (30 min) at 25 K/ min, *T*(inj) = 523, *T*(det) = 523 K, flow = 2.2 mL/min, N₂.

NMR spectra were recorded on Bruker AMX 300 spectrometer. ${}^{31}P{}^{1}H{}$ spectra was measured ${}^{1}H$ decoupled. All ${}^{1}H$ chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. ${}^{31}P{}^{1}H{}$ signals were referenced to an 85% aqueous solution of $H_{3}PO_{4}$.

2.3. High pressure NMR experiments

NMR under pressure was performed using a 5 mm pyrex glass HP-NMR tube with Teflon head (maximum pressure tolerated 13 atm). Typically, a solution of 4 \times 10⁻³ mmol of the palladium complex dissolved in CD₂Cl₂ (0.075 mL) was given into the HPNMR tube, previously evacuated at r.t. under argon. The tube was placed in a dry ice/acetone bath and a solution containing the desired amount of PPh₃, TsOH·H₂O in CD₂Cl₂/MeOH (0.075 mL/15 μ L) was

added under argon. Thus, the two solvents were used in the 10/1 (v/v) ratio in each experiment, except in the cases otherwise indicated. The tube was connected to the pressure line by using the special screw top in Teflon, then purged with CO or ethene several time (4–5) and pressurized with the gases, taking care to shake the tube in order to facilitate the solubilization of the gases. The tube was then quickly located in the NMR probe.

The NMR data of all identified complexes are reported in Table 1.

3. Results and discussion

3.1. Reactivity of I

Actually, in place of I, the corresponding aquo complex *cis*- $[Pd(H_2O)_2(PPh_3)_2](TsO)_2.2(H_2O)$ (I,H₂O) was used, because this complex is well characterized, easier to handle and because H₂O can be a reagent.

3.1.1. Reactivity of I,H₂O with PPh₃, MeOH and CO

I,H₂O and 2 equivalents of PPh₃ were dissolved in CD₂Cl₂ at 193 K under argon. From 223 K to 298 K, the ³¹P{¹H} spectrum showed singlet signals assigned to *cis*-[Pd(H₂O)₂(PPh₃)₂](TsO)₂ (hereafter indicated also as **I**,H₂O) and to uncoordinated PPh₃ in the ratio 1/1. Upon adding MeOH at 193 K, the ³¹P{¹H} signal of **I**,H₂O disappeared with concomitant appearance of new signals assigned to [Pd(H₂O)(PPh₃)₃](TsO)₂ (**I**'). Therefore, MeOH favours the displacement of one molecule of H₂O by one molecule of PPh₃, which does not occur in pure CD₂Cl₂, probably because of the affinity of H₂O to MeOH.

An alternative assignment as $[Pd(MeOH)(PPh_3)_3](TsO)_2$ is unlikely, because water has a higher coordinating capacity than methanol. Indeed, many well characterized $Pd(II)-(H_2O)$ complexes are known [26], whereas MeOH coordinates as a labile solvating molecule [9,27].

Upon admission of CO (0.3 MPa) at 193 K, a new ¹H signal appeared at 1.91 ppm for the formation of a carbomethoxy ligand [22,28]. At the same time, the ³¹P{¹H} signals of **I**' disappeared with the concomitant appearance of new signals assigned to [Pd(COO-Me)(PPh₃)₃](TsO) (**III**') (reaction (1)).

$$[Pd(H_2O)(PPh_3)_3](TsO)_2 + CO + MeOH \rightarrow I'$$

$$[Pd(COOMe)(PPh_3)_3](TsO) + H_2O + TsOH \qquad (1)$$

$$III'$$

III' is stable up to 313 K even for *ca.* 40 min. Upon warming the solution to 343 K and maintaining it at this temperature for *ca.* 20 min, partial conversion was observed. Upon cooling to room temperature, $[PdH(PPh_3)_3](TsO)$ (**IV**) was detected (30% with respect to **III**') (see later also on the reactivity of **III**, Section 3.3.2). This cationic hydride was already reported [29,30].

The formation of **IV** probably occurs *via* demethoxylation of the Pd–COOMe moiety, caused by H₂O introduced with **I**,H₂O, followed by decarboxylation of the hypothetical intermediate **a** (reaction (2)). Demethoxylation might be catalyzed by TsOH [22], which is formed in reaction (1) (see next paragraph). It is worth noting that no signal assignable to formaldehyde or its derivatives have been detected, therefore it is unlikely that the hydride forms *via* β -hydride elimination from a Pd–OCH₃ or Pd-(MeOH) species [27,31,32].

$$\begin{bmatrix} Pd(COOMe)(PPh_3)_3 \end{bmatrix} (TsO) \xrightarrow{H_2O, -MeOH} \begin{bmatrix} Pd(COOH)(PPh_3)_3 \end{bmatrix} (TsO) \xrightarrow{a} \begin{bmatrix} PdH(PPh_3)_3 \end{bmatrix} (TsO) \xrightarrow{a} (2) \begin{bmatrix} PdH(PPh_3)_3 \end{bmatrix} (TsO) \end{bmatrix}$$

Table 1

NMR	spectrosco	oic	data	for	I,	ľ,	II,	II',	III,	III′	, IV,	v	and	V	
							,								

Complex	δ ¹ H NMR [ppm]	δ ³¹ P{ ¹ H} NMR [ppm]
<i>cis</i> -[Pd(H ₂ O) ₂ (PPh ₃) ₂](TsO) ₂ .2(H ₂ O) (I)	7.48–6.99 (m, 38H, Ar) 2.28 (s, 6H, CH ₃ –TsO)	38.3 (s)
[Pd(H ₂ O)(PPh ₃) ₃](TsO) ₂ (I')	7.71–7.01 (m, 53H, Ar) 2.34 (s, 6H, CH ₃ –TsO)	35.3 (t, 1P) 31.1 (d, 2P) J _{P-P} = 13.2
trans-[Pd(COEt)(OTs)(PPh ₃) ₂] (II)	7.64–6.42 (m, 38H, Ar) 2.23 (s, 3H, CH ₃ –TsO) 2.02 (q, 2H, CH ₂ –PdCOEt) 0.26 (t, 3H, CH ₃ –PdCOEt)	20.3 (s)
[Pd(COEt)(PPh ₃) ₃](TsO) (II ')	7.65–6.87 (m, 53H, Ar) 2.31 (s, 3H, CH ₃ –TsO) 2.06 (q, 2H, CH ₂ –PdCOEt) –0.59 (t, 3H, CH ₃ –PdCOEt)	19.0 (d, 2P) 17.4 (t, 1P) $J_{P-P} = 50.0 \text{ Hz}$
trans-[Pd(COOMe)(OTs)(PPh ₃) ₂] (III)	7.61–6.67 (m, 38H, Ar) 2.36 (s, 3H, CH ₃ –PdCOOMe) 2.19 (s, 3H, CH ₃ –TsO)	18.9 (s)
[Pd(COOMe)(PPh ₃) ₃](TsO) (III')	7.61–6.67 (m, 38H, Ar) 2.33 (s, 3H, CH ₃ –TsO) 1.91 (s, 3H, CH ₃ –PdCOOMe)	19.9 (d, 2P) 15.7 (t, 1P) J _{P-P} = 39.2 Hz
[PdH(PPh ₃) ₃](TsO) (IV)	7.69–7.06 (m, 38H, Ar) 2.34 (s, 3H, CH ₃ –TsO) –7.03 (dt, 1H, J _{HPtrans} = 174 Hz, J _{HPcis} = 13.5 Hz)	30.0 (d, 2P) 21.6 (t, 1P) J _{P-P} = 28.1 Hz
<i>trans</i> -[Pd(Et)(OTs)(PPh ₃) ₂] (\mathbf{V})	7.61–6.82 (m, 38H, Ar) 2.32 (s, 3H, CH ₃ –TsO) 1.59 (q, 2H, CH ₂ –PdEt) 0.16 (t, 3H, CH ₃ –PdEt)	26.9 (s)
[Pd(Et)(PPh ₃) ₃](TsO) (V ')	7.65–6.97 (m, 53H, Ar) 2.36 (s, 3H, CH ₃ –TsO) 1.40 (q, 2H, CH ₂ –PdCOEt) 0.00 (t, 3H, CH ₃ –PdCOEt)	32.8 (d, 2P) 17.7 (t, 1P) $J_{P-P} = 40.2$ Hz

Abbreviations: s, singlet; d, doublet; t, triplet; dt, doublet of triplet; m, multiplet.

3.1.2. Reactivity of I_1H_2O with PPh₃, MeOH, CO in the presence of TsOH (reactivity of III' with H_2O)

I,H₂O, 2 equivalents of PPh₃ and 6 equivalents of TsOH.H₂O were dissolved in CD₂Cl₂/MeOH at 193 K. The solution was pressurized with 0.3 MPa of CO. At this temperature most of the starting complex was transformed into III'. The transformation was complete at 273 K. Upon increasing the temperature to 293 K in *ca.* 80 min, III' gradually converted into hydride IV (100%). Thus, because of the combined action of H₂O and TsOH, III' is already unstable at 293 K and gives IV quantitatively.

3.1.3. Reactivity of I, H_2O with PPh₃, MeOH, CO and ethene in the presence of TsOH (reactivity of IV with ethene and CO)

Once **IV** was obtained as just reported, the solution was first cooled to 193 K, then CO was replaced by a mixture of CO/ethene (1/ 1, 0.4 MPa). Upon warming to 293 K, **IV** was partially converted into **II** and [Pd(COEt)(PPh₃)₃](OTs) (**II**') (**IV**/(**II** + **II**') = 40/60) (see Section 3.2.2. for the reactivity of **II**). At this temperature, MP started forming (*ca.* 50% with respect the initial amount of **I**,H₂O in *ca.* 40 min). Upon increasing the temperature to 323 K in *ca.* 80 min, the concentration of **IV** remained practically unchanged, whereas that of **II** lowered to *ca.* 10% and catalysis to MP (330%) was observed. It will be seen in Section 3.2.2 that **II** reacts with MeOH to give MP and **IV**.

In conclusion, experiments 3.1.2 and 3.1.3 show that, in the presence of H_2O and TsOH, the Pd–COOMe moiety in unstable and is transformed into a Pd–H initiator and give further support to the explanation given in Ref. [19] on their promoting effect.

3.2. Reactivity of II

As mentioned in the Introduction, **II** was isolated after carrying out the catalytic EHCM [20]. Therefore, we chose to study the reactivity of **II** with MeOH as a model reaction for the MP forming step.

3.2.1. Reactivity of **II** with MeOH

II, dissolved in $CD_2Cl_2/MeOH$ at 193 K under argon, starts to react with MeOH at 253 K to give MP, which is formed quantitatively in *ca.* 100 min upon raising the temperature up to 323 K. The formation of MP is expected to occur with concomitant formation of a Pd–H species [33,34]. However, no hydride was detected. Instead, decomposition to Pd metal was clearly visible at the end of this time period.

3.2.2. Reactivity of **II** with MeOH and PPh_3 in the presence of TsOH

The above experiment was repeated in the presence of 2 equivalents of PPh₃ and of 6 equivalents of TsOH.H₂O. At 193 K, **II** reacts with PPh₃ to give [Pd(COEt)(PPh₃)₃](TsO) **II**' quantitatively. Above 233 K, **II**' is in equilibrium with **II**, which is the prevailing species at 293 K. At this temperature MP is formed together with hydride **IV** (reaction (3), 100% in 1 h). It is noteworthy to point out that the previous experiment was carried out in the absence of added PPh₃ and TsOH. Therefore, the use of these two reagents makes possible to detect the hydride expected to be formed in the MP generating step. In other words they stabilize the hydride.

$$\begin{bmatrix} Pd(COEt)(TsO)(PPh_3)_2 \end{bmatrix} + MeOH + PPh_3 \rightarrow \\ II \\ [PdH(PPh_3)_3](TsO) + MP \\ IV \end{bmatrix}$$
(3)

3.2.3. Reactivity of **II** with MeOH and PPh₃, in the presence of TsOH and subsequent admission first of ethene and then of CO (reactivity of **IV** first with ethene and then with CO and with MeOH)

The above experiment was repeated till all **II** was transformed into **IV** at 293 K. Then the solution was cooled to 193 K and ethene (0.3 MPa) was admitted. At 293 K, **IV** starts to react with ethene to give *trans*-[Pd(Et)(TsO)(PPh₃)₂] (**V**) (50% conversion after 50 min between 293 K and 323 K). **V** has been already reported [30]. Starting form 303 K, the ¹H signals of the ethyl ligand broaden indicating that the protons slowly interchange. Above 323 K the interchange is fast compared to the NMR scale, which causes the appearance of just one signal at 0.7 ppm. At 333–343 K all **IV** disappears and **V** starts to decompose with formation of some Pd metal.

The experiment was repeated till most of **IV** gave **V** at room temperature. The solution was then cooled to 193 K, washed with CO several times in order to take away dissolved ethene and then pressurized with CO (0.3 MPa). At 223 K, **V** reacts with CO giving **II**'. At 298 K **II**' is converted into **II**, which reacts with MeOH generating MP and **IV**, as found in Section 3.2.2.

It can be concluded that the insertion of ethene into the Pd–H bond of **IV** is slow compared to the insertion of CO into the Pd–Et bond of **V**. However, it should be pointed out that the latter complex presents an easily accessible coordination site, on the contrary of **IV** in which case ethene must displace a PPh₃ ligand.

3.2.4. Reactivity of **II** with MeOH, ethene and CO in the presence of TsOH but in the absence of PPh_3

The experiment described in Section 3.2.2 was repeated, but in the absence of PPh₃ and admitting both CO and ethene (1/1, 0.6 MPa total pressure) at 193 K from the beginning. Upon rising the temperature, **II** started to react with MeOH to give MP (1 TON in *ca.* 100 min between 253 and 323 K). During this time the intensity of the signals of **II** lowered till to disappear, without the appearance of signals in the hydride region. At the end of the experiment Pd metal was visible. MP was formed in a stoichiometric amount, no catalysis occurred even though both gases were present.

These observations suggest that after MP is formed decomposition to inactive Pd metal occurs. By comparing these results with those described just above and in Section 3.1.3, it appears that PPh₃ stabilizes the hydride that is formed in the MP generating step.

3.2.5. Reactivity of **II** with MeOH, ethene and CO in the presence of TsOH and of variable amounts of PPh₃

The above experiment was repeated in the presence of variable amounts of PPh₃. Using PPh₃ and **II** in the ratio 2/1, 4/1 and 6/1. MP was formed at *ca.* 293, 298 and 303 K, respectively. Since a prerequisite for the formation of MP is the coordination of MeOH to the metal [33], these observations suggest that PPh₃ competes with MeOH for the coordination, thus inhibiting the methanolysis of the Pd–COEt moiety.

In addition, it was observed that the catalytic activity measured in 30 min between 303 and 333 K passes through a maximum upon increasing the PPh₃/Pd ratio, being *ca.* 4, 6 and 1.5 mol of MP/Pd when the ratio is 2/1, 4/1 or 6/1, respectively. Thus, the presence of PPh₃ is essential in order to observe catalysis, because it stabilizes hydride **IV** and avoids decomposition to inactive Pd metal. However, an excess of ligand inhibits the catalysis. A similar PPh₃ influence has been observed carrying out the catalysis in an autoclave under standard conditions [19]. Quite interestingly, in the presence of a high concentration of PPh₃ (PPh₃/Pd = 6/1), the new ethyl species $[Pd(Et)(PPh_3)_3](TsO)$ (**V**') was detected during the catalysis. Thus, in the presence of relatively high concentration of PPh₃, catalysis might be inhibited also because the insertion of CO into the Pd–Et bond is retarded.

It is interesting to note that only the ethyl complex requires an larger excess of PPh₃ in order to give a tricoordinated—PPh₃ complex, which suggests that the ethyl ligand has a higher *trans*-in-fluence that the hydride, propionyl and carbomethoxy ligands.

3.3. Reactivity of III

Although all the above reported evidences are in favour of the Pd—H mechanism, the occurrence of the carbomethoxy mechanism cannot be excluded. In order to ascertain whether this mechanism plays any role, the reactivity of **III** has been investigated.

3.3.1. Reactivity of **III** with ethene in the presence of PPh₃

III and 2 equivalents of PPh₃ were dissolved in CD₂Cl₂/MeOH at 193 K. The solution was pressurized with 0.4 MPa of ethene. In place of the signals of **III**, those of **III**' appeared. The NMR spectrum remained unchanged up to 313 K. Above this temperature, **III**' started to convert into **III**, which was the only complex present for *ca.* 30 min at 343 K. Note that in this experiment MP could have been formed, but none of it was detected. In conclusion, ethene insertion into the Pd–COOMe bond does not occur even at 343 K, which is well above the temperature at which ethene inserts into the Pd–H bond of **IV** (293 K, *cfr.* Section 3.2.3) and catalysis occurs (293 K, *cfr.* Section 3.1.3).

On the contrary, using the diphosphino complexes [Pd(COO-Me)(L)(P–P)](OTf) (L = CO, CH₃CN; P–P = 1,3-bis(di-*iso*-butyl-phosphino)propane and 1,3-bis(diphenylphosphino)propane), the insertion of ethene into the Pd–COOMe bond occurs at temperature as low as 243 K under 0.1 MPa of ethene [5].

3.3.2. Reactivity of III with H_2O in the presence of $\text{PPh}_3,$ TsOH and MeOH

It should be underlined that the above experiment was carried out in the absence of TsOH and H_2O , which are key components in order to observe significant catalytic activity [19]. Hereafter, it is shown how they modify the picture depicted in Section 3.3.1.

III, 2 equivalents of PPh₃ and 6 equivalents of TsOH·H₂O were dissolved in CD₂Cl₂/MeOH at 193 K under argon. At this temperature the ³¹P{¹H} NMR spectrum did not show the presence of **III** nor of **III**', but of **I**' only and of PPh₃ in the ratio **I**'/PPh₃ = 1/1. Thus, in the presence of 6 equivalents of H₂O and TsOH the carbomethoxy group is not stable even at 193 K and reaction (1) is practically reversed. Note that, in their absence, complex **III** is stable up to 313 K (*cfr.* Section 3.3.1) and that, in their presence, but under 3 bar of CO, **III**' is stable up to 0 °C (*cfr.* Section 3.1.2). Therefore, we made this experiment to proceed further as follows.

After cooling the solution to 193 K, CO was admitted (0.3 MPa). At this temperature, most of **I**' was converted to **III**', at 273 K the conversion is complete. Upon increasing the temperature up to 293 K in 80 min the NMR signals of **III**' gradually disappear, replaced by the signals of **IV** (100% conversion). The solution was cooled again to 193 K and CO was replaced with a mixture of CO/ ethene (1/1,0.4 MPa). Upon raising the temperature up to 293 K, **IV** converted partially into **II** and **II**' and catalysis was observed as described in Section 3.1.3.

In conclusion, in the presence of H_2O and TsOH, the carbomethoxy moiety is not stable and is converted into a hydride initiator, as found in Sections 3.1.2 and 3.1.3.

4. Conclusions

In summary, the reactivity of catalyst precursor I,H₂O, the propionyl complex II and of the carbomethoxy complex III has been studied by ¹H and ³¹P{¹H} NMR spectroscopy under conditions that mime EHMC, *i.e.* in the presence of PPh₃, H₂O and TsOH. I,H₂O reacts with CO and MeOH giving III and III' in the presence of PPh₃. These carbomethoxy complexes are unstable in the presence of H₂O and TsOH and are converted into hydride IV, which is the initiator of the catalytic EHMC. The elementary steps of the cycle have been followed through the detection and the reactivity of all the key intermediates, *i.e.* the ethyl complexes V and V', the propionyl complexes II and II', which undergo methanolysis with formation of MP and of hydride IV. All the experimental evidences support the Pd–H cycle.

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