Characterization and catalytic activity of *trans*-[Pd(COCH$_2$CH$_3$)(TsO)(PPh$_3$)$_2$], isolated from the hydro-methoxycarbonylation of ethene catalyzed by [Pd(TsO)$_2$(PPh$_3$)$_2$]

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Abstract

The title complex (**I**) has been isolated after running the hydro-methoxycarbonylation (HMC) of ethene (4.5 MPa of CO/C$_2$H$_4$ = 1/1, 343 K) in MeOH, catalyzed by [Pd(TsO)$_2$(PPh$_3$)$_2$]. It has been characterized by IR, ^{1}H and ^{31}P NMR spectroscopy.

Complex (**I**) reacts with MeOH, saturated with CO, even at r.t., yielding methylpropanoate (MP) in stoichiometric amount and Pd(0) complexes and/or *trans*-[Pd(COOCH$_3$)(TsO)(PPh$_3$)$_2$] (**II**), the latter forms in the presence of PPh$_3$ and of *p*-toluenesulfonic acid (TsOH); complex (**I**) catalyses the HMC of ethene to MP; it catalyses also the HMC of a different olefin yielding also a stoichiometric amount of MP. After catalysis, complex (**I**) is recovered as such or as [Pd(TsO)$_2$(PPh$_3$)$_2$] (**III**), the latter forming when an excess of TsOH is used (Pd/TsOH = 1/8).

Complex (**II**), a potential catalytic intermediate, has been prepared under conditions similar to those employed to synthesize complex (**I**), except for the presence of ethene. This complex, dissolved in MeOH saturated with C$_2$H$_4$, does not yield MP at r.t., whilst at 353 K, it becomes a catalyst precursor for the HMC of ethene, however, it is recovered as complex (**I**). The conversion of (**II**) to (**I**) occurs with CO$_2$ evolution. For the conversion of (**I**) to (**II**), it is proposed that: (i) (**I**) reacts with MeOH yielding MP and a Pd(II)-hydride; (ii) this reacts with TsOH with hydrogen evolution and yielding complex (**III**); (iii) this reacts with CO and MeOH yielding (**II**). For the conversion of (**II**) to (**I**) it is proposed that: (i) (**II**) reacts with H$_2$O yielding MeOH and a Pd–COOH species; (ii) this evolves CO$_2$ with formation of a Pd(II)-hydride; (iii) sequential addition of ethene and CO gives (**I**).

In addition, it has also been found that catalysis is accompanied by formation of CO$_2$ also when using complex (**I**) as catalyst and that the catalytic activity passes through a maximum with increasing the concentration of water (TOF = 420 h^{-1} at 353 K, 4.5 MPa CO/C$_2$H$_4$ = 1/1, (**I**)/PPh$_3$/TsOH = 1/6/8, H$_2$O = 800 ppm). It is proposed that: (i) catalysis occurs through initial formation of a Pd(II)–H species (which form after CO$_2$ evolution from a Pd–(COOH) species formed via interaction of H$_2$O with CO), followed by the insertion of the olefin into the Pd(II)–H bond to form a Pd(II)–(alkyl) intermediate, which in turn inserts CO with formation of an acyl complex of type (**I**), which reacts with MeOH yielding the ester and Pd(II)–H back to the catalytic cycle; (ii) a carbomethoxy complex of type (**II**) does not play a major direct role in the catalytic cycle; (iii) during the catalysis Pd(II)–H consuming side reactions occur with formation of Pd(II) species of type (**II**) and/or (**III**); these species are reintroduced, as hydrides, back to the catalytic cycle via interaction with H$_2$O and CO.
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1. Introduction

Pd(II)–phosphine complexes are efficient catalyst for the carbonylation of olefins to esters or to polyketones, in particular those having weakly coordinating anions balancing the cationic charge, so that the metal has easily available coordination sites capable of activating the reacting molecules [1–5]. As a simplified rule catalysts with monophosphine or chelating ligands which open one arm give the ester, chelating ligands that retain *cis* coordination give the polyketone [6–8]. Due to its importance, this catalysis has been extended also to the use of water-soluble

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Pd = $[PdXL_2]^{n+}$

X = TsO (n = 0); X = CO, C_2H_4, H_2O, ROH (n = 1);

L = PPh_3.
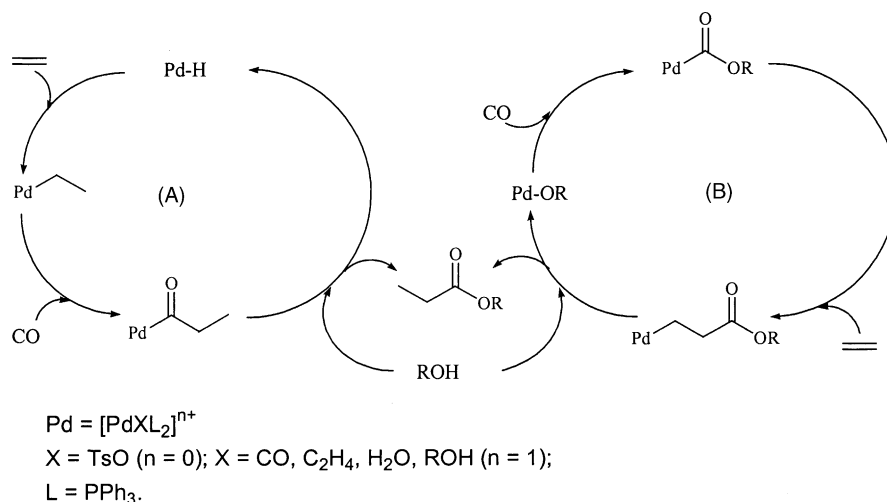
Scheme 1. Proposed catalytic cycle.

Pd(II)-sulfonated phosphine catalysts [9–11]. Hereafter, we will focus on the catalysis to the ester. Two mechanisms for the catalytic cycles have gained more acceptance (Scheme 1).

According to a simplified scheme, that does not take into account the geometry of the key active intermediates and of the transient species, one mechanism (**A**) involves the initial formation of a Pd(II)–H species, followed by sequential coordination and migratory insertion of the olefin and CO with formation of a Pd(II)–acyl species and final attack of the alkanol to give the ester and the hydride back to the catalytic cycle [12]. In favor of this mechanism, there are the findings that active Pd–acyl complexes of the type *trans*-[Pd(COR)Cl(PPh_3)_2] have been isolated from HMC experiments using *trans*-[PdCl_2(PPh_3)_2] as precursor and that these acyl complexes react with an alkanol to give the corresponding ester and that they are active when reused as catalysts [13]. Together with the acyl complex, it has been isolated also a carboalkoxy complex of the type *trans*-[Pd(COOR)Cl(PPh_3)_2] [13], a potential intermediate, which involves the insertion of the olefin into the Pd–COOR bond to form a Pd–alkyl intermediate, which undergoes alkanol protonolysis to give the final product and the Pd–alkoxy species that inserts CO giving Pd–COOR back to the catalytic cycle (mechanism **B**) [14–16]. However, it was found that the isolated carbomethoxy complex does not react with an olefin, but rather it brings to the deactivation to Pd(0) complexes [13]. Acid treatment of a deactivated catalyst can restore activity through formation of Pd(II)–H species, which give further support that catalysis undergoes through mechanism **A** [17,18].

Other more recent studies, based on multinuclear NMR and isotopic labeling investigations, are also in favor of the hydride route [19–22], including also the exceptionally active and selective system generated in situ, via the reaction of [Pd(P–P)(dba)] (P–P = 1,2(CH_2PBut_2)_2C_6H_4; dba = *trans*-(PhCH=CH)_2CO) with methanesulfonic acid for the HMC of ethene (TOF=50,000 h^{-1}, selectivity

of 99.98% at 353 K and 1 MPa of CO/C_2H_4 = 1/1) [23–26].

In favor of the Pd(II)–H mechanism, it has been also reported that the catalytic activity of the precursor [Pd(TsO)_2(PPh_3)_2], is significantly enhanced when the catalysis is carried out in the presence of a hydride source, such as H_2O, *p*-toluenesulfonic acid (TsOH), H_2 and that the same precursor catalyses the hydrogenation of olefin [27,28]. It has been also found that the cationic carbomethoxy complex *trans*-[Pd(COOCH_3)(H_2O)(PPh_3)_2](TsO), plays only a minor role, if any, in the catalysis [29].

In favor of the Pd(II)–H mechanism, there are also the findings that during the HMC of ethene using the precursor [Pd(TsO)_2(PPh_3)_2] in combination with relatively large amounts of PPh_3 and TsOH there was formation of phosphonium salts of the type (EtPPh_3)(TsO) and (EtCOCH_2CH_2PPh_3)(TsO) mediated by the metal [30].

This paper deals with the characterization, reactivity and catalytic activity of the title Pd(II)–acyl complex, which has been isolated in the HMC of ethene catalyzed by [Pd(TsO)_2(PPh_3)_2].

2. Experimental

2.1. Reagents

Carbon monoxide and ethene (purity higher then 99%) were supplied by SIAD Spa (Italy). Pd(OAc)_2 98%, AgTsO, triphenylphosphine and *p*-toluenesulfonic acid (TsOH·H_2O) were purchased from Aldrich Chemicals. Methanol (purity > 99.5%, 0.01% of water) and the other solvent were purchased from Baker and used without further purification. The deuterated solvents were Aldrich products. The complexes *trans*-[Pd(COCH_2CH_3)Cl(PPh_3)_2], [Pd(TsO)_2(PPh_3)_2] and *trans*-[Pd(COOCH_3)(H_2O)(PPh_3)_2] (TsO) were prepared according to the methods reported in the literature [13,22,29].

2.2. Equipment

The IR spectra were recorded on a Nicolet FTIR instruments mod. Nexus. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX 300 spectrometer equipped with a BB multinuclear probe operating in the FT mode at 300 and 121.442 MHz for ^{1}H and ^{31}P, respectively. Products of the HMC reaction were analyzed by GC on a HP 5890 series II apparatus equipped with a 30 m × 0.53 mm × 0.1 μm HP 5 column. In order to reveal CO_2 (TCD detector), it was used a 5.5 m × 3.18 mm SS silica gel, 60/80 packed column under these conditions: carrier gas: helium, 30 ml min^{-1}; oven: 313 K (2 min) to 373 K at 15 K min^{-1}.

The catalytic experiments were carried out in a stainless steel autoclave of ca. 250 ml of capacity, provided with a self-aspirating turbine. In order to prevent contamination by metallic species, due to corrosion of the internal surface of the autoclave, the reagents were contained in a ca. 150 ml Teflon-beaker placed into the autoclave. CO–ethene mixture (1/1) was supplied from a gas reservoir (260 ml) connected to the autoclave through a constant pressure regulator. The autoclave was provided with a temperature control (±0.5 K).

2.3. Synthesis of trans-[Pd(COCH$_2$CH$_3$)(TsO)(PPh$_3$)$_2$] (I) and of trans-[Pd(COOCH$_3$)(TsO)(PPh$_3$)$_2$] (II)

The complex [Pd(TsO)$_2$(PPh$_3$)$_2$] (III) (0.1 mmol), together with PPh$_3$ and TsOH ((III)/PPh$_3$/TsOH = 1/0.9/0.2), in 3 ml of MeOH with 5 equivalents of H_2O was added to a glass bottle placed into a stainless steel autoclave of ca. 50 ml. The autoclave was purged with carbon monoxide and pressurized with 4.0 MPa of CO–ethene (1/1) at room temperature. The autoclave was heated to 343 K for 20 min under vigorous stirring, then cooled to room temperature. The gas phase was analyzed by GC. CO_2 was present in an amount practically equivalent to Pd. The autoclave was then depressurized and opened. In the liquid phase MP was formed (TOF[1] = 50 mol of ester/mol Pd h, h^{-1}). Upon addition of 50 ml of cold water, complex (I) precipitated. It was separated by filtration, washed and dried under vacuum (68.7 mg, yield 80%).

The same results are obtained starting from Pd(OAc)$_2$/PPh$_3$/TsOH in the ratio 1/2.9/2.2.

By adding to the methanol solution 1 equivalent of LiCl instead of water the complex trans-[Pd(COCH$_2$CH$_3$)Cl(PPh$_3$)$_2$] precipitated in 85% yield (61.5 mg).

Complex (I) was synthesized also from [Pd(CO)(PPh$_3$)$_3$]/TsOH (1/2.2) or [Pd(CO)(PPh$_3$)]$_3$/PPh$_3$/TsOH (1/1.9/2.2) under the conditions just reported (60.1 mg, yield 70% and 55.8 mg, yield 65%, respectively).

Complex (II) was prepared by the same procedure used to prepare complex (I), except for the presence of C_2H_4 (60.3 mg, yield 70%). The IR spectrum shows ν_{CO} at 1668 cm^{-1}, close to that of the aquo analogous complex trans-[Pd(COOCH$_3$)(H$_2$O)(PPh$_3$)$_2$](TsO) (ν_{CO} at 1684 cm^{-1} [29]).

Complex (I) was also synthesized directly by reacting the chloride analogous trans-[Pd(COCH$_2$CH$_3$)Cl(PPh$_3$)$_2$] (0.1 mmol) with AgTsO (0.11 mmol) in 2 ml of cold dichloroethane under vigorous stirring. AgCl precipitated immediately. The suspension was quickly filtered using a micro-filter system. Complex (I) was precipitated by dropping the solution into 20 ml of n-pentane under vigorous stirring. The solid was separated by filtration, washed with water, n-pentane and ether and dried under vacuum (68.7 mg, yield 80%).

2.4. Synthesis of [Pd(CO)(PPh$_3$)$_3$] (IV) and [Pd(CO)(PPh$_3$)]$_3$ (V)

The synthesis of these complexes is reported in literature [31,32]. Here we propose a new procedure. A mixture of Pd(OAc)$_2$ (0.1 mmol) and PPh$_3$ (0.33 mmol) in 5 ml of MeOH was added to a glass bottle placed in a stainless steel autoclave of ca. 100 ml. The autoclave was purged with CO and pressurized with 5.0 MPa of CO at room temperature, then heated to the working temperature (343 K) while stirring for 30 min. The autoclave was then cooled to room temperature and depressurised. The white solid product was separated by filtration, washed and identified as [Pd(CO)(PPh$_3$)$_3$] by the elemental analysis and IR spectroscopy (71.8 mg, yield 78%).

Using the same procedure but using 1 equivalent of PPh$_3$, a reddish solid precipitated. It was separated by filtration, washed and identified as [Pd(CO)(PPh$_3$)]$_3$ by the elemental analysis and IR (89.3 mg, yield 75%).

2.5. Conversion of complex (I) to complex (II) and vice versa

Complex (I) (0.1 mmol) was allowed to react with methanol (3 ml) containing 1 equivalent of PPh$_3$ and 1 equivalent of TsOH, previously saturated with CO, for ca. 20′ at r.t.. MP formed in quantitative yield (ester/(I) = 1/1). Upon addition of cold water, complex (II) precipitated. The suspension was filtered, the precipitate was washed with cold water and dried under vacuum (60.3 mg, 70% yield). If the same experiment is carried out in the absence of PPh$_3$ and TsOH, [Pd(CO)(PPh$_3$)]$_3$ forms (107.1 mg, yield 90%) in place of complex (I).

A methanol solution of the carbomethoxy complex (II), PPh$_3$ and TsOH (0.1 mmol of (II), (II)/PPh$_3$/TsOH = 1/0.9/1.2, in 3 ml of MeOH, 800 ppm H_2O, previously washed with CO/C$_2$H$_4$) was heated at 353 K under 2.0 MPa of CO/C$_2$H$_4$ = 1/1, in a autoclave of 50 ml capacity, for 20′. The autoclave was then cooled to r.t. and slowly de-

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[1] This value is only indicative that catalysis occurs. The catalyst precursor was used in abnormal high concentration, stirring was provided by a little magnetic bar. The main aim of this experiment was to be able to isolate a complex after the reaction.

pressurised. A significant amount of MP formed ($TOF^1 = 50 \, h^{-1}$). In the gas phase CO_2 was present, practically 1 equivalent with respect to Pd. After cooling and opening the autoclave, complex (**I**) precipitated upon addition of cold water. After usual work up, it was recovered in 65% yield (55.8 mg).

2.6. Catalytic hydro-methoxycarbonylation of ethene

In a typical experiment complex (**I**) (0.1 mmol), together with PPh$_3$ and TsOH (**I**/PPh$_3$/TsOH = 1/6/8) was dissolved in 50 ml of MeOH (800 ppm of H_2O) in a Teflon beaker placed in the autoclave. The solvent was degassed with a mixture of CO/C_2H_4 before adding the catalytic precursor. The autoclave was washed by pressurizing with a 1/1 mixture of CO/C_2H_4 (ca. 0.5 MPa) and then depressurising to atmospheric pressure (this cycle was repeated five times at room temperature with stirring). After washing a gas sample was analyzed by GC: no CO_2 was detected. The autoclave was then pressurized with 0.5 MPa of the gas mixture and then heated to 353 K during ca. 10 min without stirring. The pressure was then adjusted to the desired value (typically 4.5 MPa total pressure) and, while stirring, maintained constant throughout the experiment (2 h, rate stirring 800 rpm) by continuously supplying the gasses from the reservoir. Gas samples were withdrawn at regular intervals of time (15′). CO_2 was unambiguously detected and its concentration regularly increased with time. At the end of the experiment, the autoclave was quickly cooled and carefully depressurised. The content of the beaker was analyzed by GC.
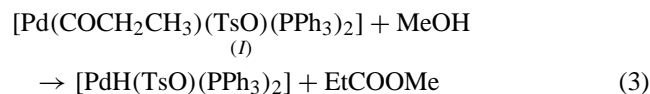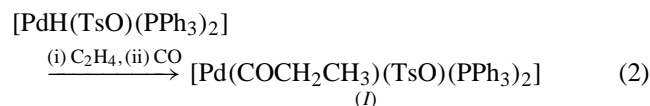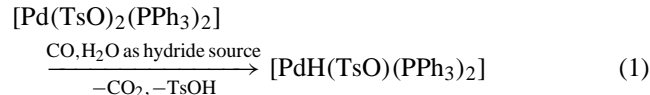
A Pd(0) complex, in combination with TsOH, was also used as catalyst precursor. Moreover, complex (**I**) was used also for the catalytic HMC of cyclohexene. A typical experiment was carried out by following the same procedure just described except for the presence of C_2H_4. Complex (**I**) was dissolved in a mixture of 10 ml of cyclohexene and 40 ml of MeOH (800 ppm of H_2O) and the autoclave was washed by pressurizing with CO; the experiments were carried out at 2.0 MPa of CO. The results are reported in Table 3.

3. Results and discussion

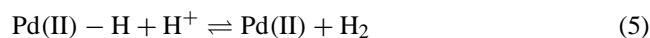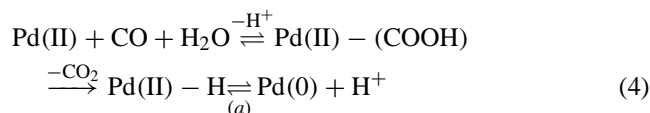### 3.1. Synthesis and characterization of trans-[Pd(COCH$_2$CH$_3$)(TsO)(PPh$_3$)$_2$] (I)

Complex (**I**) was isolated after running the HMC of ethene in MeOH catalyzed by the system [Pd(TsO)$_2$(PPh$_3$)$_2$]/PPh$_3$/TsOH or by Pd(AcO)$_2$/PPh$_3$/TsOH. (cf. 2.3). The formation of complex (**I**) (which occur with CO_2 evolution, see Section 2.3) and catalysis are likely to occur via a Pd–hydride species which forms via interaction of CO with H_2O. The hydride adds C_2H_4 and CO to give a Pd(II)–acyl intermediate of type (**I**), which undergoes attack of MeOH yielding the ester and the Pd(II)–H back to the catalytic

cycle as schematized by reactions (1)–(3):

$$[Pd(TsO)_2(PPh_3)_2]$$
$$\xrightarrow[-CO_2, -TsOH]{CO, H_2O \text{ as hydride source}} [PdH(TsO)(PPh_3)_2] \qquad (1)$$

$$[PdH(TsO)(PPh_3)_2]$$
$$\xrightarrow{(i) \, C_2H_4, (ii) \, CO} [Pd(COCH_2CH_3)(TsO)(PPh_3)_2] \qquad (2)$$
$$\underset{(I)}{}$$

$$[Pd(COCH_2CH_3)(TsO)(PPh_3)_2] + MeOH$$
$$\underset{(I)}{}$$
$$\rightarrow [PdH(TsO)(PPh_3)_2] + EtCOOMe \qquad (3)$$

It is well known that H_2O in combination with CO can interact with Pd(II) to give a hydride, which is unstable toward deprotonation with formation of Pd(0) species [33]. It is also known that an acid can stabilize the hydride by shifting equilibrium (**a**) toward left, however the acid can also react with the hydride with H_2 evolution and reformation of the Pd(II) species [33,34]:

$$Pd(II) + CO + H_2O \underset{}{\overset{-H^+}{\rightleftharpoons}} Pd(II) - (COOH)$$
$$\xrightarrow{-CO_2} Pd(II) - H \underset{(a)}{\rightleftharpoons} Pd(0) + H^+ \qquad (4)$$

$$Pd(II) - H + H^+ \rightleftharpoons Pd(II) + H_2 \qquad (5)$$

Reactions (4) and (5) are at the basis of the water gas shift reaction (WGSR) catalyzed by a homogeneous Pd(AcO)$_2$/PPh$_3$/CF$_3$COOH/H$_2$O system [33]. It has been also reported that in the presence of C_2H_4 the evolution of H_2 is inhibited and catalysis takes a different way, as the Pd(II)–H is trapped by the olefin to form a Pd(II)–Et intermediate, which inserts CO with formation of a Pd(II)–acyl intermediate, which inserts another molecule of C_2H_4 with formation of a Pd(II)–C$_2$H$_4$COEt species, which is splitted by the acid to yield diethylketone (DEK) and the initial Pd(II) precursor [33].

In the present case, complex (**III**) is dissolved in MeOH and the catalyst promotes the MP in place of DEK. Thus, MeOH attack to a Pd(II)–acyl intermediate of type (**I**) (reaction 3) is faster than the insertion of a second molecule of C_2H_4.

For the system [Pd(P–P)(dba)]–CH$_3$SO$_3$H it has been proved that the alkanol is the source of hydride, as the hydride forms only with primary or secondary alkanol and not with tertiary ones, like *t*-BuOH [26]. We have found that the acyl complex (**I**) forms also using *t*-BuOH in place of MeOH, thus in our case the source of hydride is H_2O in combination with CO interacting with Pd(II) or the acid by addition to Pd(0) (cf. reaction 4, equilibrium (**a**)).

As already mentioned, Pd(II)–H complexes are unstable toward deprotonation with formation of Pd(0). As a matter of fact, complex (**I**) can be prepared starting also from [Pd(CO)(PPh$_3$)$_3$] (or [Pd(CO)(PPh$_3$)]$_3$ in combination with

Table 1
Elemental analysis, selected IR, ^{1}H and ^{31}P NMR data for complex (**I**)

Analysis (%)				IR (cm^{-1})	^{1}H NMR δ (ppm)	^{31}P NMR δ (ppm)
	C	H	S			
Found	63.25	4.77	3.82	1688 (s, CO) 1230, 1035, 1013 (s, SO$_3$)	0.13 t (CH$_3$, 3H, CH$_2$CH$_3$) 1.92 s (CH$_3$, 3H,TsO)	17.37 s (PPh$_3$)
Calcd.	64.30	4.93	3.73		2.36 q (CH$_2$, 2H, CH$_2$CH$_3$) 7.20–7.71 m (C$_6$H$_5$, 34H, PPh$_3$ and TsO)	

Abbreviations: s, singlet; t, triplet; q, quadruplet; m, multiplet. NMR spectra taken in deuterated benzene; δ (^{31}P) values in ppm from external 85% H$_3$PO$_4$, downfield shifts being taken as positive.

PPh$_3$) and TsOH, under HMC conditions. These results give further support to the above suggestions for the formation of complex (**I**).

The synthesis of complex (**I**) was carried out also by reacting the chloride analogue *trans*-[Pd(COCH$_2$CH$_3$)Cl(PPh$_3$)$_2$] with AgTsO in dichloroethane. It has been characterized by elemental analysis, IR and NMR spectroscopy (Table 1).

The IR spectrums shows a strong absorption at 1688 cm^{-1} assigned to the $\nu_{C=O}$ of the acyl ligand [35–37]. The absorptions in the range 1230–1013 cm^{-1} are characteristic the –SO$_3^{-}$ group of the TsO ligand [29,38–40]. The ^{1}H NMR spectrum in deuterated benzene shows a quartet at 2.36 ppm and a triplet at 0.13 ppm due to the CH$_2$ and to the CH$_3$ protons of the acyl group and a singlet at 1.92 ppm due to the CH$_3$ protons of the TsO ligand. The ^{31}P NMR spectrum in deuterated benzene shows a singlet at 17.37 ppm indicating that the two triphenylphosphine ligands are in *trans* position. It has been reported that the complex *trans*-[Pd(CF$_3$COO)$_2$(PPh$_3$)$_2$] in a low-polar dioxane solvent exists as a covalent PdX$_2$P$_2$ species (^{31}P NMR at 16.5 ppm), while in a relatively high-polar 80% aqueous CF$_3$COOH medium as a cationic species [PdP$_2$(S)X]$^{+}$ or even [PdP$_2$(S)$_2$]$^{2+}$ (δ = 36.5 ppm) [33]. Moreover, the ^{31}P NMR spectrum of the chloride analogue to complex (**I**), *trans*-[Pd(COCH$_2$CH$_3$)Cl(PPh$_3$)$_2$], in deuterated benzene, shows a smglet at 19.25 ppm. Thus,

the relatively low value of the ^{31}P chemical shift suggests that complex (**I**) in benzene is a neutral species with the TsO anion coordinating the metal. However, the ^{31}P NMR spectrum of complex (**II**) and of its aquo analogous *trans*-[Pd(COOCH$_3$)(H$_2$O)(PPh$_3$)$_2$](TsO) in CD$_3$OD shows a singlet at δ = 16.51 [29].

3.2. Reactivity of trans-[Pd(COCH$_2$CH$_3$)(TsO)(PPh$_3$)$_2$] (I) and of trans-[Pd(COOCH$_3$)(TsO)(PPh$_3$)$_2$] (II)

The reactivity of these two complexes has been tested in order to give more insight into their role in the catalysis, as both of them can be considered as model catalytic intermediates. Some reactions have been carried out also in the presence of PPh$_3$ and TsOH, since they have been found to have a beneficial effect on the catalytic activity [27,28]. The results reported in Table 2 can be summarized as follows: (i) at r.t. the acyl complex (**I**) reacts with MeOH to give the expected MP in quantitative yield and a Pd(0) complex (entry 1), eventually together with the carbomethoxy complex (**II**), if in the presence of PPh$_3$ (entries 2 and 3, see Section 3.3). At higher temperature, in the presence of CO–ethene mixture, complex (**I**), in the presence of an excess of TsOH and PPh$_3$, catalyses the HMC (TOF = 380 h^{-1}), but after the reaction, it is recovered as complex (**III**) (yield 98%, entry 4, see also Section 3.4), while when (**I**)/TsOH = 1/1,

Table 2
Reactivity of Pd(II) and Pd(0) complexes

Entry No.	Complex	Additives TsOH/PPh$_3$/Pd (mol/mol)	P (MPa)		T (K)	Time (min)	Isolated species, yield (%)						
			CO + C$_2$H$_4$	CO/C$_2$H$_4$			(I)	(II)	(III)	(IV)	(V)	CH$_3$CH$_2$COOCH$_3$	
												mmol	TOF (h^{-1})
1	(**I**)	0/0/1	0.1	1/0	293	10	–	–	–	–	90	0.1	–
2	(**I**)	0/1/1	0.1	1/0	293	10	–	45	–	30	–	0.1	–
3	(**I**)	1/1/1	0.1	1/0	293	10	–	70	–	20	5	0.1	–
4	(**I**)	8/6/1	4.0	1/1	353	30	–	–	98	–	2	–	380
5	(**I**)	1/1/1	4.0	1/1	353	30	80	–	–	10	10	–	80
6	(**II**)	0/0/1	0.1	0/1	293	10	–	90	–	–	–	–	–
7	(**II**)	0/1/1	0.1	0/1	293	10	–	65	–	–	–	–	–
8	(**II**)	2/1/1	0.1	0/1	293	10	–	60	–	10	10	–	–
9	(**II**)	1.2/0.9/1	2.0	1/1	353	20	65	–	–	–	Traces	–	50
10	(**III**)	0/1/1	0.1	1/0	293	10	–	90	–	–	–	–	–
11	(**IV**)	1/0/1	0.1	1/0	293	10	–	75	–	–	–	–	–
12	(**IV**)	0/0/1	0.1	1/0	293	10	–	–	–	80	20	–	–

Run conditions: catalyst precursor: 0.1 mmol; (**I**) = [Pd(COCH$_2$CH$_3$)(TsO)(PPh$_3$)$_2$]; (**II**) = [Pd(COOCH$_3$)(TsO)(PPh$_3$)$_2$]; (**III**) = [Pd(PPh$_3$)$_2$(TsO)$_2$]; (**IV**) = [Pd(CO)(PPh$_3$)$_3$]; (**V**) = [Pd(CO)(PPh$_3$)]$_3$; MeOH: 3 ml; H$_2$O: 800 ppm.
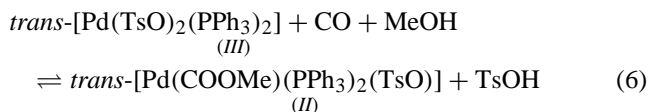
it is recovered as such it is (yield 80%, entry 5; complex (**I**) is recovered also running the experiment at r.t., in which case the TOF is significantly lower, ca. $8\,h^{-1}$); (ii) at r.t. the carbomethoxy complex (**II**) does not react with C_2H_4 in MeOH, it does not yield any MP and it is quantitatively recovered unreacted (entry 6) (or together with a Pd(0) complex, if the test in carried out also in the presence of PPh_3 and TsOH (entries 7 and 8)); (iii) at higher temperature complex (**II**) catalyses the HMC (TOF = $50\,h^{-1}$), but after the reaction, it is recovered as complex (**I**) (yield 65%, entry 9, see also Section 3.3); (iv) catalysis occurs with evolution of CO_2 (see also Sections 3.3 and 3.4).

These results prove that the acyl complex (**I**), though reactive, has been isolated from catalytic experiments because the subsequent reaction with MeOH is relatively slow and support to the suggestion that catalysis occurs via a hydride species rather then a carbomethoxy one (see Sections 3.3 and 3.4).

3.3. Conversion of trans-[Pd(COCH₂CH₃)(TsO)(PPh₃)₂] (I) to trans-[Pd(COOCH₃)(TsO)(PPh₃)₂] (II)

The results reported in Table 2 deserve further comments. Under the conditions of entry 1, the formation of the Pd(0) complex occurs within a few minutes, together with MP in quantitative yield. If the same test is carried out in the presence of PPh_3, the Pd(0) complex, that precipitates initially, re-desolves in ca. $30'$ and, upon addition of cold water, the carbomethoxy complex (**II**) precipitates. It is interesting to note that in the absence of TsOH the carbomethoxy is recovered only in 45% yield (entry 2), whilst in the presence of 1 equivalent of acid in 70% yield (entry 3). These results can be rationalized as proposed below.

Since the acyl complex (**I**) catalyses the HMC of C_2H_4 (see Section 3.4), it is likely that it reacts with MeOH according to reaction (3). However, as already mentioned, the Pd(II)–H that forms is unstable and deprotonates at equilibrium with Pd(0) and TsOH (cf. reaction (4), equilibrium (**a**)). We suggest that the acid reacts with the hydride giving complex (**III**) [33,34] (cf. reaction (5)), which reacts with CO and MeOH to give the carbomethoxy complex (**II**):

$$trans\text{-}[Pd(TsO)_2(PPh_3)_2] + CO + MeOH$$
$$\underset{(III)}{}$$
$$\rightleftharpoons trans\text{-}[Pd(COOMe)(PPh_3)_2(TsO)] + TsOH \qquad (6)$$
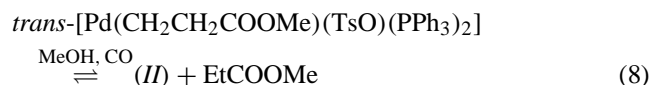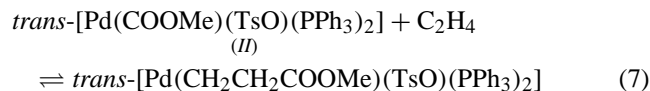$$\underset{(II)}{}$$

Supporting these suggestions, there are the facts that complex (**II**) forms in 90% from (**III**) in MeOH saturated with CO, even in the absence of the acid (entry 10), and that it forms also starting from $[Pd(CO)(PPh_3)_3]$ (**IV**) in 75% yield in the presence of TsOH, whilst in the absence of the acid, unreacted Pd(0) complex is recovered (entries 11 and 12).

It should be noted that deprotonation (4, equilibrium (**a**)) yields only 1 equivalent of acid, while the combination of reactions (3) with (5) and (6) shows that quantitative conversion to complex (**II**) requires 2 equivalents: this may explain

why the carbomethoxy complex (**II**) is obtained in less than 50% yield when the conversion of (I) is carried out without adding any TsOH (entry 2).

3.4. Conversion of trans-[Pd(COOCH₃)(TsO)(PPh₃)₂] (II) to trans-[Pd(COCH₂CH₃)(TsO)(PPh₃)₂] (I)

In principle complex (**II**), by reacting with C_2H_4, could give the ester according to reactions (7) and (8). However, in MeOH, saturated with C_2H_4, at r.t., it does not give the ester in detectable amounts and it is recovered almost quantitatively (entry 6). It does not yield any ester even the presence of 2 equivalents of TsOH (entry 8).

$$trans\text{-}[Pd(COOMe)(TsO)(PPh_3)_2] + C_2H_4$$
$$\underset{(II)}{}$$
$$\rightleftharpoons trans\text{-}[Pd(CH_2CH_2COOMe)(TsO)(PPh_3)_2] \qquad (7)$$

$$trans\text{-}[Pd(CH_2CH_2COOMe)(TsO)(PPh_3)_2]$$
$$\overset{MeOH,\ CO}{\rightleftharpoons} (II) + EtCOOMe \qquad (8)$$

Starting from complex (**II**), the ester forms only upon heating, under pressure of CO and C_2H_4, however the starting complex is recovered as complex (**I**) in 65% yield (entry 9). The conversion occurs with evolution of almost one equivalent of CO_2 and without formation of hydrogen in a detectable amount.

We propose that H_2O displaces MeOH from the carbomethoxy ligand with formation of a carbohydroxy species, which evolves CO_2 [41], yielding a Pd(II)–hydride, which, upon insertion of C_2H_4 and of CO, yields complex (**I**) which catalyses the HMC.

In principle, the transformation of complex (**II**) into complex (**I**) may occur also via formation of dimethyl carbonate. The Pd(0) complex that forms, reaction 9, is reoxidized by the acid to a Pd(II)–hydride and trapped by C_2H_4 and CO to give complex (**I**). Subsequent hydrolysis of the carbonate by H_2O would give CO_2. However, dimethyl carbonate was not detected by GC, not even in trace amounts.

$$trans\text{-}[Pd(COOMe)(TsO)(PPh_3)_2] + MeOH$$
$$\rightarrow Pd(0) + (MeO)_2CO + TsOH \qquad (9)$$
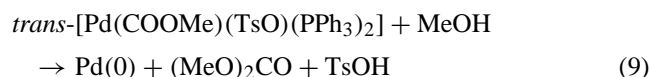
3.5. Catalytic activity of trans-[Pd(COCH₂CH₃)(TsO)(PPh₃)₂] (I)

Complex (**I**) has been tested as catalyst precursor in the methoxycarbonylation of ethene:

$$CH_2{=}CH_2 + CO + CH_3OH \rightarrow CH_3CH_2COOCH_3 \qquad (10)$$
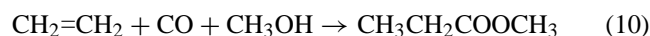
Most of the experiments have been carried in MeOH in the presence of 800 ppm of H_2O, since it has been found that this is the optimal concentration of H_2O when using the precursor (**III**) [27]. The results are reported in Table 3, together with the results obtained using other precursors. In

Table 3
Catalytic activity of Pd(II) and Pd(0) complexes

Entry no.	Complex	TsOH/Pd (mol/mol)	PPh$_3$/Pd (mol/mol)	TOF (h^{-1})	Pd$_{met}$
1	(I)	–	–	30	Yes
2	(I)	10	–	45	Yes
3	(I)	–	8	40	No
4	(I)	10	8	420	No
5	(II)	10	8	420	No
6	(II)	–	–	Traces	Yes
7	(III)	10	8	410	No
8	(III)	–	–	Traces	Yes
9*	(I)	1	8	210	No
10*	(III)	1	8	220	No
11	(IV)	10	–	410	Yes
12	(V)	10	8	400	No
13	(VI)	10		330	No

Run conditions: catalyst precursor: 0.1 mmol; MeOH: 50 ml; H$_2$O: 800 ppm; T: 353 K; P: 4.5 MPa (CO/C$_2$H$_4$ = 1/1); reaction time: 2 h; stirrer speed: 700 rpm; (VI) = [Pd(PPh$_3$)$_4$]. *MeOH = 40 ml; cyclohexene = 10 ml; P = 2.0 MPa (CO).

absence of TsOH and PPh$_3$, complex (I) leads, during 2 h, to a TOF of 30 h^{-1} (entry 1). This value is only indicative since under these conditions the complex decomposes to palladium metal. By adding an excess of TsOH only a slight increase of TOF is observed (45 h^{-1}, entry 2). Also in this case decomposition to palladium metal occurs. Practically, the same result is obtained when PPh$_3$ is added (without TsOH), but the formation of Pd metal is avoided (entry 3). The addition of PPh$_3$ and of TsOH affords the best TOF (420 h^{-1}, entry 4), practically the same as that achieved when using complex (II) or (III) under the same conditions. However, these complexes in the absence of TsOH and PPh$_3$ are inactive (entries 5–8) [27,29].

In addition, complex (I) has been used also as precursor in the catalytic HMC of cyclohexene. It gives MP in stoichiometric amount and 210 moles of methyl cyclohexanecarboxylate/mol Pd/h, showing practically the same activity as precursor (III) under the same conditions [28] (entries 9 and 10).

Quite interestingly, catalysis occurs with CO$_2$ evolution, suggesting that there is formation of Pd–COOH species that decompose to Pd–H species. In principle, starting from the acyl complex (I) as catalyst precursor, it is not necessary that the Pd(II)–H species forms again from the decomposition of Pd–COOH, because the hydride should reform after each catalytic cycle (Scheme 1 (A)). The fact that catalysis is accompanied by formation of CO$_2$ suggests that Pd–COOH species may form from Pd–COOMe species of type (II), through displacement of MeOH by H$_2$O, or from Pd(II) species of type (III) though interaction with H$_2$O and CO. It is interesting to mention that, using the precursor trans-[PdCl$_2$(PPh$_3$)$_2$], both the chloride analogous of complexes (I) and (II) have been isolated after HMC reactions [13]. A complex of type (III) could form during the catalysis through a Pd(II)–H consuming side reaction, before the

hydride is trapped by ethene, for example via reaction with the acid [33,34]. As a matter of fact, when complex (I) is used in high concentration and in the presence of an excess of TsOH, at 80 °C under 4.0 MPa of CO/C$_2$H$_4$ = 1/1, a TOF of 380 h^{-1} is obtained and it is recovered as complex (III) (98%) (Table 2, entry 4).

Another intermediate consuming side reaction can be the reaction of a Pd(II)–CH$_2$CH$_3$ intermediate with the acid that gives ethane and a complex of type (III). As a matter of fact, ethane has been detected by GC during the course of catalysis.

As already mentioned, an excess of acid may consume the active Pd(II)–H species with evolution of H$_2$, but on the other hand it may stabilize the hydrides preventing their deprotonation to inactive Pd(0) species or reoxydise them back to Pd(II)–H species. As matter of fact, also the inactive Pd(0) complexes (IV), (V) and (VI) catalyze efficiently the HMC of ethene if an excess of TsOH is used (Table 3, entries 11–13).

In conclusion, the results presented in this paper give further support to the suggestion that catalysis occurs via an initial Pd(II)–H species. In addition they suggest that H$_2$O promotes the catalysis, even when complex (I) is used as precursor, by converting species of type (II) and (III), that are likely to form during the catalysis, to Pd–(COOH) species and hence to active Pd(II)–H species.

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