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The promoting effect of chelating ligands in the oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd–Co–benzoquinone system

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Abstract

The system $Pd(OAc)_2/BQ/Co(acac)_3$ (BQ = benzoquinone), in combination with tetrabutylammonium bromide (TBAB) as a surfactant agent and a chelating ligand such as 2,9-dimethyl-1,10-phenanthroline (dmphen) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dmdpphen), is an efficient catalyst for the oxidative carbonylation of phenol to diphenyl carbonate (DPC). The best results have been obtained using the system $Pd(OAc)_2/BQ/Co(acac)_3/dmphen = 1/30/8/5$ (molar ratio) in which $[Pd] = 10^{-3}$ mol l^{-1} and TBAB/Pd = 60/1. This system gives the maximum productivity of 700 mol DPC/mol Pd h at 135°C and under $P_{tot} = 60$ atm ($CO/O_2 = 10/1$ molar ratio). The role of each component of the catalytic system is discussed and a catalytic cycle is proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chelating ligands; Oxidative carbonylation; Pd–Co–benzoquinone system

1. Introduction

The industrial method commonly employed for the synthesis of diphenyl carbonate (DPC) is based on the reaction between phenol and phosgene in the presence of bases [1]. Because the current trend in the chemical industry is to reduce the risks connected with the use of highly toxic substances such as phosgene [2], several alternative methods have been developed or proposed. Among them, the one-step oxidative carbonylation of phenol to DPC [1–4] is one of the most attractive methods.

Palladium (II) compounds are able to promote the non-catalytic carbonylation which occurs with concomitant reduction of Pd(II) to Pd(0) complexes or to Pd metal [5–9]. The catalytic oxidative carbonylation of phenol to DPC can be achieved in the presence of a

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Abbreviations: DPC, Diphenyl carbonate; TBAB, Tetrabutylammonium bromide; BQ, *p*-benzoquinone; H_2BQ, Hydroquinone; AcO, Acetate; acac, Acetylacetonate; bipy, 2,2′-bipyridyl; phen, 1,10-phenanthroline; dmphen, 2,9-dimethyl-1,10-phenanthroline; dpphen, 2,9-diphenyl-1,10-phenanthroline; dmdpphen, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

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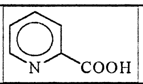
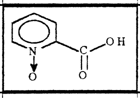
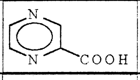
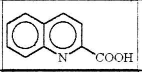
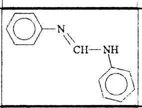
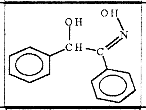
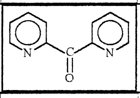
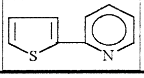
cocatalyst able to reoxidize reduced Pd(0) to Pd(II) [10–17]. In this reaction, the key step is the reoxidation one. In order to obtain an efficient catalytic cycle, a multistep electron transfer system is used [10–17] in combination with a surfactant agent. Easier in situ regeneration of Pd(II) from Pd(0) is obtained by a synergetic effect of two oxidant cocatalysts such as Co-$(acac)_3$ (or $Cu(acac)_2$) and (BQ) [10]. In these studies, simple transition metal salts were employed. The best results were obtained by using a $Pd(OAc)_2/BQ/Co(acac)_3$ system in the ratio 1/30/3, in the presence of tetrabutylammonium bromide (TBAB) as a surfactant agent (TBAB/Pd = 60/1). At 140°C, under a constant pressure of 50 atm ($CO/O_2 = 10/1$), the productivity was 400 mol DPC/mol Pd h.

Since in general, ligand coordination plays a key role in the catalytic activity of the Pd(II) compounds, in principle, a further improvement of the Pd/Co/BQ/TBAB catalytic system should be obtained by the addition of a dosed quantity of a proper ligand. We tested a series of different O–O, O–N, S–N and N–N chelating ligands that are known to coordinate Pd and that, at the same time, are stable in the presence of oxygen or other oxidizing agents. Thereafter, the results of this investigation are discussed.

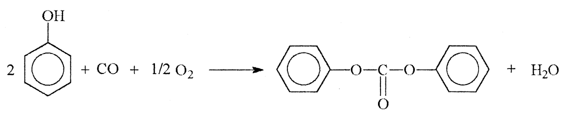
Table 1
The effect of some chelating ligands on the productivity
$Pd(OAc)_2 = 0.01$ mmol, $Co(acac)_3 = 0.02$ mmol, PhOH = 80 mmol; TBAB/Pd = 60/1, BQ/Pd = 30/1, ligand/Pd = 1/1 molar ratios; $T = 100°C$, $P = 60$ atm ($CO/O_2 = 10/1$).

Entry	Ligands		DPC (mol/molPd*h)
1	Without ligands		69
2	2-pyridin carbossilic acid		40
3	2 pyridin carbossilic acid N-oxide		33
4	2-pyrazin carbossilic acid		38
5	2-quinolin carbossilic acid		35
6	Formamidine		55
7	α-benzoinoxime		50
8	1,2-di-(2-pyridyl)-keton		30
9	2,(2' tiophenil)-pyridine		39

2. Results and discussion

2.1. On the catalytic system

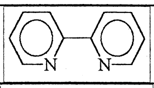
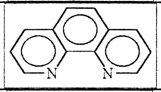
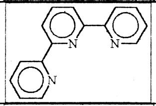
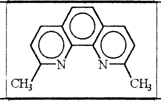
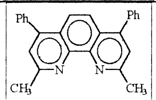
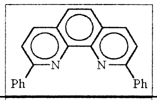
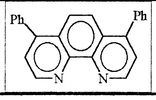
The oxidative carbonylation of phenol to DPC occurs according to reaction (1):



(1)

As already mentioned, the reaction is catalyzed by the system $Pd(OAc)_2/BQ/Co(acac)_3$, in combination with a surfactant agent, such as TBAB. Typically, the components of the catalytic system were used in the ratio $Pd(OAc)_2/BQ/Co(acac)_3/TBAB = 1/30/3/60$, which are known to give satisfactory results [10]. This catalytic system can be improved in the presence of a bidentate N–N substituted ligand such as 2,9-dimethyl-1,10-phenanthroline (dmphen) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dmdpphen). For example using dmphen, under the conditions reported in Fig. 7 (see later), a productivity as high as 700 mol DPC/mol Pd h can be achieved without formation of oxidative dimerization and trimerization by-products in a significant amount. However,

Table 2
The effect of N–N chelating ligands on the productivity
$Pd(OAc)_2 = 0.01$ mmol, $Co(acac)_3 = 0.02$ mmol, PhOH = 80 mmol; TBAB/Pd = 60/1, BQ/Pd = 30/1, ligand/Pd = 1/1 molar ratios; T = 100°C, P = 60 atm ($CO/O_2 = 10/1$).

Entry	**Ligands**		**DFC mol/molPd*h**
1	Without ligands		69
2	2,2'-bipyridyl		14*
3	1,10-phenantroline (phen)		16*
4	terpyridine		18
5	2,9-methyl-1,10-phenantroline (dmphen)		106
6	(2,9 methyl)(4,7phenyl)-1,10-phenantroline (dmdpphen)		110
7	2,9 phenyl-1,10 phenantroline (dpphen)		57
8	4,7phenyl-1,10 phenantroline		20

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* Using an excess of ligand (N–N/Pd = 4/1), DPC was not detected.

Table 3
The effect of preformed Pd(II) compounds on the productivity
Pd(II) = 0.01 mmol, PhOH = 80 mmol; Co/Pd = 2/1 (mol/mol), BQ/Pd = 30/1, TBAB/Pd = 60/1 (mol/mol), PhOH = 80 mmol; $T = 100°C$, $P = 60$ atm ($CO/O_2 = 10/1$); reaction time = 5 h.

Entry	Catalyst	Productivity mol DPC/mol Pd h
1	$Pd(OAc)_2$	69.2
2	$Pd(phen)(OAc)_2$	10.5
3	$Pd(bipy)(OAc)_2$	11.3
4	$Pd(dmphen)(OAc)_2$	95.7
5	$Pd(dmdpphen)(OAc)_2$	97.1

carbon monoxide and oxygen are consumed also by a side reaction to carbon dioxide, which is also catalyzed by palladium compounds.

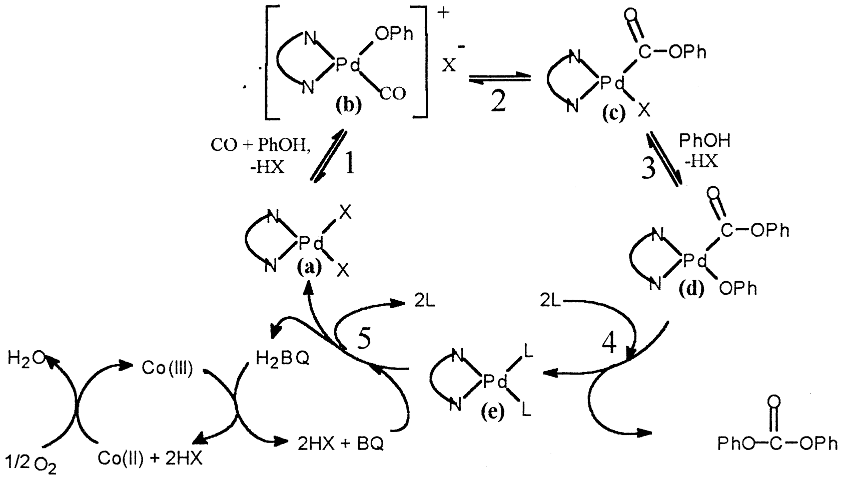
2.2. Effect of chelating ligands on the productivity

In principle, in the case of palladium, of particular interest are chelating ligands that favour the square planar coordination, thus forcing the reagents (phenol and CO) to interact in the catalytically more favoured *cis* position.

In Tables 1 and 2 are reported the chelating ligands tested together with the results obtained.

The catalytic system, without the addition of any ligand, gives a productivity of 69 mol DPC/mol Pd h (Table 1, entry 1). The productivity is depressed (40–30 mol DPC/mol Pd h) when the reaction is carried out in the presence of O–O, N–O or N–S chelating ligands (entry 2–9). Also, unsubstituted N–N ligands do not improve the productivity (see Table 2).

For example, very low values (16–14 mol DPC/mol Pd h) are obtained when a stoichiometric amount of N–N ligand, such as bipyridyl (entry 2) or 1,10-phenanthroline (entry 3), is added. A low productivity (10.5 and 11.3 mol DPC/mol Pd h) is obtained also when the preformed catalyst $Pd(phen)(OAc)_2$ or $Pd(bipy)(OAc)_2$ (Table 3, entries 2 and 3) is used in place of the system $Pd(OAc)_2$–N–N ligand. The catalytic activity is completely inhibited when a excess of these ligands are used (N–N/Pd = 4/1, see footnotes of Table 2, entries 2 and 3), probably due to the formation of the bischelate stable $[Pd(chelating)_2]^{2+}$ complex [18], which does not possess easily available coordination sites capable of interacting with reacting molecules (see the proposed catalytic cycle depicted in Scheme 1). The productivity decreases to low values (14 mol DPC/mol Pd h) also when a tris-chelate ligand such as terpyridine (Table 2, entry 4) is used, probably because there is in situ formation of a stable



Scheme 1.

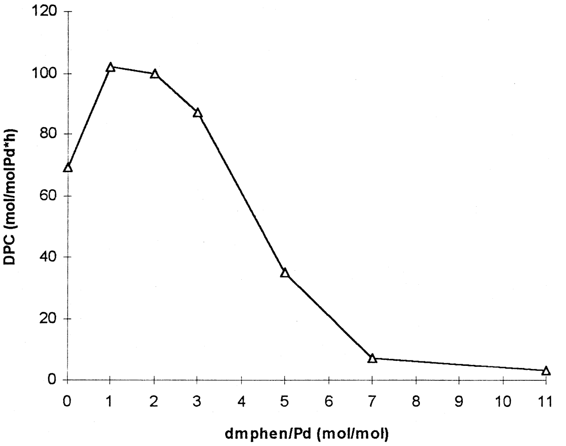


Fig. 1. Productivity as function of dmphen/Pd molar ratio. Run conditions: $Pd(OAc)_2 = 0.01$ mmol, $Co(acac)_3/Pd = 2/1$ (mol/mol), PhOH = 80 mmol; TBAB/Pd = 60/1 (mol/mol), BQ/Pd = 30/1 (mol/mol); P = 60 atm ($CO/O_2 = 10/1$ molar ratio), T = 100°C; reaction time = 4 h.

tris-chelate complex such as $[Pd(N–N–N)X]^+$, in which the coordination of two reagents, for example PhO^- and CO, is not favoured (see for example step 1 of the proposed catalytic cycle).

Quite interestingly, N–N ligands substituted with phenyl or methyl groups have a significant promoting effect. For example, using the dmphen ligand (Pd/ligand = 1/1), the productivity reaches 106 mol DPC/mol Pd h (Table 2, entry 5). In Table 2, among the substituted phenanthrolines (entries 5–8), a sharp increase in productivity is observed going from phenanthroline (16 mol DPC/mol Pd h, entry 3) to 2,9-dimethylphenanthroline (106 mol DPC/mol Pd h, entry 5) and to 4,7-diphenyl-2,9-dimethylphenanthroline (110 mol DPC/mol Pd h, entry 6). This positive effect is probably due both to the increase of the ligand electron donor properties [19–21] as well as to the steric hindrance of the methyl groups.

The catalytic activity of the preformed precursor $Pd(dmphen)(OAc)_2$ is close (95 mol DPC/mol Pd h) to that obtained using the system $Pd(OAc)_2$/dmphen = 1/1 (106 mol DPC/mol Pd h, see Table 3). This fact suggests that starting from this system, there is in situ formation of $Pd(dmphen)X_2$.

2.3. Optimization of the $Pd(OAc)_2$ / BQ / $Co(acac)_3$ / TBAB / dmphen catalytic system

Since the catalytic system $Pd(OAc)_2$/BQ/$Co(acac)_3$/TBAB/dmphen is the most promising, we focused further investigations on the role of each component of this system.

2.3.1. Effect of dmphen / Pd molar ratio on the productivity

The productivity as a function of dmphen/Pd molar ratio reaches a maximum at dmphen/Pd = 1/1 (Fig. 1). This fact suggests that the complex $Pd(dmphen)X_2$ (X = OAc, Br), which may form in situ [18], plays an important role in the catalytic cycle.

At higher dmphen/Pd values, a significant decreasing in productivity is observed, which lowers to 7 mol DPC/mol Pd h when the dmphen/Pd molar ratio is 8/1. This is probably due to the formation of the bischelate $[Pd(dmphen)_2]^{2+}$ complex [18], which is inactive in this reaction.

2.3.2. Role of the surfactant agent

Fig. 2 shows that the presence of a surfactant agent (TBAB) is essential in order to make the

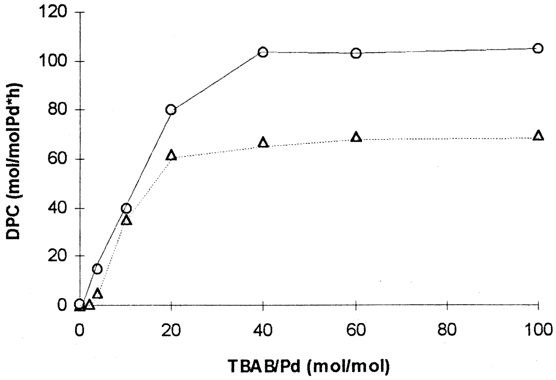


Fig. 2. Effect of the TBAB/Pd molar ratio on the productivity. Run conditions: $Pd(OAc)_2 = 0.01$ mmol, PhOH = 80 mmol, BQ/Pd = 30/1; $Co(acac)_3/Pd = 3/1$ (mol/mol); O: dmphen/Pd = 1/1 (mol/mol), △: dmphen/Pd = 0/1; P = 60 atm ($CO/O_2 = 10/1$ molar ratio), T = 100°C, reaction time 4 h.

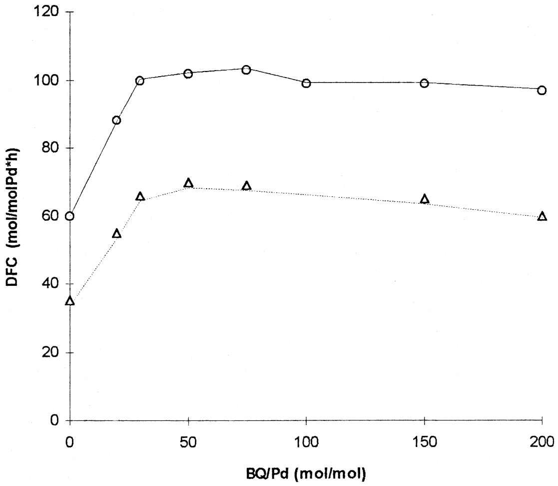


Fig. 3. Effect of the BQ/Pd molar ratio on the productivity. Run conditions: $Pd(OAc)_2$ = 0.01 mmol, $Co(acac)_3/Pd$ = 2/1 (mol/mol), PhOH = 80 mmol; TBAB/Pd = 60/1 (mol/mol), ○: dmphen/Pd = 1/1 (mol/mol), △: dmphen/Pd = 0; P = 60 atm (CO/O_2 = 10/1 molar ratio), T = 100°C; reaction time = 4 h.

catalytic cycle more efficient. The productivity reaches a plateau value of 105 mol DPC/mol Pd h when the molar ratio TBAB/Pd is larger than 40/1. When the reaction is carried out without TBAB or in the presence of a small amount of it (TBAB/Pd $\ll$ 40/1), the productivity is low and Pd metal is found at the end of each reaction.

In addition, Fig. 2 shows that, in the absence of the dmphen ligand, the productivity reaches a plateau at c.a. 70 mol DPC/mol Pd h when TBAB/Pd = 40/1. The comparison of the two curves suggests that the dmphen increases the productivity, but can not avoid the Pd metal formation and the catalyst deactivation at low TBAB/Pd value.

Thus, it is reasonable to suppose that the surfactant properties of the TBAB cation plays an important role. As a matter of fact, it has been found that in the presence of such surfactant, there is formation of nanostructured $R_4N^+X^-$-stabilised metal clusters [22–25]. In these systems, each cluster is surrounded by a monomolecular layer of ammonium salt (micelle) which functions as a stabiliser and prevents agglomeration to larger naked metal particles [24]. In the present case, it is reasonable to suppose that the surfactant inhibits palladium metal agglomeration efficiently when the ratio TBAB/Pd is > 40/1, thus making easier its reoxidation to Pd(II).

2.3.3. Effect on the productivity of p-benzoquinone

The BQ plays a fundamental role in the catalytic cycle (see Scheme 1) as it has been found when using a Pd–Co catalytic system [10]. Fig. 3 shows that the productivity increases up to a plateau of 100 mol DPC/mol Pd h when the ratio BQ/Pd is > 30/1 and that the addition of dmphen has a positive effect on the catalytic system. In fact, both curves are similar, but the one related to the dmphen ligand is shifted to a higher productivity.

2.3.4. Effect of Co/Pd molar ratio on the productivity

Using a dmphen/Pd = 1/1, the productivity increases in the presence of Co(III) and reaches a maximum of 106 mol DPC/mol Pd h when Co/Pd = 3/1 (Fig. 4). For high Co/Pd values (Co/Pd > 4/1), a slight decrease in productivity is observed until a constant value of c.a. 65 mol DPC/mol Pd h. This value is close to the

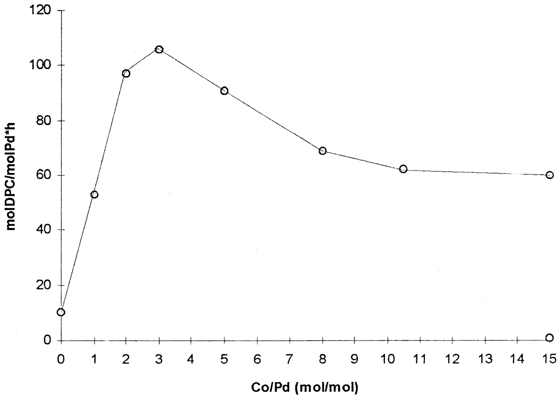


Fig. 4. Productivity as function of Co/Pd molar ratio using dmphen/Pd = 1/1. Run conditions: $Pd(OAc)_2$ = 0.01 mmol, PhOH = 80 mmol; dmphen/Pd = 1/1 (mol/mol), TBAB/Pd = 60/1 (mol/mol), BQ/Pd = 30/1 (mol/mol); P = 60 atm (CO/O_2 = 10/1 molar ratio), T = 100°C; reaction time = 4 h.

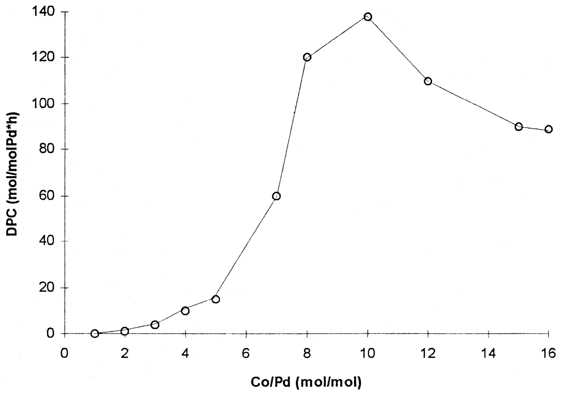


Fig. 5. Productivity as function of Co/Pd molar ratio using dmphem/Pd = 8/1. Run conditions: $Pd(OAc)_2 = 0.01$ mmol, PhOH = 80 mmol; dmphen/Pd = 8/1 (mol/mol), TBAB/Pd = 60/1 (mol/mol), BQ/Pd = 30/1 (mol/mol); P = 60 atm ($CO/O_2 = 10/1$ molar ratio), T = 100°C; reaction time = 4 h.

one obtained without addition of any ligands (Table 1, entry 1).

These results suggest that dmphen forms a complex also with Co(III) in competition with Pd(II), thus shifting equilibrium (2) to the right.

$$[Pd(dmphen)X_2] \rightleftharpoons PdX_2 + dmphen \qquad (2)$$

A further support to this hypothesis has been found by studying the effect of Co/Pd ratio on the productivity under the experimental conditions in which the productivity is very low (7 mol DPC/mol Pd h using dmphen/Pd = 8/1 and Co/Pd = 3/1). We have found that the productivity is again function of the Co/Pd molar ratio and increases up to a maximum of 110 mol DPC/mol Pd h, when the molar ratio Co/Pd increases to 12/1 (see Fig. 5).

As already mentioned, at high concentration of ligand, the productivity is rather low, probably because there is formation of relatively large amounts of inactive $[Pd(dmphen)_2]^{2+}$. The productivity can be improved by adding increasing amounts of $Co(acac)_3$ (see Fig. 5). This fact can be explained also with the formation Co–dmphen complexes. Upon increasing the concentration of $Co(acac)_3$, an increasing amount of ligand is subtracted to Pd(II) thus shifting equilibrium (3) to the more active Pd-(dmphen)X_2. The slight decrease in productivity observed at a ratio Co/Pd > 4/1 gives further support to the suggestion on the role played by equilibrium (2).

$$[Pd(dmphen)_2]^{2+} + 2\,X^- \rightleftharpoons [Pd(dmphen)X_2] + 2\,dmphen \qquad (3)$$

Fig. 6 shows the effect on the productivity varying both the Co and ligand concentration. According to the previous results, each curve reaches a maximum at different Pd/Co/dmphen ratios. Thus, it is possible to optimize the Co/dmphen/Pd ratios in order to obtain the highest productivity. In fact, using Co/dmphen/Pd = 8/5/1, at 100°C and 60 atm ($CO/O_2 = 10/1$), a productivity as high as 170 mol DPC/mol Pd h can be obtained.

2.3.5. Effect of the temperature on the productivity

The catalytic system, $Pd(OAc)_2/BQ/Co(acac)_3/dmphen = 1/30/8/5$, has been tested also at different temperatures. Fig. 7 shows that the productivity increases by increasing the temperature and reaches the maximum value of 700 mol DPC/mol Pd h at 135°C.

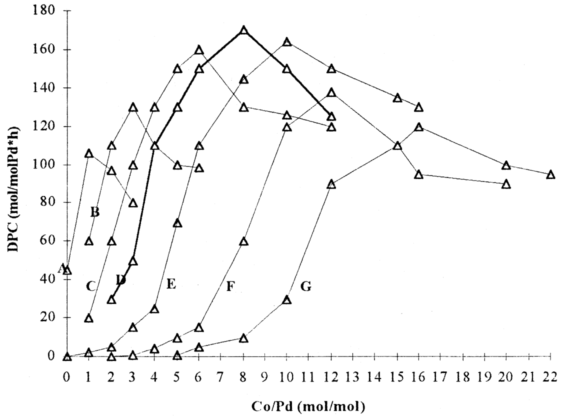


Fig. 6. Productivity as function of Co/Pd and dmphen/Pd molar ratios. Run conditions: $Pd(OAc)_2 = 0.01$ mmol, PhOH = 80 mmol; TBAB/Pd = 60/1 (mol/mol), BQ/Pd = 30/1 (mol/mol); P = 60 atm ($CO/O_2 = 10/1$ molar ratio), T = 100°C; reaction time = 4 h. Each curve have a different dmphen/Pd value: **A**) 1/1, **B**) 3/1, **C**) 4/1, **D**) 5/1, **E**) 6/1, **F**) 8/1, **G**) 12/1 (mol/mol).

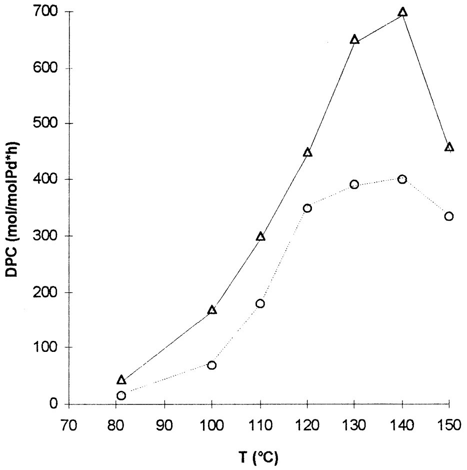


Fig. 7. Effect of the temperature on the productivity. Run conditions: $Pd(OAc)_2 = 0.01$ mmol, PhOH = 80 mmol; TBAB/Pd = 60/1 (mol/mol), BQ/Pd = 30/1 (mol/mol); O: dmphen/Co/Pd = 0/3/1, △: dmphen/Co/Pd = 1/8/5; P = 60 atm ($CO/O_2 = 10/1$ molar ratio), reaction time = 4 h.

The lowering in the productivity, observed upon increasing the temperature above 140°C, is probably due to side reactions of BQ with phenol which yields mixtures containing dimeric, trimeric compounds and polymers [26]. As a matter of fact, a large amount of a brown polymer, together with Pd metal, is found at the end of each reaction carried out above 140°C.

2.4. On the catalytic cycle

In the proposed catalytic cycle (Scheme 1), the Pd–chelating ligand complex (**a**) (X = OAc or Br) is the catalyst precursor that interacts with the phenol and CO to give complex (**b**) and HX. These ligands are forced in a cis mutual coordination, thus making easier the insertion of CO into the Pd–OPh bond to form intermediate (**c**). Complex (**c**) coordinates a second phenate species with formation of HX and PdL(COOPh)(OPh) (**d**). The reductive elimination from (**d**) gives rise to DPC and a Pd(0) complex (**e**). The reaction becomes catalytic: (i) when an efficient reoxidation system for Pd(0) to Pd(II) is used and, (ii) when a surfactant agent is added in order to avoid the catalyst deactivation due to the aggregation and precipitation of inactive Pd metal particles [10].

The reoxidation system proposed [10], is a multistep electron transfer system (see Scheme 1) composed of *p*-benzoquinone, which is reduced to hydroquinone in the presence of acid HX, reoxidizes Pd(0) to Pd(II), and of a metal cocatalyst which is reduced by hydroquinone, reoxidized to *p*-benzoquinone. Oxygen and protons, arising from the last reaction, close the cycle with reoxidation of the reduced cocatalyst and formation of water.

3. Experimental section

3.1. Materials

Carbon monoxide and oxygen (purity higher then 99%) were supplied by SIAD Spa (Italy). Phenol 99%, biochemical grade, TBAB 99% and 1,4-benzoquinone (BQ) 99% were purchased from Acros Chemicals. $Pd(OAc)_2$ 98%, $Co(acac)_3$ 98%, 2,2′-bipyridyl-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 2,9-diphenyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 2-pyridinecarboxylic acid, 2-pyridinecarboxylic acid *N*-oxide, 2-quinolinecarboxylic acid, α-benzoinoxime, 1,2-di(2-pyridyl)ketone and terpyridine were purchased from Aldrich Chemicals. The $Pd(phen)(OAc)_2$, $Pd(dmphen)(OAc)_2$, $Pd(dmdpphen)(OAc)_2$, $Pd(bipy)(OAc)_2$ palladium complexes were prepared according to methods reported in the literature [18].

3.2. Experimental setup

All the experiments were carried out in a stainless steel autoclave of c.a. 100 cm^3 of capacity, provided with a magnetic stirrer. In order to avoid corrosion, the reagents were added to a glass beaker placed inside the autoclave.

Carbon monoxide and oxygen were supplied from a gas reservoir connected to the autoclave through a constant pressure regulator. The autoclave was provided with a temperature control (±0.5°C) and sampling of gas phase.

3.3. Experimental procedure

Typical reaction conditions were: $T = 100°C$, $P = 60$ atm ($CO/O_2 = 10/1$[1] molar ratio), phenol = 80 mmol (reagent and solvent in these reactions), Pd/cocatalyst/*p*-benzoquinone = 1/2/30 and ligand/Pd = 1/1 molar ratios, with $Pd(OAc)_2 = 0.01$ mmol, reaction time 4 h. Tetrabutylammonium bromide, Pd/TBAB = 1/60 molar ratio, was also added to the reaction mixture.

In a typical experiment, known quantities of the catalyst, cocatalyst, BQ, TBAB and ligand along with the solvent (phenol) where charged into the glass bottle placed in the autoclave. Then, the autoclave was pressurized at room temperature with the mixture of carbon monoxide and oxygen. The autoclave was then heated to the working temperature while stirring. At this temperature, the pressure in the autoclave was adjusted to 60 atm and maintained constant using the pressure regulator connected to the gas reservoir. The gas consumption was measured by monitoring the pressure drop of the reservoir. After 4 h, the autoclave was cooled to room temperature and vented.

Products were characterized by gas chromatography analysis (GC) on a HP 5890 series II apparatus equipped with a 30 m × 0.53 mm × 0.1 μm FFAP column. The gas phase products (CO/CO_2 molar ratio) were analyzed by GC using an 18 ft × 1/8 SS Silica Gel, 60/80 packed column.

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[1] In all experiments the two gases were employed in this ratio to make sure to operate with a safe non explosive oxygen containing gas mixture.