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Oxidative carbonylation of ethene catalyzed by Pd(II)–PPh_3 complexes in MeOH using benzoquinone as stoichiometric oxidant

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ABSTRACT

The complexes $[Pd(COOMe)_nX_{2-n}(PPh_3)_2]$ (n = 0, 1, 2; X = TsO, OAc, ONO_2, Cl, Br), $[Pd(SO_4)(PPh_3)_2]$, $[PdCl_2(PPh_3)]_2$ and PdX_2 (X = Cl, Br, I) catalyze the oxidative ethene carbonylation in MeOH using benzoquinone (BQ) as stoichiometric oxidant. The main products dimethyl succinate (DMS) and dimethyl oxalate (DMO) are formed together with minor amounts of methyl propanoate and dimethyl carbonate. The formation of DMS unambiguously proves that ethene inserts into a Pd–COOMe bond. The influence of the CO/ethene ratio at constant total pressure and of the BQ/Pd ratio on the product distribution has been studied. Model reactions of a Pd-hydride with BQ, of trans-$[Pd(COOMe)(TsO)(PPh_3)_2]$ with ethene in the presence of BQ and of trans-$[Pd(COOMe)_2(PPh_3)_2]$ with BQ have been studied by $^{31}P\{^1H\}$ NMR. BQ consumes the Pd–hydride and directs the catalysis toward a Pd–COOMe initiator leading to DMS. In the catalysis to DMO, BQ is likely to favour the formation of a Pd–$(COOMe)_2$ species having the two carbomethoxy ligands in vicinal position such to favour the elimination of the product. The proposed catalytic cycles for the formation of the products are discussed.

1. Introduction

The carbonylation of ethene catalyzed by Pd(II)–phosphine complexes in MeOH as a solvent yields different products. As a general rule, with a monodentate phosphine, such as for example PPh_3, the main product is methyl propanoate (MP), whereas with a chelating diphosphine, such as 1,3-bis(diphenylphosphino)propane (dppp), polyketones (PKs) are formed [1–9]. An important exception occurs using a Pd(II)–(dtbpx)complex (dtbpx = 1,2-bis(di-*t*-butyl)phosphinomethyl]benzene), in which case MP is produced at a high rate and selectivity [10–13].

Catalysis to MP can occur via the so called "Pd–H" mechanism and/or the "Pd–COOMe" one. The same is true for the formation of PKs having keto (K) and ester (E) end groups. With monophosphine catalysts the "Pd–H" mechanism is the most likely to be operative. This conclusion is based on: (i) reactivity studies of trans-$[Pd(COEt)X(PPh_3)_2]$ and of trans-$[Pd(COOMe)X(PPh_3)_2]$ (X = Cl, TsO), which have been isolated after catalysis using the precursor $[PdX_2(PPh_3)_2]$ and that are related to the "Pd–H" or the "Pd–COOMe" mechanism, respectively, (ii) the promoting effect of a hydride source, such as H_2, H_2O and the acid HX, (iii) the instability of the carbomethoxy complex when treated with HX, and (iv) the products of phosphine degradation side reactions such as $EtPPh_3^+$ and $EtCOCH_2CH_2PPh_3^+$. In addition, it was found that ethene does not insert into the Pd–COOMe bond of trans-$[Pd(COOMe)X(PPh_3)_2]$ (X = Cl, TsO, HSO_4) and that catalysis is prevented in the presence of a base which favours the formation of the carbomethoxy complexes [14–21].

However, using the diphosphine complex $[Pd(H_2O)_2(dppf)](OTs)_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) in combination with relatively large amounts of TsOH (up to 160 equivalents), it has been found that catalysis occurs with formation of MP, methyl 4-oxohexanoate and the diesters dimethyl succinate (DMS) and dimethyl 4-oxoheptanoate in addition to heavier alternating CO–ethene KE or EE oligomers [22]. The formation of the diesters unambiguously proves that Pd–COOMe initiators play an important role even in the presence of relatively large amounts of TsOH, and that ethene inserts into this bond.

With the precursor $[Pd(TsO)_2(dppb)]$ (dppb = 1,3-bis(diphenylphosphino)butane) it was observed that diesters were formed at a higher rate when carrying out the catalysis in the presence of benzoquinone (BQ) [23]. It was suggested that BQ is able to convert $Pd–H^+$ initiators into $Pd–COOMe^+$ initiators through reaction (1) [2,23].

$$(P\text{-}P)Pd\text{-}H^+ + BQ + MeOH + CO \longrightarrow (P\text{-}P)Pd\text{-}COOMe^+ + H_2BQ \quad (1)$$

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This prompted us to carry out the carbonylation of ethene in MeOH in the presence of BQ using Pd(II)–PPh_3 precursors in order to establish whether catalytic reactions involving the insertion of ethene into a Pd–COOMe bond could occur. Hereafter, we present and discuss the results.

2. Experimental

2.1. Reagents

Carbon monoxide and ethene (purity higher then 99%) were supplied by SIAD Spa (Italy). MeOH, NEt_3, PPh_3, BQ and CD_2Cl_2 were purchased from Aldrich Chemicals. NEt_3 and the solvents were of commercial grade and used without further purification. BQ was purified before use (from EtOH). PdX_2 (X = Cl, Br, I, AcO) were generous gift of Chimet (Italy). The following complexes were prepared according to methods reported in literature: cis-$[PdX_2(PPh_3)_2]$ (X = TsO, NO_3, COOMe) [18,24], cis-$[Pd(SO_4)(PPh_3)_2]$ [25], trans-$[PdX_2(PPh_3)_2]$ (X = AcO, Cl, Br) [26,27], trans-$[Pd(COOMe)X(PPh_3)_2]$ (X = Cl, Br, TsO, NO_3, AcO) [16,19,24,28–30].

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 with reference to 85% H_3PO_4 as an external standard, respectively. GC analysis was performed using a HP 4890 instrument, with Agilent Chem Station, equipped with HP1 column, 10 m, 0.53 mm, film 2.65 μm; oven: 45–180°, 5 °C/min. Mass spectra were taken using a Thermo trace DSQ instrument, equipped with a thermo TR-SMS column, 30 m, 0.25 mm, film 0.25 μm, initial temperature 40 °C, final temperature 300 °C, 10 °C/min.

2.3. Oxidative carbonylation of ethene

The catalytic reactions have been carried out by using a stainless steel autoclave of ca. 80 mL provided with a magnetic stirrer. 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 Pyrex bottle placed inside the autoclave.

In a typical experiment 9.9 mg of cis-$[Pd(TsO)_2PPh_3)_2]$ (10^{-2} mmol), 108 mg of BQ (1 mmol) were dissolved in 5 mL of MeOH in a Pyrex bottle placed in a 80 mL autoclave. The autoclave was purged by pressurizing it with a mixture of CO and ethene (1/1, ca. 3 bar) and depressurizing it to atmospheric pressure (this cycle was repeated 5 times at room temperature). Then the autoclave was charged with 50 atm of CO and ethene (1/1). The autoclave was heated to 55 °C and maintained at this temperature for 1 h. Then the autoclave was rapidly cooled to 5–10 °C and the gas was carefully released. The liquid was analyzed by GC.

3. Results and discussion

3.1. Catalytic precursors, run conditions and products

Usually, the carbonylation of ethene in MeOH catalyzed by Pd(II)–PPh_3 complexes is carried out in the presence of an acid and an excess of ligand. This allows the catalysis to be carried out at a temperature as high as 100 °C without decomposition to inactive Pd metal [15,20]. In the present case, experiments were carried out in the absence of an acid, because it does not favour the formation of Pd–COOMe species.

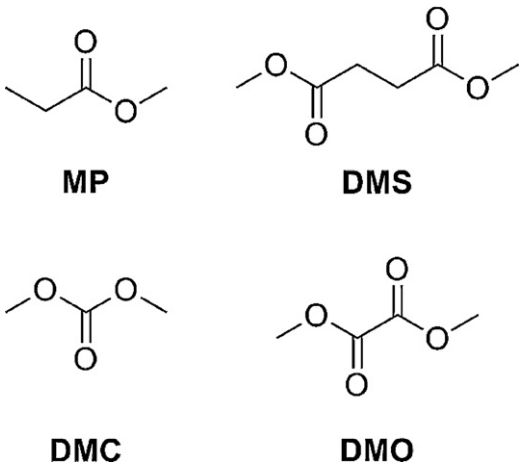
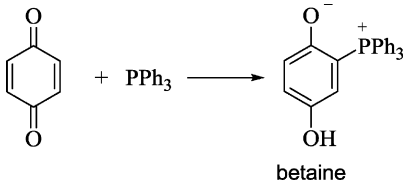


Fig. 1. Products of the catalysis.

That being stated, the precursors, the conditions used and the results for the oxidative carbonylation of ethene are reported in Table 1. Experiments were carried out at 55 °C in order to ensure a reasonable compromise between activity and stability of the catalytic system. The products obtained are shown in Fig. 1. The table also reports in which experiment some decomposition to Pd metal has been observed after the catalysis.

Preliminary experiments were carried out under conditions that favour the formation of Pd–COOMe species, i.e. in the presence of NEt_3 and of NEt_3–PPh_3. The latter experiment was carried out in order to make a comparison with the oxidative carbonylation of MeOH carried out in the presence of the base and of PPh_3, but in the absence of ethene. DMO was selectively formed [24]. In the present study, i.e. in the presence of ethene, there was formation of DMC and of DMO, but not of any diester incorporating ethene. The two experiments give practically the same result (runs 1 and 2). Decomposition to Pd metal occurred. The use of PPh_3 does not stabilize the catalyst, because the ligand is consumed in a reaction with BQ which yields betaine [31,32].



(2)

Instead, in the absence of NEt_3 and of PPh_3 there was formation of DMS (run 3). The same precursor in the absence of BQ promotes the formation of MP, which is accompanied by only trace amounts of DMS (run 4). As already mentioned, MP can be formed via both the "Pd–COOR" and the "Pd–H" mechanisms, but DMS can be formed only via the "Pd–COOMe" mechanism. Therefore, experiment 3 proves that in the presence of BQ the insertion of ethene into a Pd–COOMe bond can occur even with this monophosphine-based catalyst.

The formation of DMO, DMC and DMS is schematized below. For the formation of MP see Section 3.4.3. The methanolysis product-forming steps for DMC and DMS occur with concomitant formation of a Pd–H species. However, catalysis occurs in the presence of BQ, which sweeps away the Pd–H hydride to give a Pd–COOMe species that continues the catalysis (cf. Section 3.4.3).

Table 1
Oxidative carbonylation of ethene catalyzed by Pd(II) complexes.

Run no.	Precursor	Additive (equivalents)	TOF[a]				Pd metal
			DMC	MP	DMO	DMS	
1	$Pd(TsO)_2L_2$	NEt_3 (2)	10	–	27	–	b
2	$Pd(TsO)_2L_2$	L (1); NEt_3 (2)	10	–	28	–	b
3	$Pd(TsO)_2L_2$	–	3	2	32	24	–
4	$Pd(TsO)_2L_2$	–	–	14	–	0.7	–
5	$Pd(OAc)_2L_2$	–	9	–	36	–	b
6	$Pd(SO_4)L_2$	–	20	–	79	0.7	b
7	$Pd(NO_3)_2L_2$	–	6	8	55	4	b
8	$PdCl_2L_2$	–	–	–	4	5	–
9	$PdBr_2L_2$	–	18	–	18	5	–
10	$Pd(COOMe)_2L_2$	–	25	–	32	–	b
11	$Pd(COOMe)(TsO)L_2$	–	6	4	38	1	b
12	$Pd(COOMe)(OAc)L_2$	–	5	–	35	–	b
13	$Pd(COOMe)(NO_3)L_2$	–	3	2	79	7	b
14	$Pd(COOMe)ClL_2$	–	16	–	42	2	b
15	$Pd(COOMe)BrL_2$	–	–	–	17	6	b
16	$[PdCl_2L]_2$	–	–	3	–	8	–
17	$[PdCl_2L]_2$	L (1)	–	–	11	6	–
18	$PdCl_2$	–	–	–	2	23	–
19	$PdCl_2$	L (2)	–	–	14	10	b
20	$PdBr_2$	–	–	–	25	24	b
21	PdI_2	–	–	–	35	31	b

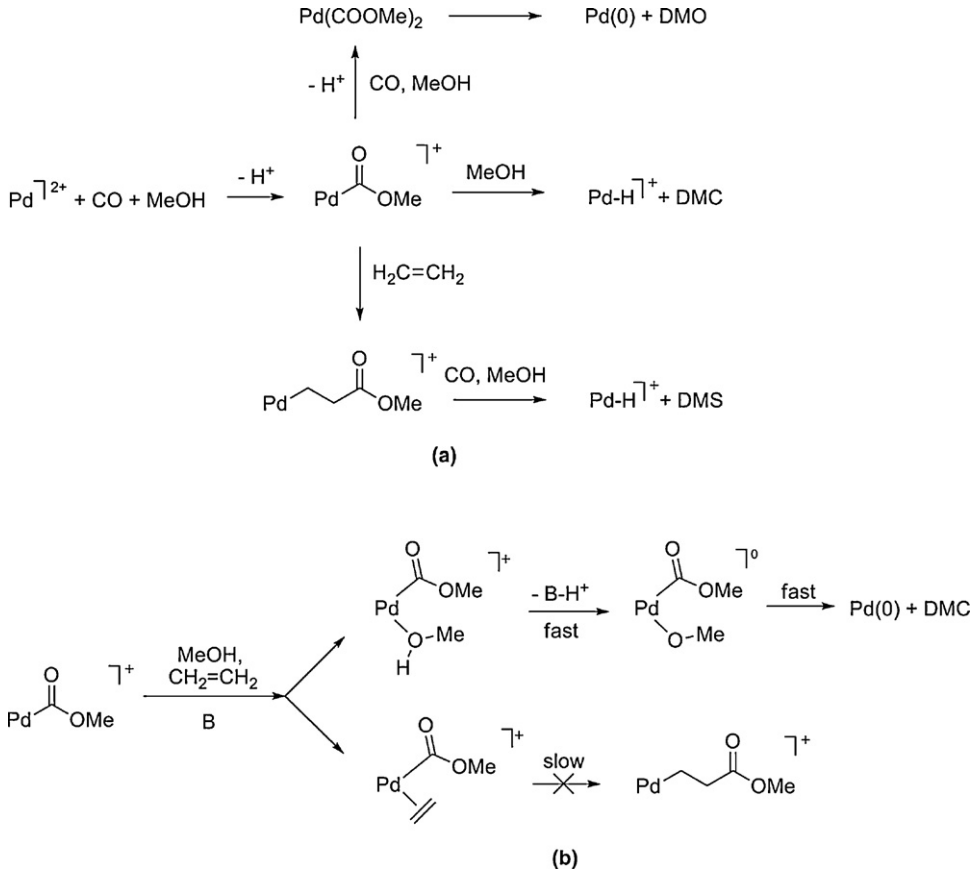
Run conditions: Pd 10^{-2} mmol; BQ 1 mmol, except in run 4, where BQ was not used; $p_{CO} = p_{ethene}$ = 25 atm at room conditions; solvent MeOH 5 mL; temperature 55 °C; reaction time 1 h. L = PPh_3.

[a] Mol product (mol Pd h)$^{-1}$.

[b] Decomposition to Pd metal.

The fact that in the presence of NEt_3 no diester incorporating ethene is formed suggests that (i) ethene insertion and MeOH attack to the Pd–COOMe species which yields DMC are competitive and ii) the base increases the nucleophilicity of MeOH toward the attack of the Pd–COOMe species, so that DMC formation occurs before ethene insertion can occur (Scheme 1(b)).

Experiments 5–9 were carried out using other precursors, which differ for the anion. The acetate (run 6) yields carbonylation



Scheme 1. Formation of DMO, DMC and DMS (B = base).

products of MeOH only, with DMO prevailing over DMC, as in the case when using the tosylate precursor in the presence of NEt_3 (runs 1 and 2). These results suggest that the acetate ligand is displaced during the course of catalysis and that it acts as a base, being the conjugated base of a weak acid. An analogous explanation can be given for the results of experiment 6, in which the SO_4^{2-} anion is the conjugated base of relatively weak HSO_4^- acid. When the anion is NO_3^-, the prevailing product is still DMO, but there is also formation of some DMS (run 7). With coordinating anions, such as Cl^- and Br^-, decomposition to Pd metal was not observed after catalysis, however the catalytic activity was significantly lower (runs 8 and 9).

Experiment 10 was carried out with the di-carbomethoxy precursor trans-[$Pd(COOMe)_2(PPh_3)_2$] in which there is not any conventional anion. There is the formation of products of the carbonylation of MeOH, DMC and DMO, without formation of DMS, which occurs when a base is used (compare run 10 with 1 and 2 and also with 5 and 6). During the course of catalysis, in the absence of a base, there is formation of HX, except in experiment 10. When catalysis is carried out in the presence of a base, as in experiment 1 and 2, or when the anion acts as base, as in experiment 5 and 6, the acid is neutralized. This might be the reason why in experiments 1, 2, 5, 6 and 10 there is formation of DMC and DMO only.

Experiments 11–15 were carried out with mono-carbomethoxy precursors. The TsO precursor yields comparable amounts of DMO, but significantly lower amounts of DMS (compare 11 with 3). Trans-[$Pd(COOMe)Cl(PPh_3)_2$] yields significantly higher amounts of DMO and DMC than the dichloride precursor, but the formation of DMS is rather low in both cases (compare 14 with 8). It is worth pointing out that trans-[$Pd(COOMe)Cl(PPh_3)_2$] is rather reactive in the presence of BQ. As a matter of fact, in the absence of BQ, it is stable because it can be synthesized in high yield even at 70 °C by pressurizing trans-[$PdCl_2(PPh_3)_2$] with CO in MeOH without giving DMC or DMO [29].

The comparison of experiments 8 with 16–19 gives an insight on the coordination of the PPh_3 ligand *during* the course of catalysis. The precursor [$PdCl_2(PPh_3)_2$] may dissociate one PPh_3 ligand or both. The dimer [$PdCl_2(PPh_3)_2]_2$ may dissociate one PPh_3 ligand per Pd centre. Since PPh_3 promptly reacts with BQ yielding betaine (reaction (2) [31,32], if during catalysis trans-[$PdCl_2(PPh_3)_2$] dissociates one PPh_3 ligand, the catalytic system becomes equivalent to half dimer plus one equivalent of betaine; if both PPh_3 ligands dissociate it is like having $PdCl_2$ plus two equivalents of betaine.

The results of experiments 8 and 17 are rather close and do not allow to have a sound picture on the coordination of PPh_3. Instead, experiments 8 and 19 give results that, in our opinion, differ enough to suggest that during catalysis neither of the two ligands dissociates from the $PdCl_2(PPh_3)_2$ precursor. The observation that, after catalysis, decomposition to Pd metal was rather extensive in the case of experiment 19, but not in experiment 8, gives further support to the suggestion that dissociation of both PPh_3 ligands does not occur.

Experiment 3 was repeated using only 1 mL of MeOH. After 1 h reaction the solvent was removed. The ^{31}P NMR spectrum of the residue in CD_2Cl_2 showed signals at 38.3, 28.4, 22.3 and 18.9 ppm in the ratios 1/0.3/0.3/0.2 for cis-[$Pd(TsO)_2(PPh_3)_2$], [$Pd(CO)(PPh_3)]_3$, betaine and trans-[$Pd(COOMe)(TsO)(PPh_3)_2$], respectively, indicating that some PPh_3 dissociated.

Experiments 20 and 21 were carried out with $PdBr_2$ and PdI_2. Though the latter is more active, there is not a significant difference in the selectivity. On the contrary, $PdCl_2$ is more selective toward the formation of DMS (92%).

Finally, we would like to add another observation. By using $PdCl_2$, the solution recovered at room conditions after catalysis was clear, whereas in the cases of $PdBr_2$ and PdI_2, the catalysis medium was dark, though apparently no Pd metal was present. Extensive decomposition to Pd metal was clearly visible after ca. 1 h, whereas in the case of $PdCl_2$ this occurred only after several hours.

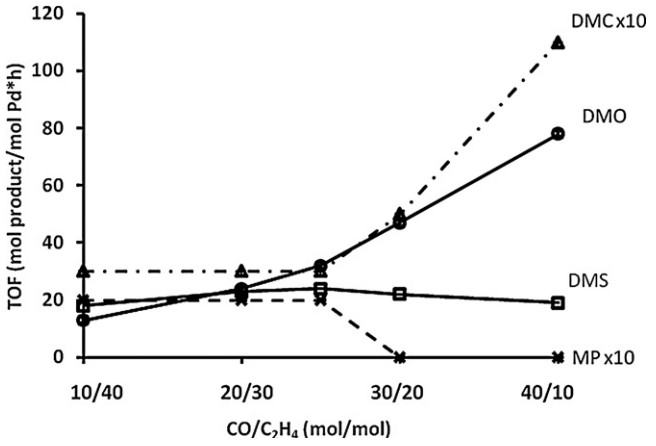


Fig. 2. Influence of the CO/ethene ratio on the TOF numbers under constant total pressure. Run conditions: $Pd(TsO)_2(PPh_3)_2$ 10^{-2} mmol; BQ 1 mmol; solvent MeOH 5 mL, total pressure 50 atm at ambient temperature; temperature 55 °C; reaction time 1 h.

3.2. Influence of the CO/ethene ratio under constant total pressure

Fig. 2 shows the product distribution at different CO pressure under constant total pressure. DMC is formed in a low amount that slightly increases with the increasing of the CO pressure. MP is formed even in a lower amount (only in trace amounts over 25 atm of CO). The TOF number for the formation of DMO increases almost linearly with the increasing of the CO pressure, on the contrary of the TOF number of DMS. The different behaviour may be rationalized as follows. It is reasonable to suppose that a mono-carbomethoxy species is involved in the formation of DMS and that a di-carbomethoxy species leads to DMO. Moreover, it is supposed that these species are in equilibrium and that the equilibrium is largely shifted toward the mono-carbomethoxy species, so that its concentration varies to little extent when varying the CO pressure and, consequently, the TOF number of DMS On the contrary, the concentration of the di-carbomethoxy species is relatively low and it can increase with the increasing of the CO pressure. In spite of the unfavorable equilibrium for the di-carbomethoxy species, the higher rate of DMO formation may be explained by assuming that the relevant catalytic cycle is faster than the one leading to DMS.

Fig. 2 shows also that the highest yield in DMS is achieved when CO and ethene are used in the ratio 1/1. It will be shown below (cf. Section 3.4.1) that the insertion of ethene into a Pd–COOMe bond is likely to be the slow step in the catalytic cycle leading to DMS. The fact that the TOF number is little influenced by the CO/ethene ratio and the fact that it is almost the same when these ratios are 10/40 or 40/10 may be rationalized by admitting that (i) the metal centre presents two coordination sites available for coordination, one more available for CO and the other for ethene and (ii) the insertion of ethene is CO assisted, so that, also in the case when the CO/ethene ratio is unbalanced the rate of ethene insertion is not much different because of the cooperation of CO, higher or lower when the pressure of ethene is lower or higher, respectively. CO assisted ethene insertion has been proposed also for the alternating chain growing in the synthesis of PKs catalyzed by a Pd(II)–dppp system [33].

3.3. Influence of the concentration of BQ

Fig. 3 shows the influence of the BQ/Pd ratio on the product distribution. The formation of DMC starts from BQ/Pd = 100/1 and

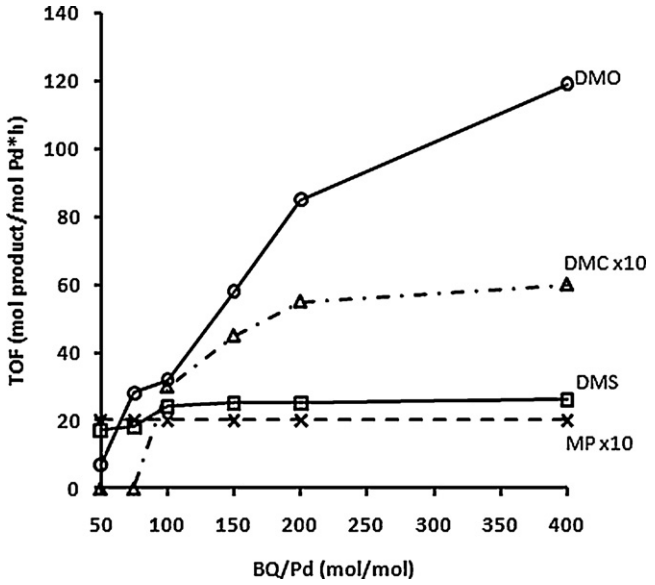


Fig. 3. Influence of the BQ/Pd ratio on the TOF numbers. Run conditions: $Pd(TsO)_2(PPh_3)_2$ 10^{-2} mmol; $p_{CO} = p_{ethene} = 25$ atm at ambient temperature; solvent MeOH 5 mL; temperature 55 °C; reaction time 1 h.

remains low. MP is formed even to a smaller extent. The TOF number of DMO increases progressively up to 119 h^{-1} when the BQ/Pd ratio is 400/1. The TOF number of DMS increases regularly up to 24 h^{-1} upon increasing the BQ/Pd ratio up to 100/1, then it increases significantly less, 26 h^{-1} when BQ/Pd = 400/1.

It is worth pointing out that above BQ/Pd = 100/1, the rate of the formation of DMS increases slightly at difference of the one of DMO. This fact does not contrast the hypothesis given above, i.e. that the mono- and di-carbomethoxy species are in equilibrium and that the equilibrium is largely shifted toward the mono-carbomethoxy species. By admitting that the concentration of the di-carbomethoxy species increases upon increasing the BQ concentration one can explain why the rate of DMO increases. Alternatively, the concentration of the di-carbomethoxy species is not significantly affected by the concentration of BQ, at the contrary of the rate of DMO formation if BQ is involved in the slow step or before it.

3.4. Model reactions and proposed catalytic cycle

As model complexes, we took into consideration the "cationic" complexes cis-$[Pd(TsO)_2(PPh_3)_2]$ and trans-$[Pd(COOMe)(TsO)(PPh_3)_2]$ because they are known to be more reactive than the corresponding neutral ones. For the catalysis to DMO we used trans-$[Pd(COOMe)_2(PPh_3)_2]$.

3.4.1. Reactivity of cis-$[Pd(TsO)_2(PPh_3)_2]$ with MeOH and CO and with CO–ethene in the presence of BQ

CO was bubbled into a solution of trans-$[Pd(TsO)_2(PPh_3)_2]$ and BQ (1/10) in CD_2Cl_2/MeOH (10/1) in an NMR tube at room temperature. The immediate formation of trans-$[Pd(COOMe)(TsO)(PPh_3)_2]$ was not accompanied by the formation of trans-$[Pd(COOMe)_2(PPh_3)_2]$. The same has been found in the absence of BQ [24]. Thus, BQ does not inhibit the formation of the mono-carbomethoxy complex, but it does not favour the formation of the di-carbomethoxy one: and yet under catalytic conditions there is formation of DMO, which is likely to occur via this intermediate.

Upon adding some NEt_3 to the above solution there was immediate formation of the di-carbomethoxy complex. Again, the same has been found in the absence of BQ [24]. Thus, BQ does not inhibit the formation of the di-carbomethoxy complex either. However, in the presence of NEt_3, catalysis yields carbonylation products of MeOH, only, without formation of any carbonylation product incorporating ethene (see experiments 1 and 2).

In another experiment the solution of cis-$[Pd(TsO)_2(PPh_3)_2]$ and BQ in CD_2Cl_2/MeOH was pressurized with 4 atm of CO in an NMR tube at room temperature. Again there was immediate formation of the mono-carbomethoxy, only. The solution was then warmed. At 35 °C, the formation of DMC started. The ^{31}P spectrum showed the presence of the starting complex (38.3 ppm) and of trans-$[Pd(COOMe)(TsO)(PPh_3)_2]$ (19.0 ppm). At 55 °C after 30 min the ^{31}P signals where replaced by signals at 28.4 ppm of $[Pd(CO)(PPh_3)]_3$ and at 23.1 ppm of betaine. DMC was formed in ca. 50% of the amount of the initial complex. Extensive decomposition occurred. For another 30 min period the amount of DMC did not increased further. No catalysis to DMC or DMO was observed.

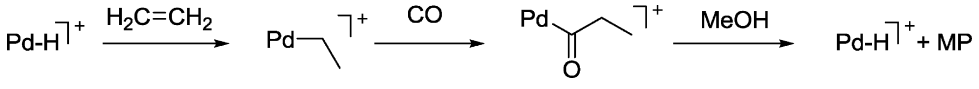
In another experiment the above solution was pressurized with CO and ethene (3 atm/3 atm). Neither in this case catalysis to DMC or DMO was observed, nor to DMS.

3.4.2. Reactivity of ethene with trans-$[Pd(COOMe)(TsO)(PPh_3)_2]$ in the presence of BQ

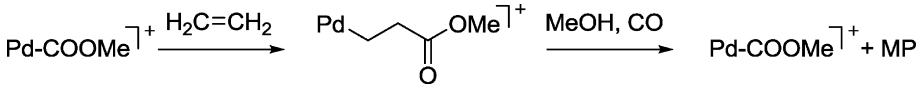
Catalysis to DMS must occur through ethene insertion into a Pd–COOMe bond, The insertion has been attempted by using the model complex trans-$[Pd(COOMe)(TsO)(PPh_3)_2]$ in the presence of BQ (10 equivalents) in an NMR tube in CD_2Cl_2 under 4 atm of ethene. No reaction occurs after 15 min at room temperature or after 20 min at 55 °C. After this period, the intensity of the signals of the starting complex (^{31}P signal at 19.0 ppm and $^{31}P\{^1H\}$ signals at 2.38 ppm and 2.25 ppm for the methyl groups of COOMe and OTs, respectively), lowers and at the same time new signals appear in the ^{31}P spectrum at 31.9 ppm, attributable to $[Pd(BQ)(PPh_3)_2]$ [34] and in the $^{31}P\{^1H\}$ spectrum at 3.4 and 3.8 ppm together with a complex pattern of signals centred at 1.02 e 1.67 ppm. Multiplets at 1.47 and 3.22 ppm and at 0.64 and 3.87 ppm have been attributed to the methylene protons of the β-chelate and of its enolate isomer arising from the ethene insertion into the Pd–COOMe bond of the diphosphino complex $[Pd(COMe)(NCCH_3)(dppp)](CF_3SO_3)$, which occurs at a temperature as low as −20 °C [35]. In our case we cannot make a sound attribution of the signals in the methylene region, we can only state that trans-$Pd(COOMe)(TsO)(PPh_3)_2$ is rather reluctant to insert ethene. This may represent the slow step in the catalysis to DMS.

3.4.3. On the formation of MP and of DMS

As already mentioned in the introduction, MP can be formed via both the "Pd–H" and the "Pd–COOMe" mechanisms.



(3)



(4)

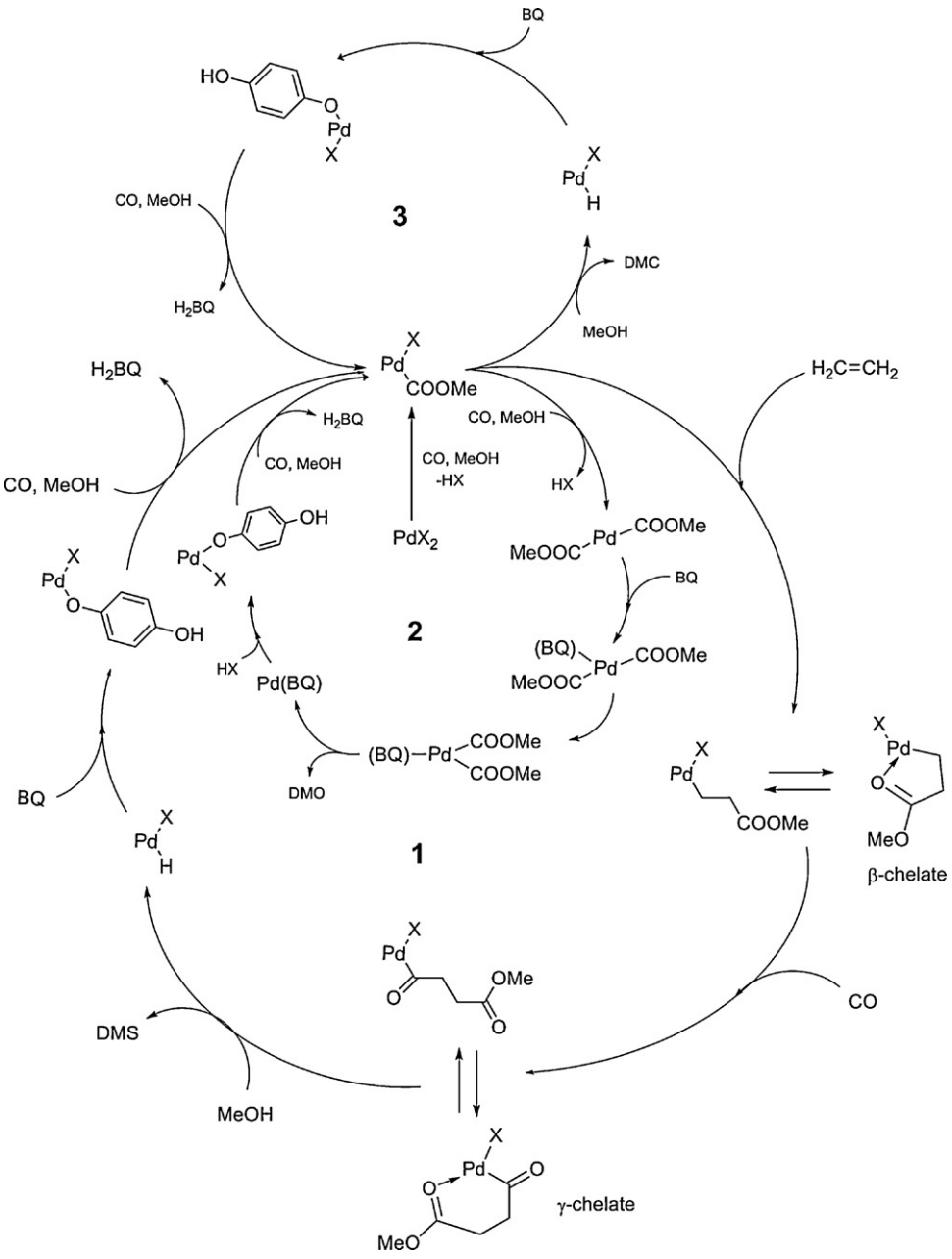


Fig. 4. Catalytic cycles for the formation of DMS (**1**), DMO (**2**) and DMC (**3**).

In order to ascertain which role the "Pd–H" mechanism could play we studied the reactivity of a Pd(II)–hydride with BQ. The hydride $[(PPh_3)_2Pd(\mu\text{–}H)(\mu\text{–}CO)Pd(PPh_3)_2](HSO_4)$ was generated from $[Pd(SO_4)(PPh_3)_2]$ in the presence of H_2SO_4 ($Pd/H_2SO_4 = 1/4$) in CD_2Cl_2/MeOH in an NMR tube under CO [20]. After ca. 1 h the NMR spectrum showed the presence of the starting complex and of $[Pd(COOMe)(HSO_4)(PPh_3)_2]$ and of the hydride in the ratio 1:0.6:3. The addition of 5 equivalents of BQ caused the immediate disappearance of the hydride. The other two complexes were in the ratio 1/0.5, which indicates that the hydride is converted for 2/3 to the sulfate and the rest to the carbomethoxy complex. After 10 min, the only complex still present was the starting sulfate.

$$Pd_2(\mu\text{-}H)(\mu\text{-}CO)L_4^{+}(HSO_4)^{-} + 2\ BQ \xrightarrow{H_2SO_4} 2\ Pd(SO_4)L_2 + 2\ H_2BQ + CO \quad (5)$$

Thus, BQ sweeps away the Pd–hydride. This might be the reason why, in the absence of BQ, catalysis takes a different route. As a matter of fact, in experiment 4 the main product is MP, which is likely to be formed via the "Pd–H" route. The presence of BQ reduces the possibility that ethene inserts into a Pd–H bond and catalysis takes a different route to DMS through the insertion of ethene into the only moiety left, i.e. a Pd–COOMe bond (compare experiment 3 with 4).

In principle, DMS could form from a mono-carbomethoxy intermediate as well as from a di-carbomethoxy intermediate. In an experiment trans-$[Pd(COOMe)_2(PPh_3)_2]$ was suspended in 1 mL MeOH containing 10 equivalents of BQ. The suspension was pressurized with 30 atm of ethene at room temperature and then kept for 1 h at 55 °C. After cooling to room temperature and

depressuring to 1 atm the suspension was collected on a filter (IR νCO at 1822 for $[Pd_3(CO)_3(PPh_3)_4]$ [35]. The GC analysis of the solution showed the presence of DMC and of DMO in the ratio ca. 15/1 and of trace amounts of DMS. Thus DMC may form also from a $Pd(COOMe)_2$ species via attack of MeOH to a Pd–COOMe bond or by decarbonylation to a Pd(COOMe)(OMe) species, followed by reductive elimination of DMC. Instead, it is unlikely that DMS is formed through simultaneous insertion of ethene into two Pd–COOMe bonds of a $Pd(COOMe)_2$ species or insertion of ethene into a Pd–COOMe moiety of a $Pd(COOMe)_2$ species, with formation of a Pd–(CH_2CH_2COOMe)(COOMe) intermediate, followed by the transfer of the other COOMe moiety and elimination of DMS.

It is more reasonable that DMS is formed through the first steps of the well known mechanism leading to PKs [2,4], i.e. the insertion of ethene into a Pd–COOMe bond, with the formation of a Pd–CH_2CH_2COOMe intermediate (which might be in equilibrium with a β-chelate isomer), followed by the insertion of CO with the formation of a Pd–$COCH_2CH_2$COOMe intermediate (which might be in equilibrium with its γ-chelate) [36], followed by the attack of coordinated MeOH [37] to yield DMS.

3.4.4. On the formation of DMO

DMO is probably formed from a di-carbomethoxy species. As reaction model we studied the reactivity of trans-$[Pd(COOMe)_2(PPh_3)_2]$ with BQ dissolved in CD_2Cl_2 in an NMR tube, under 6 atm of CO and ethene (1/1). The complex starts to react at 20 °C with formation of $[Pd(BQ)(PPh_3)_2]$ and DMO. Catalysis to DMO was observed at 60 °C. In the absence of BQ the complex is stable at a temperature of 35 °C. It can be concluded that (i) BQ destabilizes the starting complex, probably by promoting its isomerization to one having the two carbomethoxy ligands in a vicinal position, thus favouring the reductive elimination of DMO and that (ii) under these conditions the elimination of DMO is faster than catalysis.

3.4.5. Proposed catalytic cycles

As already stated, in the absence of BQ, MP may form via the "Pd–H" mechanism (reaction (3)). In the presence of BQ it may form via either cycle **3** or **4**. Fig. 4 shows the proposed catalytic cycles for the formation of DMC, DMO and DMS. The one relevant to DMO (cycle **2**) proceeds via a typical Pd(II)/Pd(0) catalytic cycle where a cis-dimethoxy intermediate yields the product and a Pd(0)–BQ complex, whose oxidation is promoted by HX to a Pd(II)–(OC_6H_4OH) intermediate, which reacts further to give H_2BQ and the Pd(II)-mono-carbomethoxy species which is common to all three cycles. In experiment 11 the precursor cannot give off HX. In this case HX is MeOH.

In cycles **1** and **3** the methanolysis product-forming steps to DMS or DMC are accompanied by the formation of a Pd–H species [22], which is promptly consumed by BQ, probably with formation of a of a Pd(II)–(OC_6H_4OH) species [38]. These two catalytic cycles do not occur through a Pd(II)/Pd(0) cycle species, as proposed for cycle **2**. In any case, all three are equivalent, because also cycles **1** and **3** might occur through a Pd(0)–BQ intermediate, whose oxidation would be promoted by HX as proposed mechanism **2**.

4. Conclusions

In summary, we have reported that Pd(II)–PPh_3 and PdX_2 (X = Cl, Br, I) complexes, in combination with BQ, catalyze the oxidative carbonylation of ethene in MeOH, yielding MP and DMS, together with DMC and DMO. The formation of DMS unambiguously proves that ethene inserts into a Pd–COOMe bond. BQ sweeps away Pd–H initiators and directs the catalysis toward Pd–COOMe ones. In the absence of BQ, DMS is not formed and catalysis takes a Pd–H route to MP. The catalytic cycles for the formation of DMC, DMO, MP and DMS are proposed on the bases of the results of the catalysis and of model reactions in an NMR tube.

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