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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.

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

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 di-carbomethoxy 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 $5\cdot10^{-3}$ 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, $6.0\cdot10^{-2}$ 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.

Table 2
Relevant ^{1}H and ^{31}P{^{1}H} NMR data of **I**, **II**, **III** and other compounds identified during the NMR experiments.

Compound	δ ^{1}H NMR [ppm]	δ ^{31}P{^{1}H} NMR [ppm]
cis-[Pd(TsO)$_2$(PPh$_3$)$_2$] (**I**)	7.48–6.99 (m, 38H, Ar) 2.28 (s, 6H, CH$_3$–TsO)	38.3 (s)
trans-[Pd(COOMe)(OTs)(PPh$_3$)$_2$] (**II**)	7.61–6.67 (m, 38H, Ar) 2.36 (s, 3H, COOMe) 2.19 (s, 3H, CH$_3$–TsO)	18.9 (s)
trans-[Pd(COOMe)$_2$(PPh$_3$)$_2$] (**III**)	7.68–7.37 (m, 30H, Ar) 2.55 (s, 6H, COOMe)	21.76 (s)
[Pd(OTs)(PPh$_3$)$_3$](TsO)	7.71–7.01 (m, 53 H, Ar) 2.34 (s, 6 H, CH$_3$–TsO)	35.3 (t, 1P); 31.1 (d, 2P); J_{P-P} = 13.2 Hz
[Pd(COOMe)(PPh$_3$)$_3$](TsO)	7.61–6.67 (m, 38H, Ar) 2.33 (s, 3H, CH$_3$–TsO) 1.91 (s, 3H, COOMe)	19.9 (d, 2P); 15.7 (t, 1P); J_{P-P} = 39.2 Hz
BQ	6.80 (s, 4H, CH)	
H$_2$BQ	6.65 (s, 4H, CH) 9.00 (brs, 2H, OH)	
DMC	3.73 (s, 6H, CH$_3$)	
DMO	3.89 (s, 6H, CH$_3$)	
PPh$_3$–BQ adduct		22.3, 16.4 (s)[a]
[Pd(COOMe)(OMe)(PPh$_3$)$_2$]	2.52 (s, 3H, COOMe) 3.25 (brs, 3H, OMe)	19.7 (s); 20.3 (s)[a]
[Pd(CO)(PPh$_3$)]$_3$		28.5 (s)
[Pd(CO)(PPh$_3$)$_3$]		22.6 (s)[a]
[Pd(BQ)(PPh$_3$)$_2$]		32.9 (s)[a]

NMR spectra were taken in CD_2Cl_2, data at 195 K. Abbreviations: s, singlet; d, doublet; t, triplet; dt, doublet of triplet; m, multiplet; dt, doublet of triplet; m, multiplet; brs, broad singlet.
[a] In CD_2Cl_2/MeOH 10%.

DMC were formed at 333 K. [Pd(BQ)(PPh$_3$)$_2$] was formed at 193 K from **I** and BQ also in the presence of NEt$_3$ (Table 1, system 1.4).

These results can be summarized as follows. **II** is formed only in the absence of a base, otherwise Pd(0) is formed. **III** is formed only through **II** and after addition of a base. Betaine acts as a base because of the presence of the Ar–O$^-$ moiety. In fact, it reacts with an acid giving a phosphonium salt [4].

The fact that Pd(0) is formed when the base is present before CO is admitted can be rationalized as follows. The presence of the base and MeOH could lead to a methoxy-palladium species and, *via* β-elimination, to a palladium hydride [17], unstable in the reaction conditions [18].

It should be noticed that the NMR experiments were carried out with MeOH diluted in CH_2Cl_2. We have found that in MeOH with dissolved NEt$_3$, in the absence of CD_2Cl_2, **I** reacts with CO (0.2 MPa) at 273 K to give [Pd(CO)(PPh$_3$)]$_3$ [19] together with both **II** and **III**. These results show that in MeOH the carbomethoxy complexes are formed even when NEt$_3$ is present before the admission of carbon monoxide, at difference of what observed in a NMR tube in which MeOH in diluted with CD_2Cl_2. Thus the concentration of MeOH (and probably also the polarity of the medium) plays an important role in directing the reactivity.

Table 3
Effect of time and base on the activity of the oxidative carbonylation reaction toward DMO using **I**, **II** and **III**.

Time [h]	**I**	**II**	**III**
	TON_{DMO}	TON_{DMO}	TON_{DMO}
0.5	0	5	6
1	0	10	14
1.5	11[a] or 9[b]	26[a]	30[a]
2	21[a] or 20[b]	37[a]	39[a]

Operative conditions: [Pd] = $1.2\cdot10^{-2}$ mol/L, Pd/BQ = 1/100, P_{CO} = 0.3 MPa, 298 K, anhydrous MeOH, 5 mL.
[a] NEt$_3$ (Pd/NEt$_3$ = 1/2), added after 1 h of reaction.
[b] PPh$_3$ (Pd/PPh$_{3\ added}$ = 1/2), added after 1 h of reaction. $TON_{DMO} = mol_{DMO}/mol_{Pd}$.

3.2. Reactivity of *II*

At 193 K, **II** reacts with PPh$_3$ and CO (Table 1, system 2.1) to give [Pd(COOMe)(PPh$_3$)$_3$](TsO) (Table 1, system 2.1; Supporting information, Fig. S3). Only with the subsequent addition of NEt$_3$ further reactions occur: a PPh$_3$ ligand is displaced from the coordination to Pd(II) and carbon monoxide and methanol interact giving **III**. This complex is stable up to 298 K, but at 313 K (better at 333 K) it decomposes with formation of [Pd(CO)(PPh$_3$)$_3$] [19], *trans*-[Pd(COOMe)(OMe)(PPh$_3$)$_2$] and of DMO and DMC (*ca.* 15% each). For the identification of the methoxy complex see below on the reactivity of **III**.

Therefore, as shown in Scheme 1, starting from both **I** or **II**, the dicarbomethoxy complex **III** is formed only after the addition of NEt$_3$ (see also Table 1, system 1.1). When the monocarbomethoxy complex **II** is formed from **I**, one equivalent of TsOH is also formed, so that one equivalent of acid is present before the addition of the base. In the absence of the base, the acid prevents the formation of the dicarboxy complex **III**. As a matter of fact, **III**, in the presence of one equivalent of acid, is unstable and gives the monocarbomethoxy complex as reported below (Table 1, system 3.1). The reason why it is necessary to add a base in order to obtain **III**, is described below.

The reactivity of **II** has been studied also with BQ, under conditions close to those of catalysis, except for the presence of NEt$_3$. A CD_2Cl_2/MeOH solution of **II**, PPh$_3$ and BQ was pressurized with CO at 193 K (Table 1, system 2.2). As shown in Fig. 1, **II** reacts immediately with CO and MeOH to give **III**, which starts decomposing at 298 K, giving 20% of DMO. Only upon increasing the temperature up to 333 K, [Pd(BQ)(PPh$_3$)$_2$], [Pd(CO)(PPh$_3$)]$_3$ are formed together with *ca.* 1.5 equivalent of DMO, an amount larger than that of the starting complex. Thus catalysis is observed. Though not so high, the catalytic activity is significant considering that, in the absence of BQ, DMO is formed in 15% yield with respect to **III** (*cfr.* system 2.1).

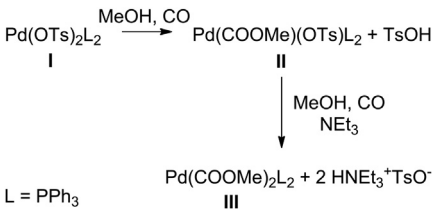
The same results have been obtained also by using a larger amount of added ligand (Table 1, system 2.3). In fact, in both cases PPh$_3$ does not interact with the complexes, but rather it is immediately consumed by the reaction with excess BQ forming "betaine".

It is noteworthy to point out that, in the presence of BQ, **III** already gives DMO at 298 K, together with the Pd(0) complexes [Pd(CO)(PPh$_3$)]$_3$ and [Pd(BQ)(PPh$_3$)$_2$], without formation of DMC and that catalysis is observed at 333 K. Whereas in the absence of BQ, **III** is stable up to 313 K with formation of DMO, DMC, *trans*-[Pd(COOMe)(OMe)(PPh$_3$)$_2$] and [Pd(CO)(PPh$_3$)$_3$]. Thus BQ modifies the reactivity of the system, in particular the reactivity of **III** toward the formation of oxalate.

3.3. Reactivity of *III*

A dicarbomethoxy species is likely to be involved in the product-forming step. Therefore, the study of the stability and reactivity of **III** is of paramount importance.

As reported above, the formation of **III** from **II** requires the addition of base. The following observations may explain the role of



Scheme 1. Formation of **II** and **III** from **I**.

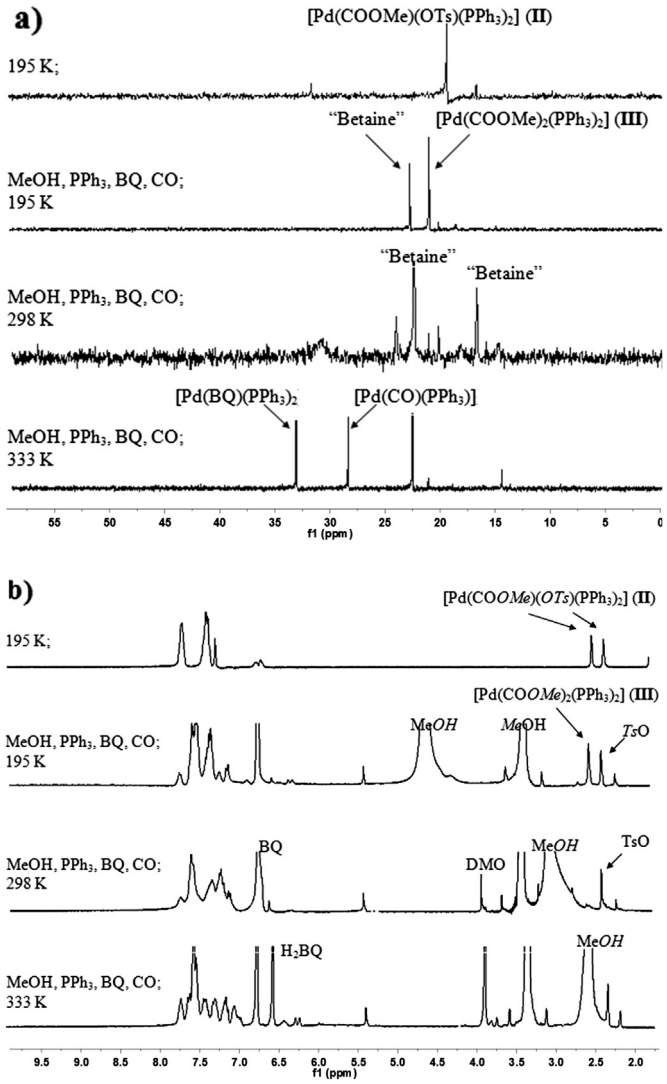
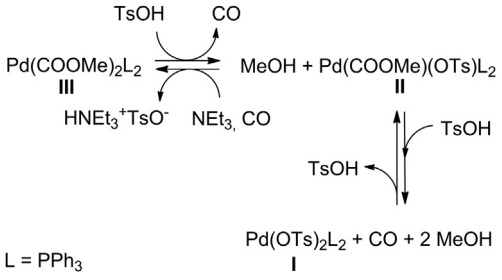


Fig. 1. Selected $^{31}P\{^{1}H\}$ (a) and ^{1}H (b) NMR spectra in CD_2Cl_2 on the reactivity of **II**, Table 1, system 2.2.

the base. When one equivalent of TsOH is added to **III** in CD_2Cl_2/MeOH under CO at 193 K (Table 1, system 3.1; Supporting information, Fig. S4), **II** is formed. This complex is stable up to 323 K even in the absence of CO. By addition of one more equivalent of TsOH, **II**, under pressure of CO, is also stable up to 323 K. However, at this temperature, by replacing of CO with argon, a slow conversion to **I** takes place. Considering that **I** reacts with MeOH and CO giving **II**, which is converted to **III** upon addition of NEt_3, the equilibria reported in Scheme 2 may be present in solution. These observations suggest that the base has the function of subtracting the acid



Scheme 2. Stability of **III** and **II** in the presence of TsOH.

formed in the reaction medium, thus eliminating the cause of instability of the dicarbomethoxy complex **III**.

In the experiment relevant to the system 2.1, the formation of a new complex tentatively formulated as *trans*-[Pd(COOMe)(OMe)$(PPh_3)_2$] is reported. This assignment is based on the following considerations. **III**, dissolved in CD_2Cl_2 under Ar (Table 1, system 3.2), starts decomposing at 313 K. Complete decomposition occurs at 333 K with formation of palladium metal and DMC. Decomposition is accompanied with the decreasing of the intensity of the signal of the Pd–COOMe moiety at 2.52 ppm from the $H(PPh_3)$/$H(COOCH_3)$ = 30/6 of **III** to 30/3. In addition, a new broad ^{1}H signal appears at *ca.* 3.25 ppm, close to that of the OMe ligand of *trans*-[Pd(X)(OMe)$(PPh_3)_2$] (X = C_6F_5, CCl=Cl_2) [20] (Fig. 2). DMC could form through an intramolecular migratory nucleophilic attack of the COOMe and OMe ligands of [Pd(COOMe)(OMe)$(PPh_3)_2$] (Scheme 3) [18].

In another experiment (Table 1, system 3.3) the stability of **III** was tested under CO starting form 193 K. **III** is stable up to 313 K, then it decomposes giving DMC and DMO (*ca.* 10% each) and Pd(COOMe)(OMe)$(PPh_3)_2$. At 333 K **III** is completely converted to the methoxy complex.

The reactivity of **III** with BQ was studied under conditions close to those of catalysis (Table 1, system 3.4; Supporting information, Fig. S5). In the presence of BQ and CO the complex is stable up to 298 K, at which temperature new signals appear attributable to

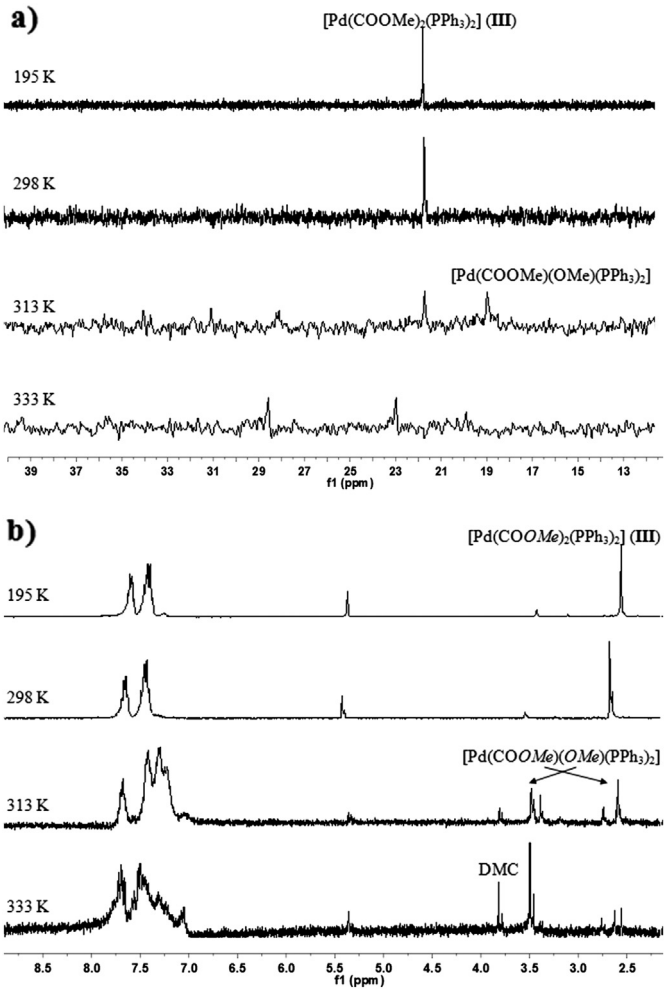
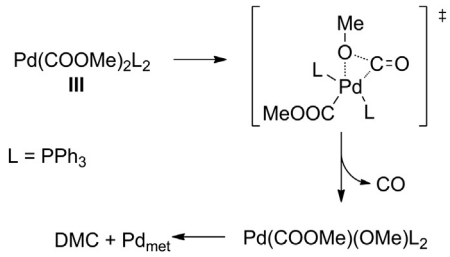


Fig. 2. Selected $^{31}P\{^{1}H\}$ (a) and ^{1}H (b) NMR spectra in CD_2Cl_2 on the reactivity of **III** in system 3.2.



Scheme 3. Putative pathway for the formation of [Pd(COOMe)(OMe)(PPh_3)$_2$] and DMC from **III**.

[Pd(BQ)(PPh_3)$_2$] and *trans*-[Pd(COOMe)(OMe)(PPh_3)$_2$] and formation of DMO becomes evident (*ca.* 10%). Although DMO is formed in a lower amount than that expected from the disappearance of the starting complex, it can be stated that BQ destabilizes the dicarbomethoxy complex and promotes both the reductive elimination of DMO as well as the decarbonylation of one Pd–COOMe moiety. At this point, in order to observe catalysis, MeOH (10% v with respect CD_2Cl_2) was added at 193 K, keeping the pressure of CO at 0.4 MPa. No change in the NMR spectra was observed up to 313 K, whereas at 333 K [Pd(BQ)(PPh_3)$_2$] and *trans*-[Pd(COOMe)(OMe)(PPh_3)$_2$] slowly disappeared with concomitant formation of **III**, DMO (*ca.* 1.2 ton) and of hydroquinone H_2BQ.

These results give significant insights into the basic aspects of the catalytic cycle, which are schematized as follows.

i) In order to observe catalysis it is necessary that complex **III** (Or any other carbomethoxy species, hereinafter for simplicity indicated as **III**) or [Pd(BQ)(PPh_3)$_2$] are formed.
ii) Complex **III** is stable up to 313 K.
iii) In the presence of BQ complex **III** is converted to [Pd(BQ)(PPh_3)$_2$] with formation of DMO at *ca.* 298 K. Thus, BQ promotes the formation of DMO, probably through a rearrangement of **III** into a species having the two carbomethoxy ligands in a closer mutual position, more favourable for the formation of the oxalate. This occurs at a temperature significantly lower than that necessary to observe catalysis.
iv) Catalysis occurs only at 333 K.
v) These evidences suggest that the reformation of **III** from [Pd(BQ)(PPh_3)$_2$] is likely to be the difficult step of catalysis.

3.4. Catalytic oxidative carbonylation of methanol using *I*, *II* and *III* as precursors

In order to demonstrate that **I**, **II** and **III** are effective catalyst precursors, the oxidative carbonylation of MeOH was performed in a (robust) glass bottle under relatively mild temperature conditions (298 K) under 0.3 MPa of CO in pure MeOH. Under these conditions, decomposition to Pd metal is avoided and catalysis occurs to a significant extent.

The results are reported in Table 3. In the absence of a base (NEt_3 or betaine), only **II** and **III** are active. It should be pointed out that when MeOH is diluted with CD_2Cl_2 in a NMR tube catalysis occurs at 333 K and at a lower rate (see Table 1, experiments 2.2 and 3.4). Catalysis is quite selective to DMO. No DMC is formed even when the monocarbomethoxy complex **II** is used, in spite of the fact that the TsO^- anion is weakly coordinating, so that the metal centre presents an easily available site for the coordination of MeOH, which in principle could lead to the carbonate.

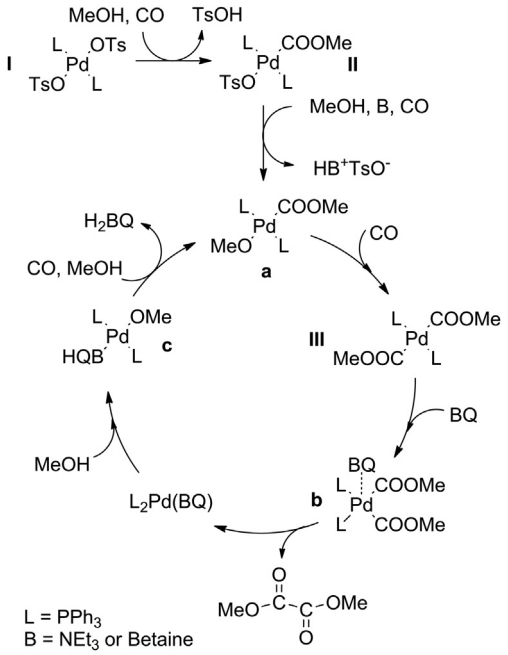
Since DMO is the only product, it is quite reasonable to suppose that the product-forming step involves a dicarbomethoxy species. By NMR spectroscopy, we observed that **III** is unstable at 298 K when in the presence of one equivalent of TsOH and gives **II** (*cfr.* system 3.1). Thus starting from **II**, a dicarbomethoxy species is formed at least to some extent in the glass bottle, enough to observe catalysis, in spite of the fact that when **III** is formed from **II**, TsOH is also formed. **III** is *ca.* 40% more active than **II** (TON 14 *versus* 10, during the first hour of catalysis and before adding a base), which might be due to the presence of TsOH when starting from the latter precursor. After 1 h, when NEt_3 is added, **II** and **III** show a significant increment in the catalytic activity.

The inactivity of **I** can be rationalized as follows. Before the addition of the base, **I** gives **II** and TsOH (*cfr.* reactivity of **I**). Further reaction with MeOH and CO to give **III** does not occur, because it would yield additional TsOH, which prevents its formation (*cfr.* system 3.1).

But, when after 1 h NEt_3 is added, catalysis occurs because **III** is formed (*cfr.* system 1.1). Catalysis is observed also when PPh_3 is used in place of NEt_3, because the base betaine is formed. In this case the role of the base is to neutralise the acid. In the first half an hour, the increment for **II** and **III** is practically the same, from 10 to 26 and from 14 to 30 mol of DMO/mol of Pd, respectively. This reinforces the above explanation on the retarding effect of TsOH. The base neutralizes TsOH and favours the formation of **III**, so that the two systems become equivalents and show the same increment of catalytic activity. In this case the role of the base is to neutralise the acid. In the first half an hour, the increment for **II** and **III** is practically the same, from 10 to 26 and from 14 to 30 mol of DMO/mol of Pd, respectively. This reinforces the above explanation on the retarding effect of TsOH. The base neutralizes TsOH and favours the formation of **III**, so that the two systems become equivalents and show the same increment of catalytic activity.

3.5. Proposed catalytic cycle

NMR evidences show that the reoxidation of [Pd(BQ)(PPh_3)$_2$] is likely to be the difficult step of the catalysis. It has been reported that the oxidation of Pd(0)–BQ complexes is acid-induced [21]. In the present case it has been shown that TsOH prevents the formation of **III**, through which DMO is likely to be formed. Not only, but a closer inspection of the activity of **III** reported in Table 3, shows that the addition of NEt_3 after 1 h catalysis speeds up the



Scheme 4. Proposed catalytic cycle for the formation of DMO.

catalytic activity. In fact, the TON before addition of the base is 14, whereas after addition is 39, with an increment of 25 units, almost double than that observed in the first hour.

Scheme 4 shows a simplified catalytic cycle and the route to **III** starting from **I** and **II**. As already reported above, precursor **I** reacts with MeOH and CO to give **II**, which, in the presence of the base, CO and MeOH is converted into **III**, the catalytic active palladium species, *via* the probable formation of intermediate **a**. BQ activates **III** to intermediate **b**, in which the two carbomethoxy ligands are in a closer position, in such away to favour their reductive elimination to DMO and [Pd(BQ)(PPh_3)$_2$]. The role of BQ as a promoter of reductive elimination from palladium complexes in C–C forming reactions is known [22,23]. The reoxidation of this Pd(0) complex occurs through the addition of MeOH to the PdBQ moiety with formation of a ((methoxy)*p*-hydroxyfenoxy)Pd(II) intermediate **c**. An intermediate of this type has been detected by NMR spectroscopy in the acid-promoted oxidation of Pd(0)–BQ complexes [21]. The subsequent reaction of **b** with CO and MeOH gives again **III**, *via* the intermediate **a**, and closes the catalytic cycle.

4. Conclusions

It has been demonstrated that not only the carbomethoxy complexes but also both BQ and the base play a role of paramount importance in the oxidative carbonylation of MeOH. In particular, it has been shown that BQ, in addition of being the oxidant, plays also an important role in promoting the reductive elimination of DMO from **III**.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.11.009.

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