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

Gianni Cavinato [a], Sarah Facchetti [b], Luigi Toniolo [b,*]

[a] *Department of Chemical Sciences, University of Padua, via Marzolo 1, 35100 Padua, Italy*
[b] *Department of Chemistry, University of Venice, Dorsoduro 2137, 30123 Venice, Italy*

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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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* Corresponding author. Tel.: +39 041 2348553; fax: +39 041 2348517.
E-mail address: toniolo@unive.it (L. Toniolo).

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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.

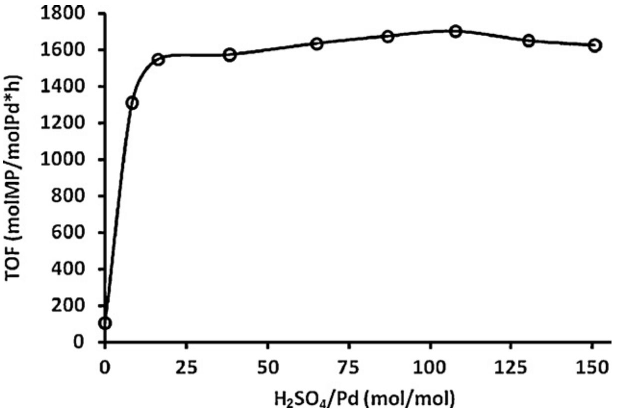

Fig. 1. Influence of the H_2SO_4/Pd ratio on the TOF. *Run conditions*: $[Pd(SO_4)(PPh_3)_2]$, 1.38×10^{-2} mmol; PPh_3, 0.22 mmol; solvent MeOH, 80 mL; $p_{CO} = p_E = 30$ bar; temperature, 100 °C; reaction time, 1 h.

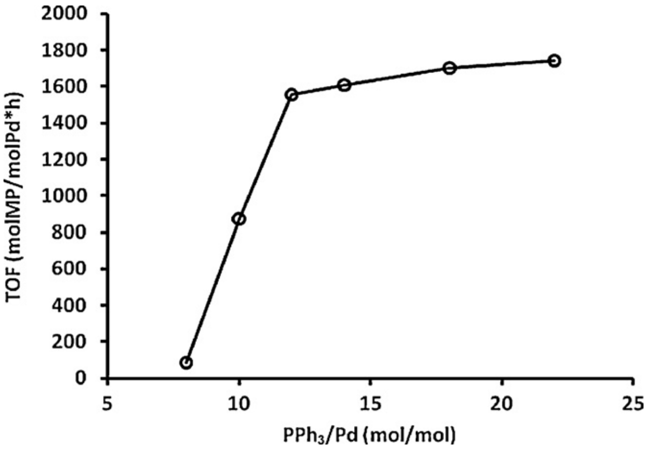

Fig. 2. Influence of added PPh_3/Pd ratio on the TOF. *Run conditions*: $[Pd(SO_4)(PPh_3)_2]$, 1.38×10^{-2} mmol; H_2SO_4, 96% 151 mg, 1.48 mmol H_2SO_4; solvent MeOH, 80 mL; $p_{CO} = p_E = 30$ bar; temperature, 100 °C; reaction time, 1 h.

(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.