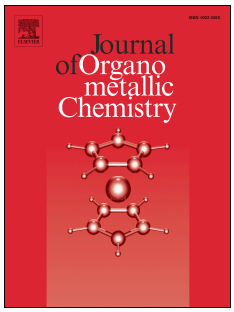
Accepted Manuscript



Efficient oxidative carbonylation of *i*PrOH to oxalate catalyzed by Pd(II)-PPh_3 complexes using benzoquinone as a stoichiometric oxidant

E. Amadio, L. Toniolo

PII: S0022-328X(14)00279-4

DOI: 10.1016/j.jorganchem.2014.05.033

Reference: JOM 18605

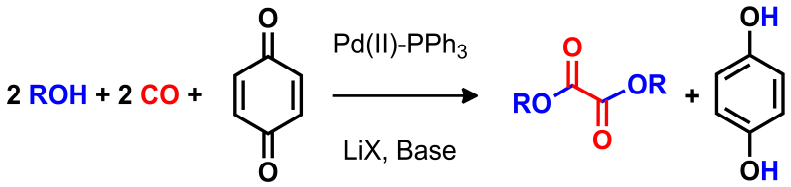
To appear in: *Journal of Organometallic Chemistry*

Received Date: 31 March 2014

Revised Date: 25 May 2014

Accepted Date: 27 May 2014

Please cite this article as: E. Amadio, L. Toniolo, Efficient oxidative carbonylation of *i*PrOH to oxalate catalyzed by Pd(II)-PPh_3 complexes using benzoquinone as a stoichiometric oxidant, *Journal of Organometallic Chemistry* (2014), doi: 10.1016/j.jorganchem.2014.05.033.



The catalytic system formed *in situ* from *trans*-[$PdBr_2(PPh_3)_2$]/Base/PPh_3/LiBr is highly active and selective in the oxidative carbonylation of *i*PrOH to the corresponding oxalate using benzoquinone as a stoichiometric oxidant. The influence of each component the catalytic system is discussed. A catalytic cycle is proposed.

Efficient oxidative carbonylation of *i*PrOH to oxalate catalyzed by Pd(II)-PPh_3 complexes using benzoquinone as a stoichiometric oxidant

E. Amadio[#], L. Toniolo[*]

Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy

Abstract

The catalytic system *trans*-[$PdBr_2(PPh_3)_2$]/NEt_3/PPh_3/LiBr is highly active and selective in the oxidative carbonylation of *i*PrOH to the corresponding oxalate using benzoquinone (BQ) as a stoichiometric oxidant. The oxalate is formed together with minor amounts of carbonate and acetone. The influence of each component the catalytic system is discussed together with the influence of the concentration of BQ, reaction time, temperature and CO pressure. NEt_3 neutralizes the acid released in the catalytic cycle, thus favouring the formation of a dicarboalkoxy intermediate. Added PPh_3 reacts with bezoquinone giving betaine, which is a base that contributes to a further enhancement of the catalytic activity. The Br^- anion might coordinate the Pd(0) which is formed in the product forming step thus stabilizing it against decomposition and making easier its reoxidation and reentering in the catalytic cycle. The catalytic activity depends only slightly on the concentration of BQ,

[#] Present address: Department of Chemical Sciences, University of Padua, via Marzolo 1, Padua, Italy

[*] Corresponding author. E-mail: toniolo@unive.it. Fax +39 (0)41 234 8517

Abbreviations : **O**, diisopropyl oxalate; **C**, diisopropyl carbonate; **A**, acetone.

suggesting that either uncoordinated BQ is not involved in the slow step of the catalytic cycle or that BQ is strongly coordinated in this the species. The catalytic activity toward oxalate increases upon increasing the concentration of NEt_3, and of PPh_3, whereas the selectivity toward carbonate and the formation of acetone remain practically constant. The increase of the pressure of CO has a similar effect, except that the formation of acetone is suppressed. It is suggested that at relatively high pressure of CO, a pentacoordinated species may be formed so that there is no place for any interaction between palladium and the C-H bond before the β-H elimination. Instead there is a nucleophilic intrasphere attack of the alkoxy ligand onto a CO ligand. After catalysis the precursor *trans*-$[PdBr_2(PPh_3)_2]$ has been detected, together with *trans*-$[PdBr(COO\textit{i}Pr)(PPh_3)_2]$ and $[Pd(BQ)(PPh_3)_2]$. PPh_3 remains coordinated to the palladium centre during catalysis. A BQ- and halides-assisted catalytic cycle is proposed. In this cycle, the reoxidation occurs though the release of a proton from an ammonium salt or a phosphonium salt, which are formed during the catalysis, with reformation of the catalyst precursor.

Keywords: Oxidative carbonylation, Isopropanol, Disopropyloxalate, Palladium(II)

1. Introduction

Alkyl oxalate is formed from an alkanol and CO in the presence of a Pd(II) salt, which is reduced to Pd metal [1,2]. When the reaction is carried out with Pd(II)-phosphine complexes, Pd(0)-phosphine complexes are formed [2-4]. To make the reaction catalytic, an oxidant must be used, such as molecular oxygen, redox couples of copper, iron, manganese, vanadium, organic nitrites, BQ or a combination of them [5-8]. The use of BQ is attractive because it avoids the co-formation of water, which causes consumption of CO and

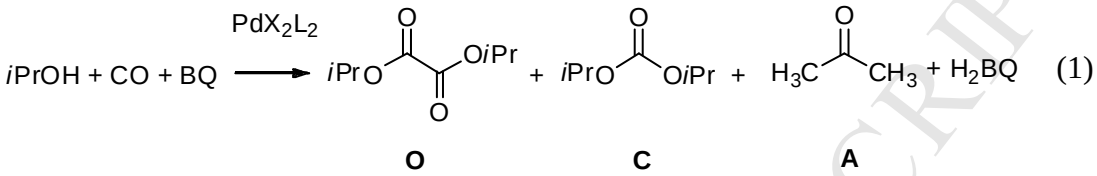
deactivation of the catalyst and it can be recycled after reoxidation of hydroquinone which is formed along with the desidered oxalate [9].

Catalysis undergoes through the formation of Pd-COOR species. Recently, the use of $[Pd(COOMe)_nX_{2-n}(PPh_3)_2]/NEt_3/PPh_3$, (n = 0, 1, 2; X = AcO, Cl, NO_2, NO_3, TsO) for the catalytic oxidative carbonylation of MeOH using BQ as an oxidant has been briefly reported [10]. Even under relatively mild temperature conditions (338 K), some decomposition to Pd metal occurred. In addition, a consumption of BQ higher than that expected was observed [10]. BQ could have been subtracted through the formation of an insoluble solid produced by BQ polymerisation promoted by a PPh_3-BQ adduct formed in *situ* [8]. Another BQ consuming reaction could have been the oxidation of MeOH to formal, which in turn can give rise to many derivatives (methyl hemi-formal and di-formal, formal oligomers, methyl formate, 4-hydroxyphenyl formate, pitches) [11]. However, formal and its derivatives were not detected. For these reasons it was not possible to give an order of activity in relation to the nature of X.

More recently, an NMR mechanistic study on the selective oxidative carbonylation of MeOH to the corresponding oxalate has been taken using the catalyst precursors $[Pd(COOMe)_n(TsO)_{2-n}(PPh_3)_2]$ (n = 0, 1, 2), which are rather reactive even under relatively mild conditions [12]. The basic steps of the catalysis have been identified. The role of the base has been elucidated, together with that of BQ, which enhances the reactivity of the dicarbomethoxy complex (n = 2) and directs the catalysis toward the oxalate selectively.

Subsequent preliminary experiments using *trans*-$[PdX_2(PPh_3)_2]$ (X = Cl, Br) in *i*PrOH showed that the mass balance between BQ, H_2BQ and the products (diisopropyl oxalate (**O**), diisopropyl carbonate (**C**) and acetone (**A**), (reaction (1)) was reasonably well respected. Acetone does not give rise to any derivative in a significant amount and is easily quantifiable by GC analysis. Moreover, decomposition to Pd metal did not occur even under relatively severe conditions (363 K, 9.0 MPa of CO, 2 h). This prompted us to further investigate the

catalysis in *i*PrOH. The choice of using a *sec*-alkanol was also decided for two more reasons: i) the formation of the corresponding ketone could have given us further insights on the formation of the products, and ii) would allow us to find the conditions to reduce or eliminate the fomation of the ketone. The use of a tertiary alkanol would not be useful in the light of these two points. Hereafter, the results are presented and discussed.



2. Experimental section

2.1. Reagents

Carbon monoxide and ethene (purity higher than 99 %) were supplied by SIAD Spa (Italy). *i*PrOH, PPh_3, PhCN, NEt_3, LiCl, LiBr, LiI, H_2SO_4, BQ, CD_2Cl_2, $CDCl_3$, were purchased from Aldrich Chemicals. $Pd(AcO)_2$ and $PdCl_2$ were purchased from Chimet SpA (Italy). $CDCl_3$ was stored together with molecular sieves and under argon. BQ was recristallized from Et_2O. The other chemicals were used as received. *Trans*-$[PdCl_2(PhCN)_2]$, *trans*-$[PdX_2(PPh_3)_2]$ (X = Cl, AcO, TsO) were prepared according to literature procedures [13-16].

2.2. Instrumentation

IR spectra were recorded in nujol mull or in KBr on a Nicolet FTIR instrument mod. Nexus. NMR spectra were recorded on Bruker 300 MHz spectrometers. ^{31}P spectra were measured ^{1}H decoupled. All ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. ^{31}P signals were referenced to an 85 % aqueous solution of H_3PO_4. GC analysis was performed on: a) Hewlett-Packard Model 6890 chromatograph fitted with HP5, 30 m × 0.32 μm × 0.25 μm column (detector: FID; carrier gas: N_2, 0.7 mL/min; oven: 40 °C (3.5 min) to 250 °C at 15 °C/min). b) Hewlett-Packard Model 5890

Series II chromatograph fitted with 20 % Carbowax 20 M on 80-100 mesh Chromosob W, 1 m × 2.3 mm ID packed column (detector: FID; carrier gas: N_2; 25 mL/min; oven: 80°C).

2.3. Preparation of the complexes

2.3.1. Synthesis of trans-[$PdBr_2(PPh_3)_2$]

To a suspension of *trans*-[$PdCl_2L_2$] (0.10 mmol) in 5 mL of *i*PrOH/$CHCl_3$ (1/1) a solution of LiBr (2.4 mmol) and PPh_3 (0.2 mmol) in 5 mL of *i*PrOH was added under stirring at room temperature. After two hours, the solution was concentrated to half the volume and 5 mL of Et_2O was added. The microcrystalline solid was filtered off, washed several times with *i*PrOH and Et_2O and dried under vacuum. Yield: 96 %. Elem. anal. Calcd for $C_{36}H_{30}Br_2P_2Pd$: C, 54.68; H, 3.82; found: C, 53.61; H 3.92. NMR: ^{1}H 7.75-7.41 (m, 30H, Ph), $^{31}P\{^1H\}$ 23.2 (s).

2.3.2. Synthesis of cis-[$Pd(SO_4)(PPh_3)_2$]

To a 0.1 mmol of *trans*-[$Pd(OAc)_2(PPh_3)_2$] in 20 mL EtOH a slight excess of H_2SO_4 was added dropwise. After *ca*. 10 minutes a yellow solid precipitated. The suspension was stirred for 30 more minutes. After adding 20 mL petrol ether, the solid was collected on a filter, washed with H_2O, EtOH, petroleum ether and dried under vacuum. Yield 80 %. Elem. anal. Calcd for $C_{36}H_{30}O_4SP_2Pd$: C, 58.69, H, 4.08; found:C, 59.05; H, 4.06. NMR: ^{1}H 7.66-6.94 (m, 30H, Ph), $^{31}P\{^1H\}$ 35.0 (s).

2.3.3. Synthesis of trans-[$PdBr(COOiPr)(PPh_3)_2$]

A mixture of *trans*-[$PdBr_2(PPh_3)_2$] (0.1 mmol), PPh_3 (0.1 mmol) and NEt_3 (0.2 mmol) in 6 ml of *i*PrOH in a glass bottle, that was placed into an autoclave. The autoclave was purged wth CO and pressurized with 5.0 MPa at room temperature. After heating at 368 K for 4 h under stirring, the autoclave was cooled to room temperature and depressurized. The

microcrystalline product was separated by filtration, washed with the alkanol and dried under vacuum. Yield 82%. Elem. anal. Calcd for $C_{40}H_{37}BrO_2P_2Pd$: C, 59.49; H, 4.58; found: C, 58.99; H5.28. IR (KBr): 1665 cm^{-1} (ν_{CO}). NMR: ^1H 7.75-7.41 (m, 30H, Ph), 3.66 (m 1 H, OCH), 0.32 (d, 6 H, CH_3), $^{31}P\{^1H\}$ 20.04 (s).

2.4. Catalytic oxidative carbonylation of iPrOH

Typically, 5 mL of a solution of NEt_3 in anhydrous *i*PrOH was introduced into a *ca*. 20 mL glass bottle containing 10^{-3} mmol of catalyst precursor and the desired amount of ligand and BQ. The glass bottle was then placed into an autoclave of *ca*. 50 mL volume. The autoclave was first purged several times with CO, then pressurized and heated to the desired pressure and temperature. The solution was stirred with a magnetic bar. After the desired reaction time, the autoclave was rapidly cooled to 273 K and then slowly depressurized. The solution was analyzed by GC using *n*-undecane and toluene as internal standards.

3. Results and discussion

3.1. Influence of the counter anion on the activity and selectivity of $[PdX_2(PPh_3)_2]$

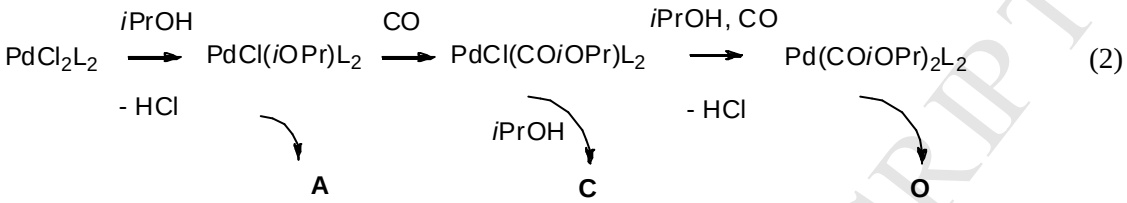
The influence of the anion on the activity and selectivity of the title complexes has been studied using precursors having X = TsO, AcO, Cl, Br; $X_2 = SO_4$ (Graph 1). At the end of catalysis, some decomposition to Pd metal was observed when X = TsO, AcO and $X_2 = SO_4$, thus the comparison can be made with only the other two precursors. The bromide one is more active and selective that the chloride one.

Insert **Graph 1**

3.2. Influence of NEt_3

The use of NEt_3 in combination with the precursor *trans*-$[PdCl_2(PPh_3)_2]$ has a beneficial effect on the catalytic activity toward **O** and only a minor effect on that toward **C** and **A**

(Graph 2). The formation of these products is schematized by reaction (2) and occurs with release of HCl. The base subtracts the acid and favours the formation of the dicarboxy intermediate, as it has been found for the synthesis of *trans*-[$Pd(COOMe)_2(PPh_3)_2$] from *trans*-[$Pd(COOMe)(TsO)(PPh_3)_2$] in MeOH under CO [9, 12].



(2)

Insert **Graph 2**

3.3. Influence of halides

The influence of X = Cl, Br, I on the activity and selectivity was studied using *trans*-[$PdCl_2(PPh_3)_2$] as catalyst precursor in combination with LiX. The results are reported in Table 1. The catalytic activity increases in the presence of LiBr up to a TOF = 228 h^{-1} for **O**, when Br/Pd = 24/1. The rate of formation of **C** is slightly influenced. Acetone and/or some derivatives such as ketals or mesityl oxide were not detected when Br/Pd > 6/1, thus the formation of **A** is completely inhibited. Cl^- has a minor effect, excess I^- depresses significantly the activity. These results may be accounted with a different coordinating capacity of the anions on the palladium centre. While the Cl^- ion is less binding than Br^-, I^- is too much, thus making its displacement by the reagents difficult [17]. A similar trend has been observed in the palladium catalysed carbonylation of aryl halides [18].

Insert **Table 1**

The fact that **A** does not form in the presence of added halide provides a further evidence that the halide plays an important role. The coordination of the halide may inhibit the β-hydride extraction of the Pd-OR species, responsible to the formation of **A** [19]**,** without compromising the formation of the Pd-OR and Pd-COOR moieties, because, at least when LiBr is used, the activity toward **O** and **C** is enhanced.

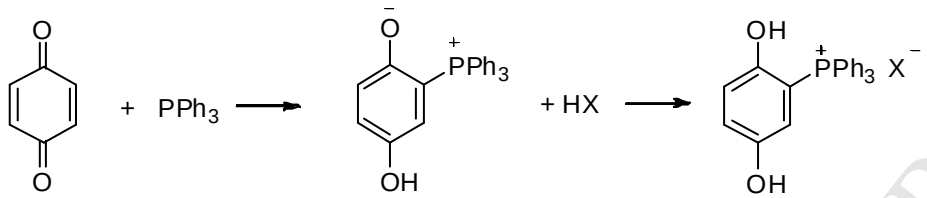
The following considerations may help to rationalize the promoting effect of Br^-. After catalysis the complexes *trans*-[PdBr(COOPr*i*)(PPh_3)$_2$] and [Pd(BQ)(PPh_3)$_2$] were detected (see *3.8.*). Amatore *et al.* and Neghishi *et al*. demonstrated that [Pd(0)(PPh_3)$_2$] is unstable in the absence of halide ions and that the partial or total saturation of the coordination shell of a zerovalent palladium complex by halide ions, with formation of anionic complexes Li[Pd(PPh_3)$_2$X] or Li_2[Pd(PPh_3)$_2X_2$], prevent decomposition [20,21]. Not only, but the negative charge of Pd(0) when coordinated by the anion enhances its reactivity toward oxidation [22-24]. In our case, Br^- could enhance the catalytic activity by stabilizing [Pd(BQ)(PPh_3)$_2$] as anionic species of the type [PdBr(BQ)(PPh_3)$_2$]$^-$ or [$PdBr_2$(BQ)(PPh_3)$_2$]$^{2-}$ and making their reoxidation easier without compromising the coordination of the reagents (see *3.9*) .

3.4. Influence of added PPh_3

The influence of added PPh_3 has been studied using the most active system reported in Table 1, *i.e.* entry 5. The catalytic activity significantly increases upon addition of PPh_3 and reaches a plateau when the P/Pd ratio (15-20)/1 (Graph 3). It is known that BQ gives an adduct with PPh_3 with formation of (2,5-dihydroxyphenyl)phosphonium (betaine) [25], which may act as a base because of the presence of an Ar-O^- moiety (reaction (3)) [26] . However, this cannot be the only effect of betaine, because Graph 2 shows that upon increasing the NEt_3/Pd ratio over *ca.* 10/1 the catalytic activity does not increase further. Thus, betaine might

favour catalysis by coordinating Pd(0) which is formed in the product-generating step (see *3.8*), like Cl^- and Br^- do.

Insert **Graph 3**



(3)

3.5. Influence of reaction time and of BQ

Upon increasing the reaction time from 1 to 3 h the TOF and the selectivity to **O** slightly decrease (Table 2). Since during the course of catalysis the concentration of BQ decreases considerably, it arises that the catalytic activity depends only slightly on the concentration of BQ. This suggests that either uncoordinated BQ is not involved in the slow step of the catalytic cycle or that BQ is strongly coordinated in the species involved in this step.

3.6. Effect of temperature

Upon decreasing the temperature, the activity decreases as expected, but the selectivity toward **O** increases (Table 2). Indeed, the apparent activation energy is higher for the formation of **C** (19.3 $Kcal \cdot K^{-1} \cdot mol^{-1}$) than for **O** (15.1 $Kcal \cdot K^{-1} \cdot mol^{-1}$) (Graph 4).

Insert **Table 2**

Insert **Graph 4**

3.7. Effect of the CO pressure

Graph 5 shows that upon increasing the pressure of CO the TOF toward **O** steadily increases, whereas that of **C** is little influenced. **A** is formed in low quantities at low CO pressure only (0.7 TOF at 1.3 MPa). This fact is rationalized as follows. Acetone is formed from a Pd-*i*OPr intermediate via β-H elimination [19]. At relatively high pressure of CO, this intermediate inserts CO giving a Pd-CO*i*OPr intermediate before the β-H elimination can occur (*cfr*. Graph 2), so that acetone is not formed. At relatively high pressure of CO, a pentacoordinated species may be formed so that there is no place for any interaction between palladium and the C-H bond before the β-H elimination. Instead there is a nucleophilic intrasphere attack of the alkoxy ligand onto a CO ligand.

Insert **Graph 5**

3.8. On the coordination of PPh_3 to palladium during catalysis

The highest catalytic activity has been obtained using the precursor *trans*-$[PdBr_2(PPh_3)_2]$ in combination with relatively large amounts of added PPh_3 and LiBr. Since BQ reacts with the ligand, the question is: does coordinated PPh_3 dissociates during the catalysis, so that the metal centre is no longer coordinated by this ligand? In order to give an answer, the catalytic activity of $PdBr_2$ was compared to that of *trans*-$[PdBr_2(PPh_3)_2]$. As shown in Table 3, $PdBr_2$ is significantly less active and selective than *trans*-$[PdBr_2(PPh_3)_2]$ (entries 1 and 3) also in the presence of added PPh_3 (entry 2). In this last case, the ligand was first added to a solution of BQ in *i*PrOH before adding $PdBr_2$, LiBr and NEt_3. With this procedure, PPh_3 was subtracted in advance by BQ, so that there was no free ligand left to react with $PdBr_2$ to give *trans*-$[PdBr_2(PPh_3)_2]$. In entry 2 the activity is higher than that of entry 1 probably because of the positive effect of betaine, that is formed from BQ and PPh_3 (see *3.4.*), but it is significantly different from that of entry 3. These results suggest that dissociation of the ligand does not occur to a significant extent during catalysis.

Insert **Table 3**

As a further demonstration, we carried out a reaction using a relatively large amount of *trans*-[$PdBr_2(PPh_3)_2$] in *i*PrOH at 363 K, under 8.5 MPa of CO, together with relatively small amounts of LiBr and BQ (Pd/Br/BQ = 1/4/5), hopefully making the recovery of the precursor after catalysis easier, yet ensuring catalysis to occur to some extent. GC analysis of the solution after 1 h showed the following: i) formation of only 0.1 mol of **O** per mole of Pd (**C** and **A** did not form); ii) most of the BQ was still present (*ca.* 4.8 BQ/Pd), thus the mass balance was reasonably respected. The solid recovered after filtration was recognized by IR and NMR as the starting complex *trans*-[$PdBr_2(PPh_3)_2$]. The $^{31}P\{^1H\}$ spectrum of the solution after reaction did not show any signal, indicating that no other complexes or betaine were present. It may be concluded that dissociation of the PPh_3 ligand from *trans*-[$PdBr_2(PPh_3)_2$] does not occur.

In order to favour catalysis the above experiment was repeated, but in the presence of NEt_3 (Pd/Br/NEt_3/BQ = 1/4/2/5). After 1 h reaction, GC analysis of the solution showed the presence of **O**, **C** and **A** (TOF 3.6, 0.1 and 1.0 h^{-1}, respectively) and of H_2BQ (*ca.* 4.3 H_2BQ/Pd). All BQ was consumed. Thus, also in this case the mass balance was reasonably respected. After concentration, the yellow solid recovered by filtration was recognized as a mixture of the precursor *trans*-[$PdBr_2(PPh_3)_2$], *trans*-[PdBr(COO*i*Pr)$(PPh_3)_2$] and [Pd(BQ)$(PPh_3)_2$] ($^{31}P\{^1H\}$ at 32.9 (s) in CD_2Cl_2 [12, 25]). By removing the solvent from the solution obtained after filtration, the pitchy residue that was left. The NMR of this residue dissolved in CD_2Cl_2 showed the presence of *trans*-[PdBr(COO*i*Pr)$(PPh_3)_2$], H_2BQ and of another unknown compound ($^{31}P\{^1H\}$at 33.7 ppm), but not that of betaine ($^{31}P\{^1H\}$ at 23.3 and 16.4 (s) ppm in CD_2Cl_2). Therefore, also during catalysis, dissociation of a PPh_3 ligand does not occur.

3.9. Proposed catalytic cycle

Three complexes were detected after catalysis, *i.e.* the precursor, *trans*-[PdBr(COO*i*Pr)(PPh_3)$_2$] and [Pd(BQ)(PPh_3)$_2$] (see *3.8.*). In addition, the formation of **O** is likely to occur *via* a [Pd(COO*i*Pr)$_2$(PPh_3)$_2$] intermediate [12]. Thus these complexes might be involved in the catalytic cycle.

Even the BQ plays an active role in the mechanism as the oxidant and also assisting the catalyst reactivity towards **O** formation. Indeed, it has been shown that in catalysis conditions, but in the absence of BQ, *trans*-[PdBr(COO*i*Pr)(PPh_3)$_2$] is stable for several hours. In fact, it is synthesized in high yield when the precursor is treated with CO in *i*PrOH in the presence of NEt_3 at 80-90 °C under 4.0-8.0 MPa of CO (see experimental). Whereas in the presence of BQ high catalytic activity toward **O** is observed. Thus, BQ modifies the reactivity of the monocarboxy complex and favours the formation of a dicarboxy intermediate and also the reductive elimination of **O**, since no dicarboxy species was detected after catalysis. [Pd(BQ)(PPh_3)$_2$] was detected also when all BQ was consumed, so it is rather stable.

All these evidences are in agreements with the already reported catalytic cycle for the oxidative carbonylation of MeOH to dimethyl oxalate [12]. In more detail, it was suggested a catalytic cycle in which the reoxidation of [Pd(BQ)(PPh_3)$_2$] complex may occur through the addition of MeOH to the PdBQ moiety with formation of a (MeO)(*p*-hydroxyphenoxy)Pd(II) intermediate. Similarly, this reoxidation and the catalytic cycle may occur also with *i*PrOH.

However, a further reaction mechanism could be here proposed taking into account the above reported halides effect (Scheme 1).

Insert **Scheme 1**

In particular, as mentioned in *3.3*, Br^- might coordinate this Pd(0) complex, with formation of anionic complexes of the type [PdBr(BQ)(PPh_3)$_2$]$^-$ or [$PdBr_2$(BQ)(PPh_3)$_2$]$^{2-}$, whose negative charge might making easier their reoxidation. Therefore, the reoxidation may

alternatively occur through release of a proton from BH^+Br^- with reformation of the catalyst precursor $PdBr_2(PPh_3)_2$, similarly to what proposed for palladium-benzoquinone catalyzed oxidation reactions [22,27]. Protonation of BQ of a (BQ)Pd(0) moiety has been found to occur in a redox reaction which yields Pd(II) and hydroquinone [28]. As already mentioned the formation of O from the monocarboxy intermediate might be a BQ assisted process in which this electron deficient olefin might coordinate to the metal centre forming a $[Pd(COOR)_2(PPh_3)_2]$·BQ adduct complex. However, this intermediate was not isolated or detected in solution and nor we could prepare it.

In order to give a further support to the proposed cycles and the essential role of BH^+Br^- we run the catalysis in *i*PrOH using $L_2Pd(COOR)_2$ as a precursor (R = OMe; all the efforts to isolate the complex with R = O*i*Pr failed). The results are shown in Table **4**. The first experiment was carried out in the absence of $Et_3NH^+Br^-$ whereas the other experiment was carried out in the presence of two equivalents of this salt, which are formed when starting from L_2PdBr_2 as a precursor. In both cases catalysis occurs to a significant extent, but with better performance when with the salt, though not as high as that observed in an experiment reported in 3.5., which is also reported in Table 4 (Entry 3) for a comparative purpose.

Insert **Table 4**.

4. Conclusions

Trans-$[PdBr_2(PPh_3)_2]$/NEt_3/PPh_3/LiBr is an efficient catalytic system for the oxidative carbonylation of *i*PrOH to the corresponding oxalate. Only minor amounts of carbonate and acetone are formed. The role of each component the catalytic system is discussed. During catalysis the $[Pd(PPh_3)_2]$ moiety does not dissociate the ligand. *Trans*-$[PdBr_2(PPh_3)_2]$, *trans*-

[$PdBr(COOiPr)(PPh_3)_2$] and [$Pd(BQ)(PPh_3)_2$] were detected after catalysis. A BQ- and halides-assisted catalytic cycle is proposed.

Acknowledgements

The financial support of MIUR (Rome) is gratefully acknowledged.

References

[1] M. Graziani, P. Uguagliati, G. Carturan, J. Organomet. Chem. 27 (1971) 275-278.

[2] F. Rivetti, U. Romano, J. Organomet. Chem. 174 (1979) 221-226.

[3] F. Rivetti, U. Romano, Chim. Ind. 62 (1980) 7-12.

[4] F. Rivetti, U. Romano, J. Organomet. Chem. 154 (1978) 323-326.

[5] D.M. Fenton, P. J. Steinwald, J. Org. Chem. 39 (1974) 701-704.

[6] A.M. Gaffney, J.J. Leonard, J.A. Sofranko, H.-N. Sun, J. Catal. 90 (1984) 261-269.

[7] S. Uchiumi, K. Ataka, T. Matsuzaki, J. Organomet. Chem. 576 (1999) 279-289.

[8] S.P. Current, J. Org. Chem. 48 (1983) 1779-1780.

[9] R.J. Radel, J.M. Sullivan, J.D. Hatfield, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 566-570.

[10] E. Amadio, G. Cavinato, A. Dolmella, L. Toniolo, Inorg. Chem. 49 (2010) 3721-3729.

[11] D.M. Pearson, R.M. Waymouth, Organometallics, 28 (2009) 3896-3900.

[12] E. Amadio, L. Toniolo, J. Organomet. Chem., 750 (2014) 74-79.

[13] J. R. Doyle, P.E. Slade, H.B. Jonassen, Inorg. Synth. 6 (1960) 216-219.

[14] J. M. Jenkims, J.C. Verkade, Inorg. Synth. 11 (1968) 108-111.

[15] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, J. Chem. Soc. 3632-3640 (1965).

[16] G. Cavinato, A. Vavasori, L. Toniolo, A. Dolmella, Inorg. Chim. Acta 357 (2004) 2737-2447.

[17] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533-3539.

[18] V. Calò, P. Giannoccaro, A. Nacci, A. Monopoli, J. Organomet. Chem. 645 (2002) 152-157.

[19] W. Clegg, G.R. Eastham, M.R.J. Elsegood, B.T. Heaton, J.A. Iggo, R.P.Tooze, R.Whyman, S. Zacchini, Organometallics 21 (2002) 1832-1840.

[20] C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc. 113 (1991) 8375-834.

[21] E. Negishi, T. Takahashi, K. Akiyoshi, J. Chem. Soc., Chem. Commun. (1986) 1338-1339.

[22] B.V. Popp, J.L. Thorman, S.S. Sthal, J. Mol. Catal. A: Chem. 251 (2006) 2-7.

[23] C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314-321.

[24] C. Amatore, A. Jutand, A. Suarez J. Am. Chem. Soc. 115 (1993) 9531-9541.

[25] V.R. Khabibulin, A.V. Kulik, I.V.Oshanina, L.G. Bruk, O.N. Temkin, V.M. Nosova, Yu.A. Ustynyuk, V.K. Bel'skii, A.I. Stash, K.A. Lysenko, M.Y. Antipin, *Kinet. Katal.* 48 (2007) 228-244.

[26] F. Ramirez, S. Dershowitz, J. Am. Chem. Soc. 78 (1956) 5614-5622.

[27] N. Decharin, S.S. Stahl, J. Am. Chem. Soc. 133 (2011) 5732-5735.

[28] H. Grennberg, A. Gogoll, J.-E. Backwall, Organometallis, 12 (1993) 1790-1793.

Table 1

Influence of the halide anions on the performance of *trans*-[$PdCl_2(PPh_3)_2$] in the oxidative carbonylation of *i*PrOH.

Entry	Pd/LiX [mol/mol]	Activity TOF [mol/(mol*h)]			Selectivity [%]		
		O	**C**	**A**	**O**	**C**	**A**
1	---	88	20	15	72	16	12
2	6 Cl	60	13	0	82	18	0
3	24 Cl	77	12	0	87	13	0
4	6 Br	125	31	0	80	20	0
5	24 Br	228	32	0	88	12	0
6	6 I	85	8	0	91	9	0
7	24 I	14	2	0	88	12	0

Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, Pd/PPh_3/NEt_3/BQ = 1/4/10/700, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa, T 363 K, 1 h.

Table 2

Influence of reaction time and temperature on the performance of *trans*-[$PdBr_2(PPh_3)_2$] in the oxidative carbonylation of *i*PrOH.

Entry	t [h]	T K	Activity TOF [mol/(mol*h)]			Selectivity [%]		
			O	**C**	**A**	**O**	**C**	**A**
1	1	363	455	45	0	91	9	0
2	2	363	386	44	0	90	10	0
3	3	363	370	40	0	90	10	0
4	2	343	120	10	0	92	8	0
5	2	323	28	2	0	93	7	0

Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, $Pd/PPh_3/NEt_3/LiBr/BQ$ = 1/22/10/24/1400, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa.

Table 3

Effect of added PPh_3 on the activity and selectivity of $PdBr_2$.

Entry	Catalyst	Pd/PPh_3 [mol/mol]	Activity TOF [mol/(mol*h)]			Selectivity [%]		
			O	**C**	**A**	**O**	**C**	**A**
1	$PdBr_2$	0	87	15	0	85	15	0
2	$PdBr_2$	22	170	18	0	90	10	0
3	$[PdBr_2(PPh_2)_2]$	22	455	45	0	91	9	0

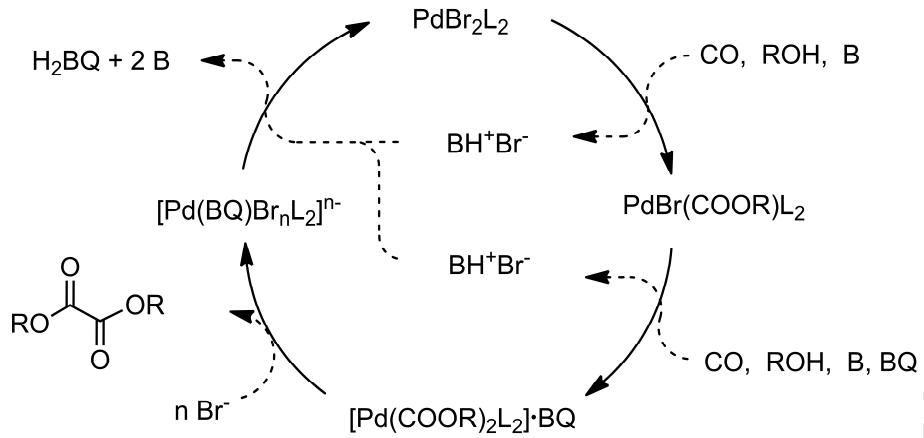
Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, Pd/NEt_3/LiBr/BQ = 1/10/24/1400, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa, T 363 K, 1 h.

Table 4

Activity of $[Pd(COOMe)_2(PPh_3)_2]$ with or without $BrNHEt_3$ compared to $[PdBr_2(PPh_3)_2]$ ones.

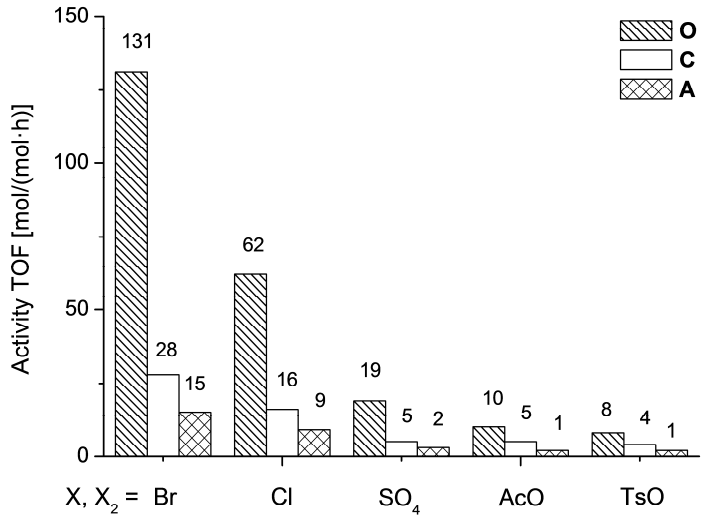
Entry	Complex	$BrHNEt_3$/Pd [mol/mol]	NEt_3/Pd [mol/mol]	LiBr/Pd [mol/mol]	Activity TOF [mol/(mol*h)]		
					O	**C**	**A**
1	$[Pd(COOMe)_2(PPh_3)_2]$	0	10	26	254	37	0
2	$[Pd(COOMe)_2(PPh_3)_2]$	2	8	24	361	50	0
3	$[PdBr_2(PPh_3)_2]$	0	10	24	455	45	0

Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, Pd/PPh_3/BQ = 1/22/1400, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa, T 363 K, 1 h.

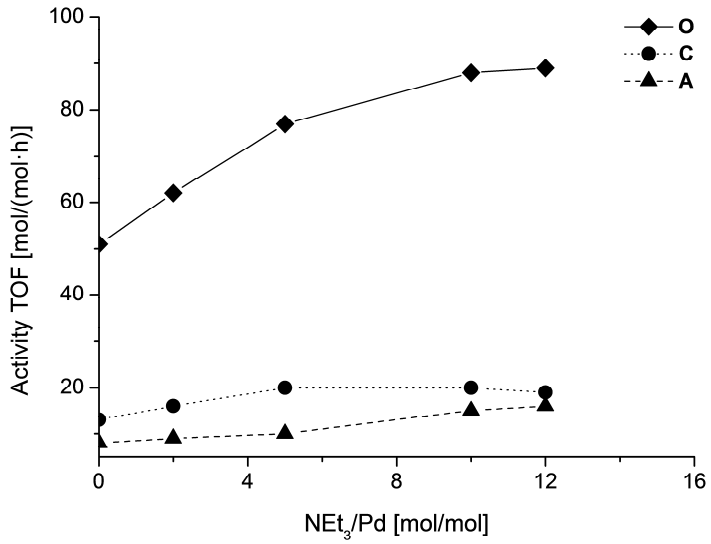


R= *i*Pr
B = NEt_3, Betaine
L = PPh_3

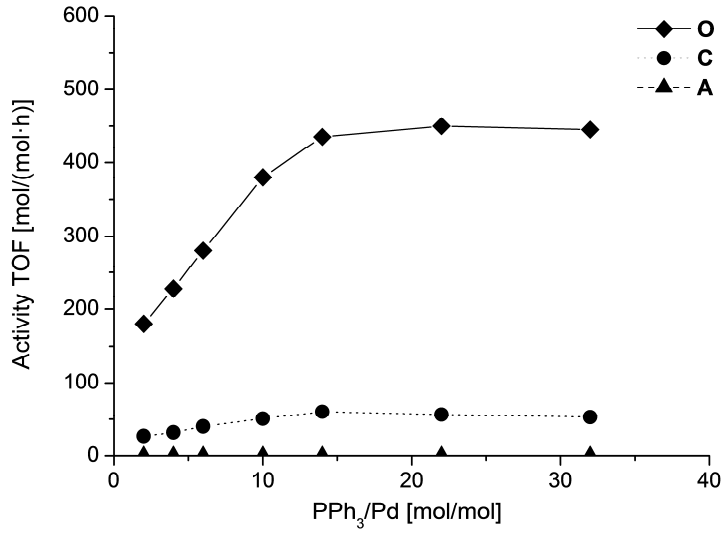
Scheme **1**. Simplified catalytic cycles.



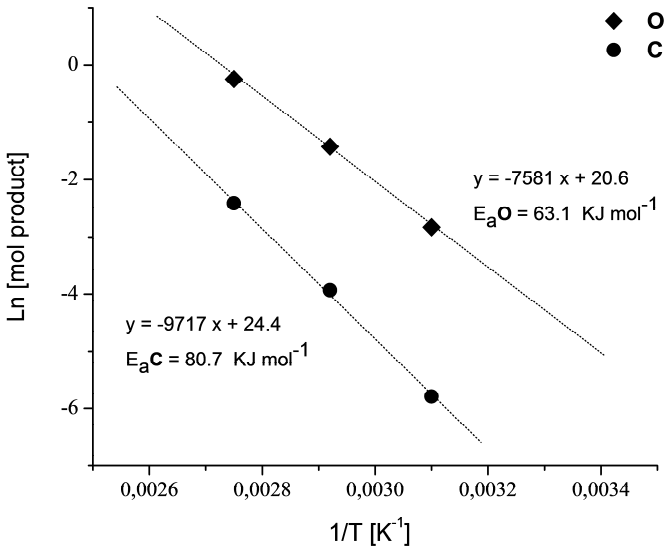
Graph 1. Influence of the anion on the performance of $[PdX_2(PPh_3)_2]$ in the oxidative carbonylation of *i*PrOH. Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, $Pd/PPh_3/NEt_3/BQ$ = 1/4/2/700, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa, T 363 K, 1 h.



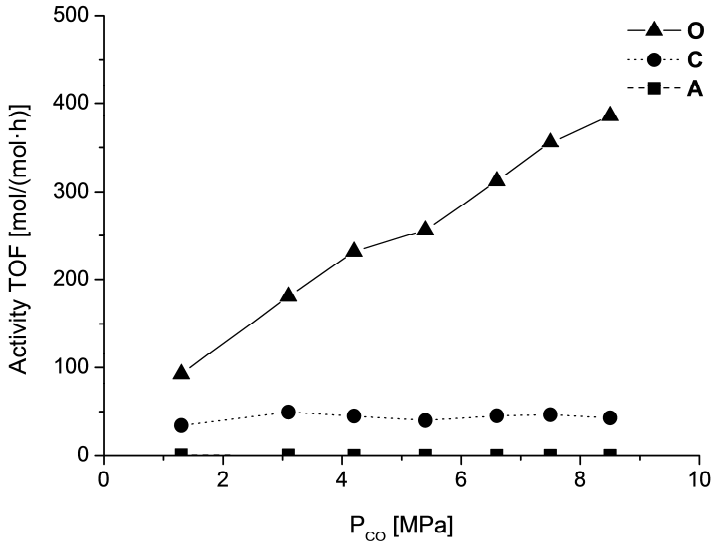
Graph 2. Influence of NEt_3/Pd molar ratio on the performance of *trans*-$[PdCl_2(PPh_3)_2]$ in the oxidative carbonylation of iPrOH. Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, Pd/PPh_3/BQ = 1/4/700, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa, T 363 K, 1 h.



Graph 3. Influence of PPh_3/Pd molar ratio on the performance of *trans*-[$PdBr_2(PPh_3)_2$] in the oxidative carbonylation of *i*PrOH. Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, Pd/NEt_3/LiBr/BQ = 1/10/24/1400, 5 mL anhydrous *i*PrOH, P_{CO} 8.5 MPa, T 363 K, 1 h.



Graph 4. Arrhenius plot. For the conditions see Table 2.



Graph 5. Influence of P_{CO} on the performance of *trans*-[$PdBr_2(PPh_3)_2$] in the oxidative carbonylation of *i*PrOH. Conditions: [Pd] = $2 \cdot 10^{-4}$ mol/L, Pd/PPh_3/NEt_3/LiBr/BQ = 1/22/10/24/1400, 5 mL anhydrous *i*PrOH, T 363 K, 2 h.

Research Highlights

- $PdX_2(PPh_3)_2$ is a catalyst precursor for the oxidative carbonylation of *i*PrOH
- benzoquinone is used as a stoichiometric oxidant
- NEt_3, PPh_3 and LiBr increase significantly activity and selectivity
- diisopropyl oxalate is formed with minor amounts of diisopropyl carbonate and acetone