



# New carboalkoxybis(triphenylphosphine)palladium(II) cationic complexes: Synthesis, characterization, reactivity and role in the catalytic hydrocarboalkoxylation of ethene. X-ray structure of *trans*-[Pd(COOMe)(TsO)(PPh<sub>3</sub>)<sub>2</sub>] $\cdot$ 2CHCl<sub>3</sub>

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## ABSTRACT

The cationic complexes *trans*-[Pd(COOR)(H<sub>2</sub>O)(PPh<sub>3</sub>)<sub>2</sub>](TsO) have been synthesised by reacting *cis*-[Pd(H<sub>2</sub>O)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](TsO) $\cdot$ 2H<sub>2</sub>O with CO in ROH (R=Me and Et), practically under room conditions, or by methathetical exchange of *trans*-[Pd(COOMe)Cl(PPh<sub>3</sub>)<sub>2</sub>] with Ag(TsO) (R=*n*-Pr, *iso*-Pr, *n*-Bu, *iso*-Bu, *sec*-Bu). They have been characterised by IR, <sup>1</sup>H NMR and <sup>31</sup>P NMR spectroscopies.

The X-ray investigation of *trans*-[Pd(COOMe)(TsO)(PPh<sub>3</sub>)<sub>2</sub>] reveals that the palladium center is surrounded in a virtually square planar environment realized by two PPh<sub>3</sub> trans to each other, the carbon atom of the carbomethoxy ligand and an oxygen atom of the *p*-toluensulfonate anion, with two crystallization molecules of CHCl<sub>3</sub>. The Pd–O–S angle, 151.9(3)°, is very wide, probably due to the interaction of one CHCl<sub>3</sub> molecule with the complex inner core. The carbomethoxy derivatives react with R'OH yielding the corresponding R' carboalkoxy derivative (R' = Et, *n*-Pr and *iso*-Pr); ethene does not insert into the Pd–COOMe bond; decarbomethoxylation occurs when treated with TsOH/H<sub>2</sub>O in MeOH at 50 °C.

All the carboalkoxy are precursors for the catalytic carboalkoxylation of ethene if used in combination of PPh<sub>3</sub> and TsOH, better in the presence of some water. Experimental evidences are more in favor of the so-called “hydride” mechanism rather than the “carbomethoxy” mechanism.

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## 1. Introduction

Pd(II)-carboalkoxy complexes are involved as key intermediates in several catalytic carbonylation reactions, such for example the oxidative carbonylation of alkanols to carbonates and oxalates, or of olefins and alkynes to diesters or unsaturated esters [1–3], the double carbonylation of organic halides [4,5], the carbonylation of olefins to polyketones [6,7]. They have been proposed as key intermediates also in the hydroesterification of an olefin to monoesters [8–11].

Methods of synthesis are based on the reaction of Pd(II) complexes with CO and an alkanol, eventually in the presence of a tertiary amine, or an alkoxide [12–17] or on the oxidative addition of chloro or cyano formate or phenylcarbonate to Pd(0) complexes [18–22]. Most of the syntheses reported up to now are relevant to carbomethoxy derivatives. The synthesis of neutral Pd(II) com-

plexes of the type *trans*-[Pd(COOR)X(PPh<sub>3</sub>)<sub>2</sub>] (X=Cl and CN) with R bulkier than Me (up to cyclohexyl) has been also reported [19–24].

The cationic carbomethoxy complex *trans*-[Pd(COOMe)(H<sub>2</sub>O)(PPh<sub>3</sub>)<sub>2</sub>](TsO) has been synthesised from the neutral *trans*-[Pd(COOMe)Cl(PPh<sub>3</sub>)<sub>2</sub>] by methathetical exchange with Ag(TsO). Its role in the catalytic hydrocarbomethylation of ethene has been investigated [25].

In the present paper we extend the study to the synthesis and characterization of the new cationic carboalkoxy complexes *trans*-Pd(COOR)(H<sub>2</sub>O)(PPh<sub>3</sub>)<sub>2</sub>(TsO), with R = Et, *n*-Pr, *iso*-Pr, *n*-Bu, *iso*-Bu, *sec*-Bu, together with further studies on the reactivity of the methyl analogue in relation to the catalytic hydrocarbomethylation of ethene. We also reported the X-ray diffraction structure of *trans*-[Pd(COOMe)(TsO)(PPh<sub>3</sub>)<sub>2</sub>] $\cdot$ 2CHCl<sub>3</sub>.

## 2. Experimental

### 2.1. Materials

Carbon monoxide and ethene (purity higher than 99%) were supplied by SIAD Spa (Italy). Methanol was purchased from Baker

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(purity >99.5%, 0.01% of water) and Pd(OAc)<sub>2</sub>, Ag(TsO), NEt<sub>3</sub>, PPh<sub>3</sub> and *p*-toluenesulfonic acid were purchased from Aldrich Chemicals. NEt<sub>3</sub> and the solvents were commercial grade and used without further purification. [Pd(COOR)Cl(PPh<sub>3</sub>)<sub>2</sub>], [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], [Pd(H<sub>2</sub>O)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](TsO)<sub>2</sub> and [Pd(TsO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] complexes were prepared according to the methods reported in the literature [24–27].

## 2.2. General procedure

The IR spectra were recorded in nujol mull on a Nicolet FTIR instruments mod. Nexus. <sup>1</sup>H and <sup>31</sup>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 121.5 MHz for <sup>1</sup>H and <sup>31</sup>P, respectively. All the samples were dissolved in deuterated methanol used also as internal reference for the assignment of the chemical shifts.

## 2.3. Preparation of trans-[Pd(COOR)(H<sub>2</sub>O)(PPh<sub>3</sub>)<sub>2</sub>](TsO) (R = Me and Et)

0.1 mmol of [Pd(H<sub>2</sub>O)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](TsO)<sub>2</sub> was dissolved in 2 ml of MeOH or EtOH, previously saturated with CO at r.t. The solution was kept under 2 atm of CO for 5–10 min and then poured into 20 ml of cold water under vigorous stirring. A white precipitated formed immediately. The suspension was filtered, the solid was washed with cold water, *n*-pentane, and dried under vacuum (yield 77%).

## 2.4. Preparation of trans-[Pd(COOR)(H<sub>2</sub>O)(PPh<sub>3</sub>)<sub>2</sub>](TsO) with R bulkier than Et

AgTsO was slowly added to trans-[Pd(COOR)Cl(PPh<sub>3</sub>)<sub>2</sub>] (0.1 mmol) suspended in 2 ml of ROH. The solution was stirred for few minutes at 15 °C till complete precipitation of AgCl and then quickly filtered using a micro-filter system. The solution was dropped directly into 20 ml of cold water, under vigorous stirring. A white solid precipitates which was separated by filtration, washed with cold water, *n*-pentane and dried under vacuum (yield 75%). This procedure gives good results also when R=Me or Et. If the filtered methanol solution is poured into warm water (50 °C), the complex trans-[Pd(COOR)(TsO)(PPh<sub>3</sub>)<sub>2</sub>] separates.

## 2.5. Reactivity

The reactivity tests under pressure higher than 2 atm were carried out by dissolving the carboalkoxy complex (0.1 mmol) in the appropriate alkanol (2 ml) in a 5–10-ml glass bottle placed in an autoclave of ca. 50 ml volume. The autoclave was first washed several times with the appropriate gas (CO or ethene), then pressurised and warmed to the desired pressure and temperature. The solution was stirred with a magnetic bar. After the desired reaction time was over the autoclave was rapidly cooled to r.t. (or even to 0 °C) and then slowly depressurised. A little sample was taken apart for GC analysis. The rest was quickly poured into water. The precipitate was collected on a filter, washed with cold water and *n*-heptane, dried under vacuum. The nature of the solid was established by IR and NMR spectroscopy.

The reactivity was tested with alkanols, acids (HCl, AcOH and TsOH), water, water/TsOH and with ethene. In order not to be redundant, the conditions of the tests are reported together with the results and the discussion in the next section.

**Table 1**  
Crystal and refinement data.

Complex	
Formula	C <sub>47</sub> H <sub>42</sub> O <sub>5</sub> P <sub>2</sub> SCl <sub>6</sub> Pd
Molecular wt	1099.9
Color	colorless
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n (No. 14)
<i>a</i> (Å)	19.558(3)
<i>b</i> (Å)	12.155(2)
<i>c</i> (Å)	21.453(4)
β (°)	103.87(1)
<i>V</i> (Å <sup>3</sup> )	4951(1)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.476
<i>F</i> (000)	2232
Crystal dimens (mm)	0.20 × 0.20 × 0.20
θ limits (°)	3.5/29.6
No. of independent data	11938
No. of data with <i>I</i> > 2σ ( <i>I</i> )	3892
No. of variables	560
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.058
w <i>R</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.110
Largest peak in ( <i>F</i> (e Å <sup>-3</sup> ))	0.824
GOF <sup>c</sup>	0.763

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR(F^2) = \left[ \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2 \right]^{1/2}$$

$$^c GOF = \left[ \sum w(|F_o|^2 - |F_c|^2)^2 / (n - p) \right]^{1/2}$$

## 2.6. Hydroesterification of ethene using the carboalkoxy complexes reported in Table 1 as catalyst precursors in the relevant ROH

The precursor was used as such or also in combination with PPh<sub>3</sub> and PPh<sub>3</sub>/TsOH as reported in Section 3. All the experiments were carried out in a stainless steel autoclave of ca. 250 ml of capacity following the same procedure already reported, using the solvent with 800 ppm of water in order to compare the activity with that previously reported using related precursors [25,28,29].

## 2.7. X-ray data collection, structure solution and refinement

The X-ray data collection was performed at room temperature with a STADI 4 CCD STOE area detector diffractometer on single-crystal mounted in a thin-walled glass capillary with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were obtained by slow evaporation of a CHCl<sub>3</sub>/*n*-hexane solution of the complex at -10 °C. A summary of the X-ray analysis is listed in Table 1.

The structure was solved by direct methods and refined by full-matrix least-squares based on *F*<sup>2</sup>, where all non-hydrogen atoms were assigned anisotropic displacement parameters. As commented in Section 3.2, the solvent molecules suffer from high thermal motions. The final Fourier difference maps showed no significant features, the largest maxima (less than one electron) close to the chlorine atoms. All calculations were made with programs of the SHELXTL/PC system and SHELXL93 program [30].

## 3. Results and discussion

### 3.1. Synthesis and characterization of the carboalkoxy complexes reported in Table 2

Complexes (**1a** and **b**) have been prepared by reacting [Pd(TsO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] or [Pd(H<sub>2</sub>O)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](TsO)·2H<sub>2</sub>O with CO in ROH

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