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Synthesis, characterization and X-ray structure of *trans*-[Pd(COOCH₃)(H₂O)(PPh₃)₂](TsO), a possible intermediate in the catalytic hydroesterification of olefins (TsO = *p*-toluenesulfonate)

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Abstract

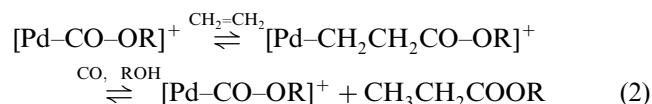
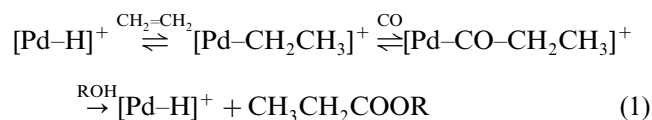
The complex *trans*-[Pd(COOCH₃)(H₂O)(PPh₃)₂](TsO) (**I**) has been synthesized by reacting *trans*-[Pd(COOCH₃)Cl(PPh₃)₂] with AgTsO in methanol. It has been characterized by IR, ¹H and ³¹P NMR spectroscopy. Crystals of *trans*-[Pd(COOCH₃)(H₂O)(PPh₃)₂](TsO)·(CH₃OH) (**II**) have been obtained by re-crystallization of **I** in methanol. The structure of the complex has been determined by X-ray analysis. It shows a slightly distorted square planar conformation around the central palladium. The coordinated water molecule and the clathrated methanol form a contact with the uncoordinated TsO⁻ anion, suggesting hydrogen bond interaction. Since **I** is a possible intermediate in the catalytic hydroesterification of olefins, its catalytic activity in the hydroesterification of ethylene has been tested at 100 °C under 45 atm of a 1/1 mixture of ethylene and CO in methanol as solvent, also in the presence of PPh₃ and TsOH. Without addition of PPh₃ and TsOH, **I** affords to traces of methylpropionate together with Pd(0) complexes and Pd metal. The same results are obtained when complex **I** is tested in the presence of PPh₃, except that in this case formation of palladium metal is avoided. Using the system **I**/PPh₃/TsOH = 1/6/8, a TOF (mol of ester/mol Pd·h) of 1800 h⁻¹ is obtained. We propose that the role of the acid TsOH is to favor the formation of a Pd–hydride intermediate and/or to reactivate the Pd(0) species, stabilized by the excess of PPh₃, via an oxidative addition of the acid. Since the acid does not favor the formation of Pd–alkoxy species we suggest that complex **I** plays only a minor role in catalysis and that this occurs via a Pd–hydride species.

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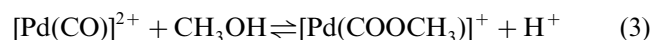
Keywords: Synthesis; Catalytic hydroesterification; Olefins

1. Introduction

Pd(II)–phosphine complexes in which the cationic charge is balanced by weakly coordinating anions, such as TsO⁻, have been successfully employed as catalyst precursor in the carbonylation of olefins [1–3]. It is widely accepted that in such reactions the catalytic cycle starts from the insertion of the olefin into a Pd–hydride or into a Pd–carboalkoxy species:



The Pd(II)–hydride species forms from the precursor and a hydrogen source such as an acid, water or hydrogen, while the Pd–carboalkoxy species forms by interaction of a Pd–carbonyl species with the alkanol [3–9]:



In a previous paper we used the preformed

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[Pd(TsO)₂(PPh₃)₂] complex as catalyst precursor for the hydroesterification of ethylene and the role of the addition of TsOH and PPh₃ was discussed [3]. Such a precursor was inactive without addition of both PPh₃ and TsOH whereas using the [Pd(TsO)₂(PPh₃)]/PPh₃/TsOH = 1/6/8 system, under 45 atm of a 1/1 CO–ethylene mixture and at 100 °C, a TOF (mol of ester/mol Pd·h) of approximately 1900 h⁻¹ was obtained. In addition, we found that the catalyst activity was influenced by the presence of water which can promote or depress the reaction [3]. Palladium complexes are also able to catalyze the WGSR via formation of Pd(II)–hydride intermediate. In such a reaction coordination of water to the Pd-center has been proposed [10,11]. On the basis of these results we proposed that a Pd–hydride species plays a major role in the catalysis.

In this paper we report the synthesis and the characterization of *trans*-[Pd(COOCH₃)(H₂O)(PPh₃)₂](TsO) (**I**) complex and the X-ray structure of **I** with a clathrated methanol molecule. To our knowledge, Pd–carboalkoxy species having weakly coordinating anions have not yet reported in literature and although several monoquo cationic transition-metal complexes are known, there have been very few palladium aquo-complexes reported [12–15].

In addition, since a Pd–carboalkoxy species may be involved in the catalytic cycle we tested the catalytic activity of **I** in the hydroesterification of ethylene.

2. Experimental

2.1. Materials

Methanol (purity > 99.5%, 0.05% of water), CD₃OD₃ and *n*-pentane were purchased from Baker; Pd(OAc)₂, TsOH and PPh₃ were Aldrich products. These products and the solvents were used without purification. The complex *trans*-[Pd(COOCH₃)Cl(PPh₃)₂] was prepared as described in literature [9]. Carbon monoxide and ethylene were supplied by SIAD Company ('research grade', purity > 99.9%).

2.2. General procedure

The IR spectra were recorded in nujol mull on a Nicolet FTIR instruments mod. Nexus.

¹H and ³¹P NMR spectra were recorded on a Bruker AMX 300 spectrometer equipped with a BB multi-nuclear probe operating in the FT mode at 300 and 121.442 MHz for ¹H and ³¹P, respectively. All samples examined were dissolved in deuterated methanol (CD₃OD) used also as internal reference for the assignment of the chemical shifts.

Products of the hydroesterification 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.

2.3. Synthesis of **I** and of its methanol clathrated **II**

AgTsO is slowly added to *trans*-[Pd(COOCH₃)Cl(PPh₃)₂] (0.1 mmol) suspended in 2 ml of methanol. The solution is stirred for a few minutes at 15 °C till complete precipitation of AgCl and then quickly filtered using a micro-filter system. By dropping directly the solution into 50 ml of cold water (15 °C), under vigorous stirring, complex **I** precipitates as a white solid which is separated by filtration, washed with cold water, *n*-pentane and dried under vacuum (yield 80%).

The solid product was separated by filtration, washed with water/*n*-pentane and ether and dried under vacuum (yield higher than 70%). It was identified by elemental analysis, IR and NMR spectroscopy. By re-crystallization of complex **I** from methanol/water (4/1, v/v) at -10 °C, after several days, crystals of the methanol clathrated of complex **I**, suitable for X-ray diffraction studies, were obtained.

2.4. Hydroesterification of ethylene in methanol, employing **I** as catalyst precursor

All the experiments were carried out in a stainless steel autoclave of approximately 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 added in a approximately 150 ml Pyrex glass beaker placed into the autoclave. Carbon monoxide–ethylene 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 °C).

The catalytic activity of complex **I** was tested as follows. Complex **I** (0.1 mmol) was dissolved in 50 ml of methanol. The autoclave was pressurized ($P_{\text{tot}} < 5$ atm) at room temperature with a mixture of carbon monoxide and ethylene (1/1). The autoclave was then heated to the working temperature (100 °C) while stirring. At this temperature the pressure in the autoclave was adjusted at 45 atm and maintained constant by a pressure regulator connected to the gas reservoir throughout the experiment (2 h). The gas consumption was monitored by following the pressure drop in the reservoir. The autoclave was then cooled to room temperature and vented. The content of the glass bottle was analyzed by GC analysis. Complex **I** was tested also (i) in combination of PPh₃ and (ii) in combination of PPh₃ and TsOH.

All experiments were carried out in the presence of 800 ppm of water in order to compare the reactivity of **I** with the reactivity of [Pd(TsO)₂(PPh₃)₂] [3].

2.5. Crystal data for II

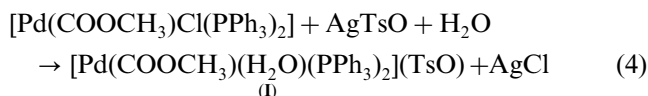
$M_r = 911.27$, triclinic, space group $P\bar{1}$, $a = 9.224(2)$, $b = 11.004(3)$, $c = 11.583(3)$ Å, $\alpha = 74.84(3)^\circ$, $\beta = 104.55(3)^\circ$, $\gamma = 90.85(2)^\circ$, $V = 1096.8(5)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.38$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 5.92$ cm⁻¹, $T = 293(2)$ K.

A prismatic colorless crystal of dimension $0.22 \times 0.26 \times 0.30$ mm was centered on a four-circle Philips PW1100 diffractometer operating in θ - 2θ scan mode with graphite-monochromated Mo K α radiation, following standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption, as described by North et al. [16]. No correction was made for extinction. The structure was solved by heavy atom method. Refinement was carried out by full-matrix least-squares; the function minimized was $\sum w(F_o^2 - F_c^2)^2$, with weighting scheme $w = 1/[\sigma^2(F_o^2) + 1.41P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in calculated positions and refined as riding, including free torsion of the methyl groups, with fixed isotropic thermal parameters (1.2 U_{eq} of the parent carbon atom). For a total of 521 parameters, $wR' = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.079$, $S = 1.21$, and conventional $R = 0.034$, based on the F values of 4358 reflections having $F_o^2 = 2\sigma(F_o^2)$. Structure refinement and final geometrical calculations were carried out with SHELXL-97 program [17]; drawings were produced using ORTEP II [18].

3. Results and discussion

3.1. Synthesis and characterization of complex I and complex II

The synthesis of complex I was carried out by reacting *trans*-[Pd(COOCH₃)Cl(PPh₃)₂] with AgTsO in methanol:



By dropping the pale yellow solution in water at 15 °C complex I precipitates as a white solid.

The elemental analysis and the characterizing IR and NMR data are reported in Table 1. The IR spectrum shows two broad absorptions at 3489 and 3412 cm⁻¹, which are attributed to $\nu_{\text{as}}(\text{O}-\text{H})$ and $\nu_{\text{s}}(\text{O}-\text{H})$, respectively, of a water molecule coordinated to the metal [12–15,19] and a strong absorption at 1684 cm⁻¹ assigned to the ν (C=O) of the carboalkoxy ligand [9]. The

absorptions at 1230, 1035 and 1013 cm⁻¹ are characteristic the $-\text{SO}_3^-$ group of the TsO⁻ anion [19–25].

The ³¹P NMR spectrum in CD₃OD shows singlets at 16.51 ppm indicating a *trans* position of the two triphenylphosphine ligands [9]. The ¹H NMR analysis shows singlets at 2.58 ppm due to the CH₃ protons of the alcoxy group and at 2.36 ppm due to the CH₃ protons of the TsO⁻ anion. On the basis of elemental analysis, IR and NMR spectra, the complex I can be formulated as *trans*-[Pd(COOCH₃)(H₂O)(PPh₃)₂](TsO).

The X-ray structure of methanol clathrated complex II is shown in Fig. 1 together with the atom labeling. The most relevant structural parameters are reported in Table 2.

It consists of monomeric palladium cations and TsO⁻ anions, together with clathrated methanol molecule in the ratio 1:1:1. The complex shows a slightly distorted square planar conformation around the central palladium with deviations of the atoms from the P(1), P(2), O(1), C(37) best mean plane $-0.033(4)$; $-0.035(4)$; $0.031(4)$; $0.036(4)$ Å, respectively.

The triphenyl phosphine groups in *trans* position display a staggered conformation with respect to the P–P axis. The Pd–P bond lengths of 2.359(2) and 2.350(3) Å are slightly larger than those reported for the neutral [Pd(OCOCH₃)(COOCH₃)(PPh₃)₂] [26] (2.338(1), 2.339(1) Å). The almost planar methoxycarbonyl group, forms a dihedral angle of 80.4(4)° with the coordination plane.

The Pd–O(1)_(water) bond distance of 2.160(7) Å is comparable with the value found in the complex cation [Pd(TsO)(H₂O)(dppp)](TsO) [14] (2.138(4) Å). The coordinated water molecule forms a contact with O(1)··O(6) of the uncoordinated TsO group of 2.698(7) Å and the O(7) of the clathrated methanol is in contact with O(5) of the TsO⁻ anion (O(7)··O(5) 2.62(1) Å ((O(7)–H··O(5) 1.84(9) Å) with an angle of 172.6(8)° suggesting hydrogen bond interaction (the water protons were not detected).

3.2. Catalytic tests of complex I

The catalytic activity of complex I in the hydroesterification of ethylene has been checked as described in Section 2.

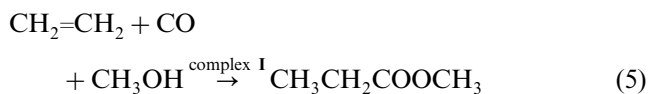


Table 3 shows the results obtained carrying out the hydroesterification of ethylene using I as catalyst precursor in the presence of different amounts of PPh₃ and TsOH.

By reacting complex I in methanol without adding PPh₃ and TsOH, methylpropionate forms in less than

Table 1
Elemental analysis, selected IR, ^1H and ^{31}P NMR data of **I**

Analysis (%)	IR			^1H NMR δ (ppm)	^{31}P NMR δ^a (ppm)	
	C	H	S			
Found	61.92	4.51	3.64	1684 (s, CO) 3489, 3412 (m, OH)	2.36 s (CH ₃ , 3H, TsO) 2.58 s (CH ₃ , 3H, OCH ₃)	16.51 s (PPh ₃)
Calc.	61.47	4.81	3.65	1230, 1035, 1013 (s, SO ₃)	7.20–7.71 m (C ₆ H ₅ , 34H, PPh ₃ and TsO)	

Abbreviations: s = singlet, m = multiplet.

^a δ (^{31}P) values in ppm from external 85% H₃PO₄, downfield shifts being taken as positive.

Table 2
Selected bond distances (Å), bond angles (°) for **II**

Pd–P(1)	2.359(2)	Pd–P(2)	2.350(3)
Pd–C(37)	1.976(9)	Pd–O(1)	2.160(6)
C(37)–O(2)	1.315(10)	C(37)–O(3)	1.182(11)
O(2)–C(38)	1.461(9)	O(4)–S	1.439(7)
O(5)–S	1.439(7)	O(6)–S	1.452(5)
S–C(39)	1.775(9)		
C(37)–Pd–O(1)	174.6(3)	P(2)–Pd–O(1)	87.7(2)
P(2)–Pd–C(37)	87.9(3)	P(1)–Pd–O(1)	96.3(2)
P(1)–Pd–C(37)	88.2(3)	P(1)–Pd–P(2)	176.04(8)
Pd–C(37)–O(3)	124.5(8)	Pd–C(37)–O(2)	111.4(6)
O(2)–C(37)–O(3)	124.1(8)	C(37)–O(2)–C(38)	116.7(7)
O(5)–S–O(6)	110.6(4)	O(4)–S–O(6)	113.8(4)
O(4)–S–O(5)	113.4(5)		

stoichiometric amount with respect to complex **I**, which decomposes to Pd(0) species, such as [Pd(CO)(PPh₃)₃]

and [Pd₃(CO)₃(PPh₃)₃], and palladium metal (entry 1) [27,28].

The same results are obtained when complex **I** is tested in the presence of PPh₃ (entry 2). In this case the formation of palladium metal is avoided and the precursor is reduced to [Pd(CO)(PPh₃)₃].

Reduction can take place through the reaction scheme:

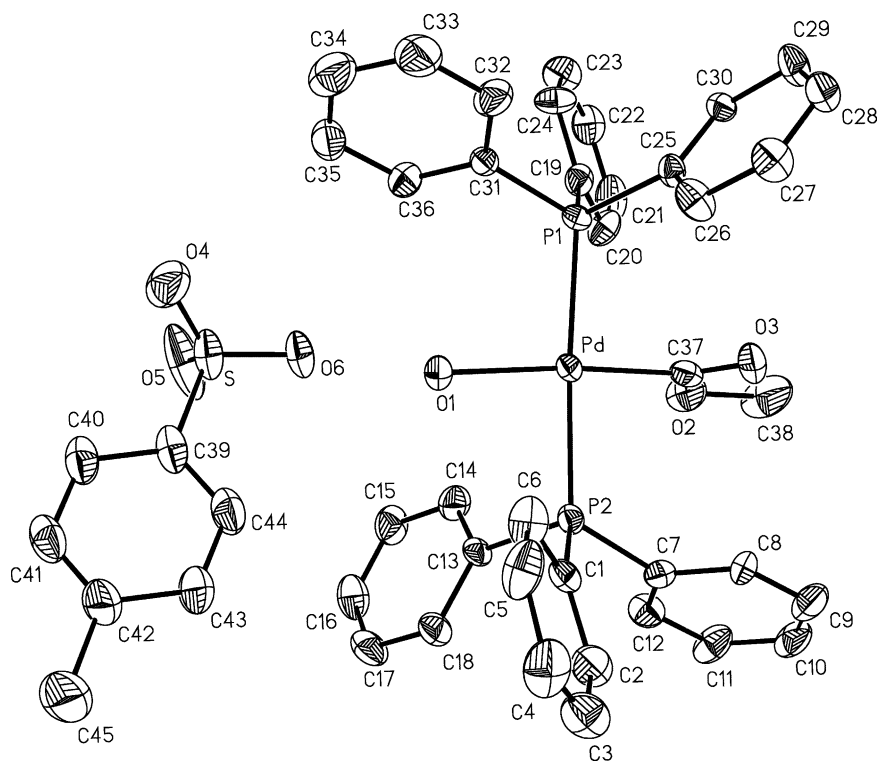
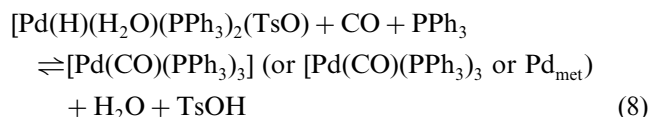
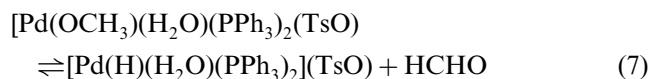
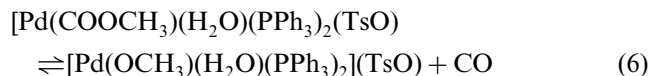


Fig. 1. ORTEP plot of [Pd(COOCH₃)(H₂O)(PPh₃)₂](TsO). The non-hydrogen atoms are represented at 30% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

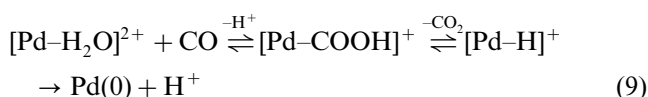
Table 3
Reactivity of **I** in the hydroesterification of ethylene

Entry no	PPh ₃ / I molar ratio	TsOH/ I molar ratio	TOF mol/mol Pd/h	Pd metal
1	0	0	traces	yes
2	6	0	traces	no
3	0	8	traces	yes
4	6	8	1800	no

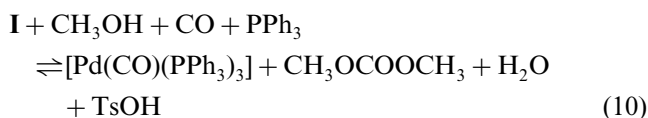
Run conditions: **I** = 0.1 mmol, methanol = 50 ml, H₂O = 800 ppm, *T* = 100 °C, *P* = 45 atm (CO/ethylene = 1/1), stirrer speed = 700 rpm, reaction time = 2 h.

Complex **I** may be in equilibrium with the Pd–methoxy species *trans*-[Pd(OCH₃)(H₂O)(PPh₃)₂](TsO) (Reaction (6)), which forms a Pd–hydride species via Reaction (7) [29]. Under the reaction conditions, the Pd–hydride species is unstable and decomposes to a Pd(0) species (Reaction (8)), which is inactive in the carbonylation of ethylene.

In addition, complex **I** may decompose to Pd(0) also via interaction of H₂O and CO on the metal center:



The alternative pathway to reduce the complex **I** to a Pd(0) complex with formation of dimethyl carbonate (Reaction (10)) [30,31] can be excluded because the carbonate has not been detected by the GC analysis.

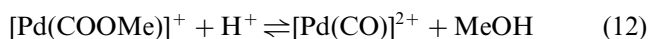


No significant catalytic activity is observed when complex **I** is tested in the presence of TsOH (TsOH/Pd = 8/1: entry 3).

Instead, when complex **I** is used in the presence of both PPh₃ and TsOH [(**I**)/PPh₃/TsOH = 1/6/8], a TOF of 1800 h⁻¹ is achieved (entry 4), which is comparable with the TOF obtained using the precursor [Pd(TsO)₂(PPh₃)₂], under the same experimental conditions (ca. 1900 h⁻¹) [3]. The acid prevents the reduction to unactive Pd(0) species or reoxidized these species:



Moreover, it is known [9] that in the presence of an acid the formation of Pd–alkoxy species is not favored:



These results suggest that complex **I** plays only a minor role in catalysis and that catalysis occurs via a Pd–H species according to the reaction scheme (1).

4. Supplementary material

Tables of additional material, including atomic coordinates, full listing of bond lengths/angles and anisotropic thermal parameters are available from the Cambridge Crystallographic Data Centre, CCDC No. 183064. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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