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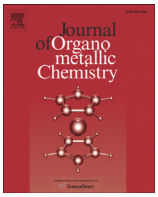

Mechanistic studies on the selective oxidative carbonylation of MeOH to dimethyl oxalate catalyzed by $[Pd(COOMe)_n(TsO)_{2-n}(PPh_3)_2]$ ($n = 0, 1, 2$) using *p*-benzoquinone as a stoichiometric oxidant

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ABSTRACT

The reactivity of the complexes *cis*-$[Pd(OTs)_2(PPh_3)_2]$ (**I**), *trans*-$[Pd(COOMe)(OTs)(PPh_3)_2]$ (**II**) and *trans*-$[(COOMe)_2(PPh_3)_2]$ (**III**), regarding the catalytic oxidative carbonylation of MeOH to dimethyl oxalate (DMO) using benzoquinone (BQ) as a stoichiometric oxidant, has been studied in CD_2Cl_2/MeOH (10/1, v/v) by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. **I** reacts with CO and MeOH at 193 K giving **II**, which is transformed into **III** upon addition of a base. The same occurs in the presence of BQ. Instead, if the base is added before admission of CO, $[Pd(BQ)(PPh_3)_2]$ is formed. Starting also from **II**, complex **III** is formed only after addition of a base. The base neutralizes TsOH which is formed in the transformation of **I** to **II** and **III**. **III** is unstable in the presence of 1 equivalent of TsOH and it is transformed into **II**. At 333 K, under 0.4 MPa of CO, **III** decomposes with formation of DMO and dimethyl carbonate (DMC) (15%) each), whereas, in the presence of BQ, **III** is unstable already at 298 K, with formation of only DMO (10%). Catalysis to DMO is observed at 333 K. Thus BQ enhances the reactivity of **III** and directs the catalysis selectively to DMO.

I, **II** and **III** have also been used in catalytic experiments in pure MeOH at 298 K, under 0.3 MPa of CO. **II** and **III** are active even in the absence of a base (TOF *ca.* 30 h^{-1}). **I** is active only after addition of a base. A catalytic cycle is proposed.

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1. Introduction

The catalytic oxidative carbonylation of an alkanol to the corresponding carbonate and oxalate can be conveniently performed in the presence of palladium-based catalysts [1].

The use of oxygen implies the formation of water, which causes consumption of CO and prevents further formation of the product. The use of triethyl orthoformate as dehydrating agent was proposed by D.M. Fenton et al. for the oxidative carbonylation of ethanol catalyzed by $PdCl_2$ in combination with a redox couple, typically Cu(I)/Cu(II) chlorides [2]. The problem of the formation of water was overcome using an alkyl nitrite in a two step process for the industrial production of alkyl oxalates catalyzed by Pd/C [1]. The use of BQ as a cooxidant in combination with oxygen was reported using $PdCl_2$ [2] and $Pd(AcO)_2/Co(AcO)_2/PPh_3$ [3] For the latter system, the function of the phosphine was not reported, for example whether it reacted with the acetates forming complexes of the type $M(AcO)_2(PPh_3)_2$. As a matter of fact, PPh_3 could have reacted with BQ with formation of PPh_3–BQ adduct (betaine) [4–6] before interacting with the metals. BQ can be used also in the absence of oxygen. This avoids the formation of water since BQ is reduced to hydrobenzoquinone (H_2BQ) [7]. Recently, we have reported the use of BQ for the oxidative carbonylation of MeOH, catalyzed by the pre-formed Pd(II)-PPh_3 complexes $[Pd(COOR)_nX_{2-n}(PPh_3)_2]$ ($n = 0, 1, 2$; X = Br, Cl, NO_2, ONO_2, OAc, OTs) in combination with NEt_3. DMO is selectively produced. After catalysis, the complexes $[Pd(BQ)(PPh_3)_2]$, $[Pd(CO)(PPh_3)_3]$ and $[Pd(CO)(PPh_3)]_3$ have been found in the reaction mixture [8]. No dicarboalkoxy species has been detected, in spite of the fact that the formation of oxalate is likely to occur through a dicarboalkoxy intermediate [9–11].

In addition to being an oxidant, BQ can play other roles by participating in both the formation and transformation of key intermediates into the reaction products by interacting with the catalytically active metal complex. It can change properties of the

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Abbreviations: BQ, benzoquinone; DMO, dimethyl oxalate; DMC, dimethyl carbonate.

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reaction centre and, consequently, the mechanism and the direction of the reaction. For example, using $PdCl_2$ or $[Pd(CO)Cl]_n$ in the oxidative carbonylation of MeOH, the corresponding oxalate or carbonate was formed in the presence or absence of BQ, respectively [12,13]. Another example is the following. *trans*-$[Pd(COOMe)Cl(PPh_3)_2]/NEt_3$ catalyzes the selective oxidative carbonylation of MeOH to oxalate at 65 °C using BQ as an oxidant, even though this complex is stable in the absence of BQ [8]. As a matter of fact, it can be prepared in high yield by carbonylation of *trans*-$[PdCl_2(PPh_3)_2]$ in MeOH in the presence of NEt_3 at 343 K [14].

To the best of our knowledge, no detailed mechanistic studies have been reported on the oxidative carbonylation of an alkanol to oxalate. As above mentioned, *cis*-$[Pd(OTs)_2(PPh_3)_2]$ (**I**), *trans*-$[Pd(COOMe)(OTs)(PPh_3)_2]$ (**II**) and *trans*-$[(COOMe)_2(PPh_3)_2]$ (**III**) have been used as catalyst precursors using BQ as an oxidant [8]. It is reasonable to suppose that starting from (**I**), the formation of the oxalate occurs though the intermediacy of a mono- and a dicarbomethoxy species of type **II** and **III**. Taking advantage of the fact that these complexes are rather reactive, but stable enough to be prepared as solid compounds, we took them into consideration for an NMR study relevant to this catalysis. Hereafter, the results of this investigation are discussed.

2. Experimental section

2.1. Reagents

MeOH, NEt_3, $TsOH{\cdot}H_2O$, PPh_3, BQ, CD_2Cl_2 and CD_3OD were purchased from Sigma–Aldrich. CD_2Cl_2 and CD_3OD were stored over 4 Å molecular sieves under Ar. Carbon monoxide (purity higher than 99%) was supplied by SIAD Spa (Italy).

Cis-$[Pd(OTs)_2(PPh_3)_2]$ (**I**) [15], *trans*-$[Pd(COOMe)(TsO)(PPh_3)_2]$ (**II**) [16], trans-$[Pd(COOMe)_2(PPh_3)_2]$ [8] were prepared according to literature procedures.

2.2. Instrumentation

NMR spectra were recorded on Bruker AMX 300 spectrometer. All ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. $^{31}P\{^1H\}$ signals were referenced to an 85% aqueous solution of H_3PO_4. NMR under pressure was performed using a 5 mm pyrex glass HP-NMR tube with Teflon head (maximum pressure tolerated 1.3 MPa).

2.3. High pressure NMR experiments

Typically, a solution of $5{\cdot}10^{-3}$ mmol of the palladium complex dissolved in CD_2Cl_2 (0.15 mL) was poured under argon, at r.t., into the 5 mm pyrex glass HP-NMR tube, previously evacuated by a vacuum pump. The tube was then quickly placed in a liquid N_2/acetone bath cooled at 193 K. To the cooled solution was added, under argon flow, a solution containing the desired amount of PPh_3 and/or BQ, NEt_3, MeOH (30 μL to reach 10% of final volume) in 0.15 mL of CD_2Cl_2. The tube was connected with the pressure line by using the special screw top in Teflon, then purged several times (4–5) and pressurized with CO or Ar (the maximum pressure used at this temperature was 0.6 MPa) taking care to shake the tube in order to favour the solubilization of the gases. The tube was then heated at the desired temperature in the NMR probe. Further addition of liquid (such as NEt_3 and MeOH) was performed by injecting the desired amount with a syringe to a depressurized NMR tube cooled at 193 K. A similar procedure was followed for the addition of the solid compounds. In this case the solution to be injected was prepared by solubilising the solid in a little vial cooled at 193 K under CO or Ar atmosphere using a small part of the solution already present in the tube as solvent. In both cases the resulting NMR tube was immediately pressurized at the desiderate pressure at 193 K.

The multicomponent systems studied and the ^1H and $^{31}P\{^1H\}$ NMR data of **I**, **II**, **III** and other complexes/compounds identified in the NMR experiments are reported in Tables 1 and 2, respectively.

2.4. Carbonylation of **I** in MeOH–NEt_3

0.1 mmol of **I** dissolved in 2 mL of MeOH–NEt_3 ($Pd/N = 1/6$) was treated with CO at 273 K. The solution, initially light brown, turned orange–red in a few minutes and, at the same time, a precipitate was formed. After 20′, neither DMO nor DMC were detected by GC. The NMR and IR spectra of the solid recovered after filtration (40 mg) showed the presence of $[Pd(CO)(PPh_3)]_3$ and **III**. Upon adding cold water to the filtrate, a white solid was precipitated (8 mg), identified as **II**.

2.5. Oxidative carbonylation of MeOH using **I**, **II**, and **III** as catalyst precursors

In a glass bottle equipped with a syringe cup for sampling, $6.0{\cdot}10^{-2}$ mmol of precursor and 6 mmol of BQ were added to 5 mL of dry MeOH, previously saturated with CO at 298 K under a flux of the same gas. The bottle was quickly pressurized at 0.3 MPa. After 1 h, NEt_3 or PPh_3 were added ($Pd/N = 1/2$, $Pd/addedPPh_3 = 1/2$). Samples were withdrawn and analyzed by CG every 30′ for a period of 2 h. The results are reported in Table 3.

3. Results and discussion

3.1. Reactivity of I

I reacts with CO at 193 K giving an unidentified species ($^{31}P\{^1H\}$ 23.01 ppm), which reacts with MeOH to yield **II**, which is transformed into **III** upon addition of NEt_3 (Table 1, system 1.1; Supporting information, Fig. S1). These results have already been reported [8]. **II** is formed also in the presence of BQ (Table 1, system 1.2). Above 313 K, **III** begins to be unstable, at 333 K decomposition to palladium metal is evident, accompanied with the formation of DMO and DMC in approximately equal amounts, 15% of each one.

In another experiment, **I** was treated with BQ and PPh_3 at 193 K and then CO was admitted (Table 1, system 1.3; Supporting information, Fig. S2). There was formation of $[Pd(BQ)(PPh_3)_2]$ [5,6], no other Pd(0) complex was formed. All PPh_3 disappeared because of the reaction with excess of BQ forming "betaine" [4–6]. At 298 K the NMR spectra did not change significantly, neither DMO nor

Table 1
Multicomponent systems studied by NMR spectroscopy.

Designation	System
1.1	**I** + (CO) + (MeOH) + ($8NEt_3$)
1.2	**I** + (MeOH, 5BQ, CO)
1.3	**I** + (MeOH, $6PPh_3$, 10BQ) + (CO)
1.4	**I** + (MeOH, $6NEt_3$, 10BQ) + (CO)
2.1	**II** + (MeOH, $1PPh_3$, CO) + ($8NEt_3$)
2.2	**II** + (MeOH, $1PPh_3$, 10BQ, CO)
2.3	**II** + (MeOH, $6PPh_3$, 10BQ, CO)
3.1	**III**+(MeOH, CO)+(1TsOH) + (1TsOH) − (CO)
3.2	**III**
3.3	**III** + (CO)
3.4	**III** + (5 BQ, CO) + (MeOH)

Note: the components that were mixed or added together are in brackets; the value near the component represents the equivalent with respect to Pd; MeOH 10% in volume with respect to CD_2Cl_2. CO in all cases 0.4 MPa.

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