

# Catalysis with a palladium giant cluster: phenol oxidative carbonylation to diphenyl carbonate conjugated with reductive nitrobenzene conversion

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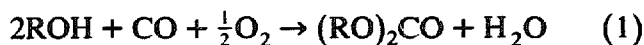
## Abstract

Giant palladium-561 clusters were found to be effective in catalysis of the oxidative carbonylation of phenol to diphenyl carbonate, conjugated with the reductive carbonylation and reduction of nitrobenzene under CO pressure.

**Keywords:** Palladium clusters; Oxidative carbonylation; Conjugated reactions; Phenol; Nitrobenzene; Diphenyl carbonate

## 1. Introduction

Carbonylation of alcohols and phenols into dialkyl and diaryl carbonates is known to be a redox reaction:



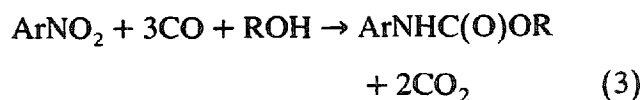
where CO molecule is oxidized to a carbonate moiety and a hydroxyl containing substrate loses two H atoms to form H<sub>2</sub>O molecule. Reaction (1) can be performed in the presence of Cu, Hg, or Pd compounds, and palladium catalysts appear to be the most common [1–3]. Although reaction (1) looks fairly promising, its feasibility is still restricted by the synthesis of

(MeO)<sub>2</sub>CO from methanol and CO [4,5] and the literature concerning the catalysts for the synthesis of diaryl carbonates is mainly limited by patents [6].

On the other hand, Pd complexes enter the triad (Pd [7–10], Ru [11–15], Rh [16,17]) of the efficient catalysts for the reductive carbonylation of nitroarenes to aryl isocyanates:



or to carbamates:



It seemed promising to combine CO oxidation (reaction 1) and nitroarene reduction (reactions 2, 3) within a unified Pd-based catalytic

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system. Low-valent palladium clusters, e.g. giant palladium clusters (GPC) of Pd-561 family could serve as such catalysts due to the expected capability of both facilitating the nucleophilic attack of ROH molecule to CO and acting as the electron reservoir for the reduction of ArNO<sub>2</sub> molecule. Previously the clusters of Pd<sub>561</sub>Phen<sub>60</sub>(OAc)<sub>180</sub> (GPC I) and Pd<sub>561</sub>Phen<sub>60</sub>(PF<sub>6</sub>)<sub>60</sub>O<sub>60</sub> (GPC II) idealized formulations have been found to be highly efficient catalysts for the oxidation of low alkenes, alcohols and formic acid with dioxygen [18–23]. No data are available so far on the reactivity of giant palladium clusters toward nitroarenes, phenols, and CO.

In this context, we studied the reactions of phenol and nitrobenzene with CO in the presence of GPC I, Pd(I), and Pd(II) compounds.

## 2. Experimental

### 2.1. Materials

All gases, organic solvents and reagents were reagent grade. The solvents and substrates were dried additionally before the experiments by standard methods [24], and their purity was checked by GLC.

GPC I and palladium(I) carbonyl complexes, [Pd(CO)(OAc)]<sub>4</sub>, [Pd(CO)Cl]<sub>n</sub>, and [Pd(CO)Br]<sub>n</sub> were prepared by the methods published elsewhere [18,19,25–27].

### 2.2. Experimental procedure

The reactions at ambient pressure were carried out in a magnetically stirred glass reaction vessel, 10 ml in a volume, supplied with a thermostating water jacket, water-cooled reflux condenser and gas inlet tube connected with gas burette. Typically, the vessel was charged with phenol or a solution of phenol in THF or in other solvent. The reactor was evacuated, then filled with an appropriate gas (CO, Ar or O<sub>2</sub>), and stirred in this atmosphere for a specified

time. After the reaction stopped, which took usually 30–60 min, gaseous reaction products were measured with a volumetric burette and analyzed by GC on a LKhM-80 gas chromatograph (3 mm × 2 m column packed with Polysorb 1, TCD). In the experiments in neat phenol as a solvent, the reaction mixture was dissolved in 5 ml of benzene before analysis. The liquid products of the reaction were identified by GC–MS with an Automass 150 (Delsi–Nermag) instrument (capillary column with OV 101, EI ionization, 70 eV). The concentrations of the reaction products were measured by GLC with a Varian 3600 gas chromatograph (capillary column with DB17-15N, FID).

In the experiments under elevated pressures (100–150 atm), the reactions were carried out in a stainless steel pressure vessel of 7 ml volume. The reaction mixture was placed in a glass beaker inside the autoclave to prevent contact of the reagents with metal walls. The apparatus was evacuated, then charged with CO or CO + O<sub>2</sub> gas mixture to a necessary pressure, then sealed and kept for a necessary time period, 2–3 h, within an air-circulating thermostat (±2°C). Typically, the autoclave was charged with phenol, nitrobenzene, palladium cluster, tetramethylammonium bromide and CO or CO + O<sub>2</sub> gas mixture (100 atm at room temperature). When the reaction stopped, the autoclave was cooled to an ambient temperature. Gas phase products were slowly discarded, under a manometric control (±2 Torr), into a preliminarily pumped off (to 1–2 Torr) round-bottom flask of 1 l in a volume to measure the total amount of the gaseous reaction products. After measuring the final pressure, it was adjusted to 760 Torr with Ar added. The reaction products were identified and quantified by GC–MS and GLC such as mentioned above.

#### 2.2.1. Reactions of palladium(I) carbonyl acetate with phenol

A. Palladium carbonyl acetate (100 mg, 0.52 mmol with respect to the [Pd(CO)(OAc)] monomer unit) was dissolved in melted phenol

(1.2 g) and stirred at 90°C under Ar for 30 min. Only traces (on the level of  $\approx 0.1\%$  based on  $[\text{Pd}(\text{CO})(\text{OAc})]$ ) of diphenyl carbonate (DPC), phenyl salicylate (PS), and phenyl acetate were found by GC–MS and GLC.

B. Palladium carbonyl acetate (100 mg, 0.52 mmol with respect to the  $[\text{Pd}(\text{CO})(\text{OAc})]$  monomer unit), tetramethylammonium bromide (70 mg, 0.45 mmol), and 1.0 g of phenol were kept under CO (140 atm) for 3 h at 150°C. DPC, PS, and phenyl acetate were found in the reaction products in the yields of 0.8, 3.2, and 7.3%, respectively, based on  $[\text{Pd}(\text{CO})(\text{OAc})]$  unit.

C. In an experiment similar to that in B, carried out under a CO + O<sub>2</sub> gas mixture (120 + 5 atm), afforded 25% of DPC, 5.0% of PS, and 46% of phenyl acetate.

### 2.2.2. Reaction of GPC I with phenol and oxygen-free CO

GPC I (100 mg,  $1.23 \times 10^{-3}$  mmol) was dissolved in 0.5 g of phenol and kept for 3 h under CO (150 atm) at 150°C. Neither organic products nor CO<sub>2</sub> were detected by GC–MS and GLC.

### 2.2.3. Reaction of GPC I with phenol and CO + O<sub>2</sub> gas mixture.

GPC I (100 mg,  $1.23 \times 10^{-3}$  mmol) was dissolved in 0.5 g of phenol and kept for 3 h under CO + O<sub>2</sub> (145 + 5 atm) at 150°C. No organic reaction products were detected by GC–MS and GLC. Reaction gas contained 1.02% of CO<sub>2</sub> (360 mol per mol of GPC I).

### 2.2.4. Reaction between CO and nitrobenzene in a phenol solution.

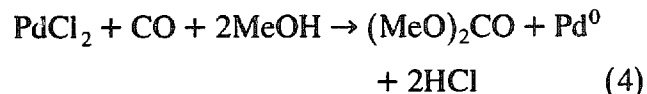
A. GPC I (100 mg,  $1.23 \times 10^{-3}$  mmol) was dissolved in a mixture of phenol (0.5 g) and nitrobenzene (0.1 g) and kept in CO atmosphere (150 atm) at 150°C for 3 h. DPC (5.5 mg, 21 mol/mol I), phenylisocyanate (PIC, 7.8 mg, 60 mol/mol I), and aniline (2.3 mg, 20 mol/mol I) were found in the reaction products by GC–MS and quantified by GLC.

B. GPC I (100 mg,  $1.23 \times 10^{-3}$  mmol) and tetramethylammonium bromide (70 mg, 0.45 mmol) were dissolved in a mixture of phenol (0.25 g) and nitrobenzene (0.1 g) and kept under CO (140 atm) at 150°C for 3 h. DPC (68.4 mg, 260 mol/mol I), PIC (17.6 mg, 120 mol/mol I), along with phenyl ester of phenylcarbamic acid (11.8 mg, 45 mol/mol I), diphenylurea (3.9 mg, 15 mol/mol I), and aniline (8.0 mg, 70 mol/mol I) were found among the reaction products.

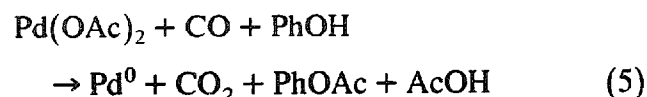
## 3. Results and discussion

### 3.1. Oxidations by Pd(+2) and Pd(+1)

Dimethyl carbonate is known to be formed when reducing Pd(+2) halides by CO in a methanol solution [2–4]:



Our experiments showed that Pd(+2) acetate was readily reduced by CO (1 atm) in a phenol solution at 50°C to give CO<sub>2</sub> and phenyl acetate, according to Eq. (5):



No DPC was found in the reaction products.

Pd(+1) complexes are also reduced by CO to give CO<sub>2</sub> and Pd<sup>0</sup>. Unlike Pd(+2), in this case phenol can be involved into redox CO + Pd(I) reaction. Only traces of diphenyl carbonate, phenyl acetate, and phenyl salicylate were found in the products of the reaction between tetranuclear palladium (+1) carbonyl acetate and phenol at 90°C in Ar or air atmosphere (Table 1, entries 2, 3). However, under CO pressure (120–140 atm) and, particularly, with the additive tetramethylammonium bromide, the yields of DPC, PS, and phenyl acetate increased substantially. DPC was formed in a fairly appreciable yield (42% based on coordinated CO) as

Table 1  
Organic products of the reaction of Pd(I) carbonyl complexes with low alcohols and phenol <sup>a</sup>

Entry	Pd complex	ROH, solvent, temp./°C	<i>p</i> (CO)/atm	<i>p</i> (O <sub>2</sub> )/atm	Yield based on CO coordinated in Pd (I) complex (%)		
					R <sub>2</sub> CO <sub>3</sub>	ROAc	PS
1	PCA	EtOH, 20	0	0.2	10	35	–
2	PCA	PhOH, THF, 20–60	0	0 <sup>b</sup>	≈ 0.1	≈ 0.1	≈ 0.1
3	PCA	PhOH, 90	0	0.2	≈ 0.1	≈ 0.1	≈ 0.1
4	PCA <sup>c</sup>	PhOH, 150	140	0	0.8	7.3	3.2
5	PCA <sup>c</sup>	PhOH, 120	120	5	25	46	5.0
6	[Pd(CO)Cl] <sub><i>n</i></sub>	PhOH, 120	120	0	42	0	0
7	[Pd(CO)Br] <sub><i>n</i></sub>	PhOH, 120	120	0	0.3	0	0

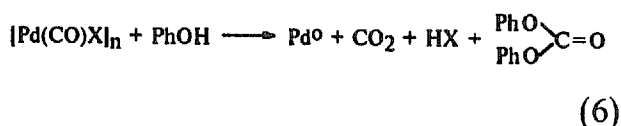
<sup>a</sup> 3 h time of reaction.

<sup>b</sup> Argon (1 atm).

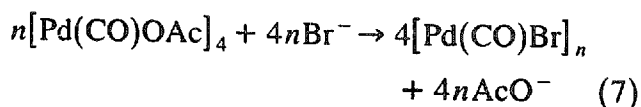
<sup>c</sup> 2 mol l<sup>-1</sup> of NMe<sub>4</sub>Br was added.

the product of the reaction between polymeric [Pd(CO)Cl]<sub>*n*</sub> and phenol (Table 1, entry 6), whereas the other polymeric palladium (+1) halide, [Pd(CO)Br]<sub>*n*</sub>, yielded much less DPC (Table 1, entry 7).

The difference in the productivities on DPC between two Pd(+1) carbonyl halides (Table 1, entries 6, 7) is poorly understood. Its origin could be due to different solubilities of these polymeric complexes in a reaction medium. It is worth noting that, in contrast to PCA, no phenyl salicylate was formed in the case of palladium carbonyl halides as starting complexes, whose reaction with phenol proceeded mainly according to Eq. 6:



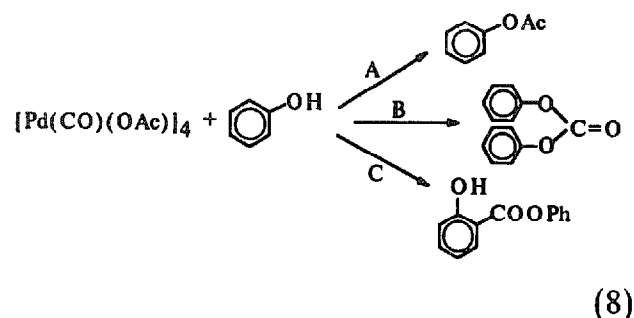
A sharp difference in the productivities on PS and DPC between the experiments with [Pd(CO)(OAc)]<sub>4</sub> + Me<sub>4</sub>NBr and [Pd(CO)Br]<sub>*n*</sub> (Table 1, entries 5, 7, respectively) suggests that the expected metathetic reaction of PCA with bromide salt (Eq. 7)



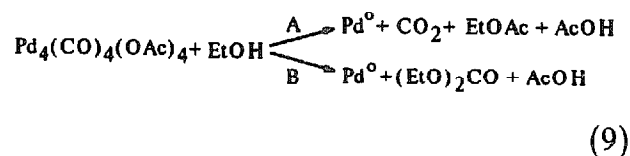
does not produce the same carbonyl bromide complex as the polymeric Pd(+1) carbonyl bromide, prepared by the standard procedure [27],

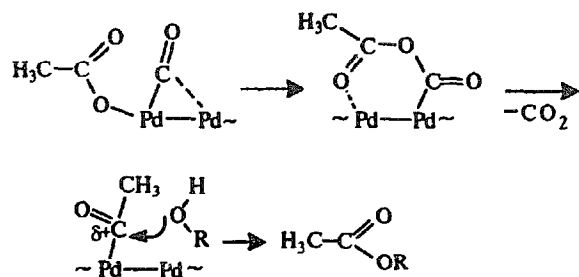
that was used as the starting compound in our experiments. A mixed-ligand Pd(+1) carbonyl bromoacetate complex seems to be responsible for the simultaneous formation of DPC and PS in the experiment with [Pd(CO)(OAc)]<sub>4</sub> + Me<sub>4</sub>NBr (Table 1, entries 4, 5).

Thus, in the reaction of palladium (+1) carbonyl acetate with phenol, three pathways were observed, that led to the formation of phenyl acetate, diphenyl carbonate, and phenyl salicylate (Eq. 8, routes A, B, and C respectively):



Meanwhile, low molecular aliphatic alcohols, e.g. ethanol, when used instead of phenol for redox decomposition of PCA, were found to form both alkyl acetate and dialkyl carbonate [28], similarly to pathways A and B of the reaction with phenol (Table 1, entry 1):





Scheme 1.

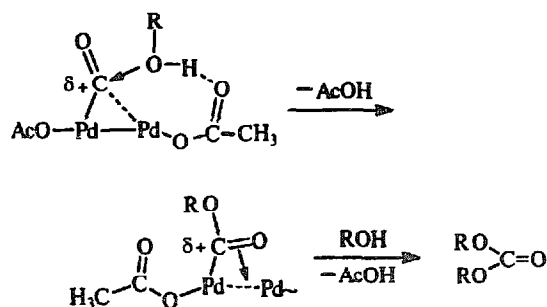
The nucleophilicity of ethanol is known to be higher than that of phenol. In this context, the difference in the reactivity of PCA toward EtOH and PhOH indicates the important role of the nucleophilicity of the hydroxyl containing reagent attacking the coordinated CO group for the reactions under study.

Esterification of the  $\text{OAc}^-$  anion by reactions (8A, 9A) seems to be an uncommon reaction. It can be explained by the insertion of CO into  $\text{Pd-OAc}$  bond to form unstable intermediate  $\text{Pd-C(O)-OAc}$  which can easily eliminate  $\text{CO}_2$  to form coordinated acetyl ligand [26] giving aryl or alkyl acetate upon attack by the ROH molecule, as depicted in Scheme 1.

Phenyl acetate seems to be formed upon carbonylation of  $\text{Pd(OAc)}_2$  (Reaction 5) in a similar way, by the reaction of phenol with the  $\text{Ac}^+$  group bound to Pd (+2) atom.

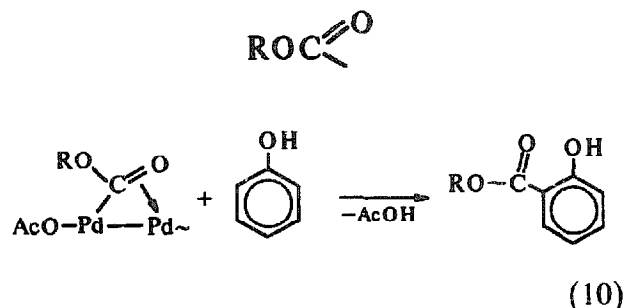
Formation of carbonates by reactions 8B and 9B can be explained as the result of the nucleophilic attack of ROH molecules to CO ligand as depicted in Scheme 2.

The third pathway of the reaction between PCA and phenol (Reaction 8C) resulting in



Scheme 2.

formation of salicyl ester may be considered as evidence for the attack on the aromatic ring of phenol molecule by coordinated group:



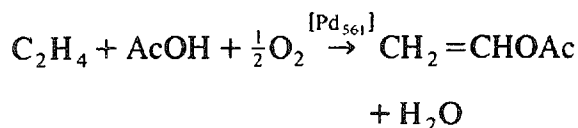
(10)

### 3.2. Oxidations with GPC

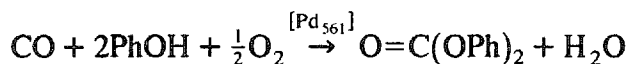
According to previous TEM, HREM, elemental analysis, and EXAFS data [18,19,29–31], the molecule of GPC I consists of a positively charged metal core containing 500–600 densely packed Pd atoms (561 atoms in an idealized icosahedron or a cubooctahedron-shaped core), ca. 60 neutral 1,10-phenanthroline (phen) ligands and ca. 180 outer-sphere acetate ( $\text{OAc}^-$ ) anions, the last counterbalancing the positive charge of the metal core. Average formal charge of palladium atoms in a molecule of GPC I is ca.  $+1/3$  (i.e. the total charge of metal core,  $+180$ , divided by the total number of Pd atoms, 561, is equal to  $+0.321$ ). On the basis of electrostatic considerations (the Gauss theorem), the positive charge of the cluster nucleus (possessing metal properties, e.g. a weak Van Vleck-type temperature-independent paramagnetism [8,12]), is expected to be mostly located on the 252 outer-layer Pd atoms resulting in  $(+180):(252) \cong +2/3$  formal charge of these metal atoms. Therefore, the outer-layer Pd atoms could exhibit some electrophilicity towards nucleophilic reagents such as CO and ROH.

Our experiments showed that oxygen-free CO is not oxidized by giant palladium clusters I and II at 1–100 atm and 20–90°C, unlike the complexes of Pd (+2) and Pd (+1). These data show palladium ( $+2/3$ ) to be incapable of CO oxidation. Nevertheless, being based on the analogy

with the GPC-catalyzed oxidation of alkenes [19,30]



one could expect co-oxidation of CO and phenol by dioxygen to take place in the presence of GPC I or GPC II:



Contrary to this expectation, neither DPC nor PS were found in the reaction product. CO<sub>2</sub> was formed readily in the presence of O<sub>2</sub>, when a solution of GPC I in a neat phenol or the GPC slurry in THF, CH<sub>2</sub>Cl<sub>2</sub>, or acetonitrile contacted with CO + O<sub>2</sub> (95:5 to 90:10) gas mixture, even at a pressure of 1 atm. Increasing both in pressure (up to 150 atm) and temperature (up to 150°C) resulted in only GPC-catalyzed reaction (11) to form CO<sub>2</sub>:

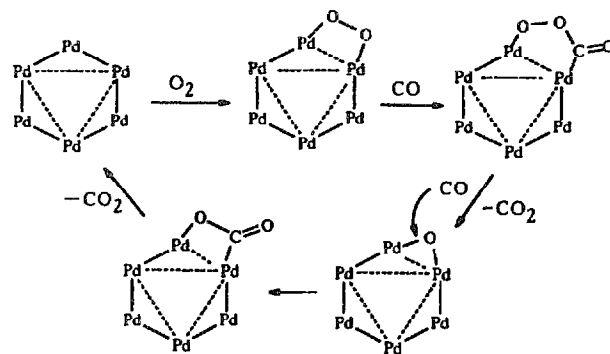


These facts imply that the electrophilicity of Pd atoms of GPC I is inadequate to provide the nucleophilic attack of PhOH molecule to coordinated CO group. Unlike alkenes, in the case of CO a new reaction route arises that includes insertion of CO molecule into Pd–O bond that is formed upon coordination of O<sub>2</sub> molecule with GPC (Scheme 3<sup>1</sup>). This route seems to gain in the competition with the above mentioned electron-mediator mechanism which is operative in the case of alkene oxidation.

In an attempt to suppress this route in favour of that of electron transfer, another oxidant, nitrobenzene, was taken instead of dioxygen.

### 3.3. Oxidation by nitrobenzene with GPC catalyst

As the next step of the study, we tested GPC I as the catalyst for the carbonylation of nitrobenzene. Our experiments showed that



Scheme 3.

phenylisocyanate (PIC) was formed, according to reaction (2), in 12% yield based on nitrobenzene taken, when a slurry of GPC I in nitrobenzene (0.3 g ml<sup>-1</sup>) was kept under CO (100–150 atm) at 150°C for 3 h (see Table 2, entry 2). This fact prompted us to carry out this reaction in the presence of phenol.

In accordance with the anticipations mentioned above, DPC was obtained in 5–10% yield based on phenol taken when contacting CO with a solution of GPC I (0.3 g l<sup>-1</sup>) in nitrobenzene–phenol mixed solvent (1:1 or 1:2 by weight) at 150°C 3 h (Table 2, entries 3–5).

PIC was detected by GC–MS analysis in the reaction products in the yield being as great as 30 to 50% of that found for DPC (Table 2). It is reasonable that PIC, if it was formed, could not be retained intact in a proton containing medium. Moreover, the reduction of nitrobenzene in such a medium was hardly expected to result in the same products (PIC mainly) as those in an aprotic solvent, neat nitrobenzene. Thus, phenyl ester of phenylcarbamic acid, PhNHCOOPh, diphenylurea, PhNhCONHPh, and aniline, PhNH<sub>2</sub> were identified as the products of the nitrobenzene reduction.

In contrast to a low selectivity of the oxidative carbonylation of phenol by Pd(+1) carbonyl complexes (see above), neither PS nor

<sup>1</sup> From here on the metal core of the Pd-561 cluster is denoted conditionally as the Pd<sub>6</sub> hexagon.

Table 2  
Oxidative carbonylation of phenol catalyzed by GPC <sup>a</sup>

Entry	$p(\text{CO})/\text{atm}$	Oxidant, concentration/ $\text{mol l}^{-1}$	$[\text{PhOH}]/\text{mol l}^{-1}$	Yield <sup>b</sup>	
				DPC <sup>c</sup>	PIC
1	145	$\text{O}_2$ , 5 atm	10.6	0	0
2	150	$\text{PhNO}_2$ , 7.5 <sup>d</sup>	0	–	12/67
3	150	$\text{PhNO}_2$ , 2.7	7.6	3.7/21	10/60
4	140	$\text{PhNO}_2$ , 2.7 <sup>d</sup>	7.6	46/260	21/120
5	140	$\text{PhNO}_2$ , 4.8 <sup>d</sup>	5.3	41/230	24/135

<sup>a</sup> 150°C, 3 h reaction time.

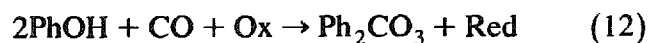
<sup>b</sup> The yields (%) are calculated with respect to one Pd atom of GPC I; those shown in brackets are catalyst turnovers, i.e. the number of mol of products per mol of GPC I.

<sup>c</sup> No PS was found by GC and GC-MS in the reaction products of all runs.

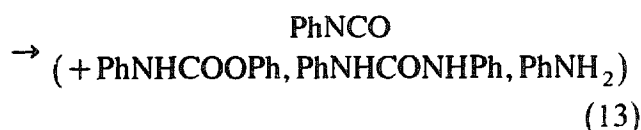
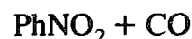
<sup>d</sup>  $\text{NMe}_4\text{Br}$  ( $2 \text{ mol l}^{-3}$ ) was added.

any other products of phenol oxidation were found in the GPC catalyzed reaction with nitrobenzene. Therefore, the conjugation of two processes:

(1) oxidative carbonylation of phenol

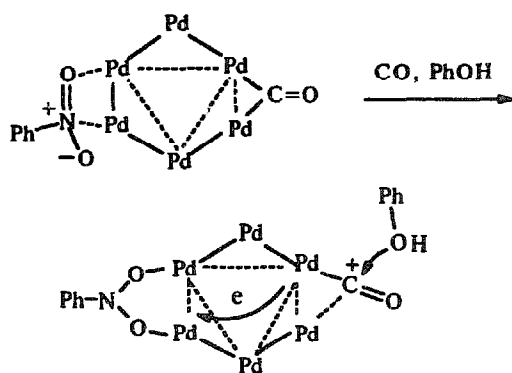


(2) reductive carbonylation and reduction of nitrobenzene:



occurred in the presence of GPC, where Ox was nitrobenzene and Red was PIC, aniline and others.

The conjugation of reactions (12) and (13) can be understood, in the framework of Scheme



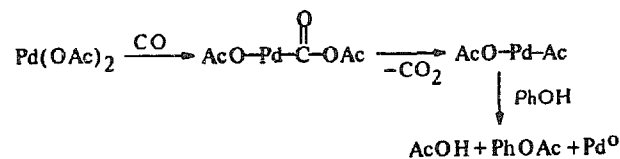
Scheme 4.

4, where the metal core of Pd-561 cluster is an electron transfer mediator.

As was mentioned above (see Section 3.1), low molecular Pd(+2) complexes and Pd(+1) clusters were readily reduced by the action of CO (or by coordinated CO) in phenol solution, according to Eqs. (5) and (6), forming Pd<sup>0</sup>, normally in the form of metal nanoparticles. Such metal particles could be expected to function as electron transfer mediators in conjugation of reactions of type (12)–(13), similarly to giant clusters. The study on this subject is in progress now, and its results will be published elsewhere.

#### 4. Concluding remarks

Our study showed that palladium complexes of various oxidation states (+2, +1, +2/3) differ substantially in their reactivity toward CO + phenol reagent system. In the case of Pd(+2) acetate, the pathway predominates that includes insertion of CO into Pd–OAc bond followed by CO<sub>2</sub> elimination to form Pd–acyl complex [26], whose reaction with phenol gives phenyl acetate:



This pathway is also realized to some extent in the case of Pd(+1) carbonyl acetate, though it is suppressed by halide anions in favour to the DPC formation.

Phenyl salicylate observed unexpectedly in the experiments with Pd(+1) carbonyl acetate can originate from at least two different reactions. First, it could result from the carbonylation of phenol molecule by Pd-coordinated CO group by breaking the C–H bond in the *ortho*-position of its aromatic ring followed by oxidative phenoxylation of the aldehyde formed. Alternatively, it can be formed by the attack of Pd-coordinated PhOCO group on the aromatic ring of phenol molecule by Eq. 10. The lack of PS in the products of the reactions of Pd(+1) carbonyl halides with phenol indicates the first pathway not to be realized in this case<sup>2</sup>.

The formation of DPC seems to be related to cluster catalysis. Nevertheless, palladium (+2/3) giant cluster appeared to be incapable of catalyzing any reactions but CO to CO<sub>2</sub> oxidation in the CO–PhOH–O<sub>2</sub> system. Contrary to our expectations, based on analogy with oxidative reactions of alkenes, GPC could not facilitate the nucleophilic attack of PhOH molecule to coordinated CO. In fact another pathway was realized in this system, that was the attack of CO to coordinated O<sub>2</sub> to form CO<sub>2</sub> as depicted in Scheme 3.

Another oxidant, nitrobenzene, was also found to be capable of converting CO to CO<sub>2</sub> in the presence of GPC. However, in this case another reaction pathway proceeding in parallel (Scheme 3), gains in the competition with direct CO oxidation. An electron transfer from the coordinated CO to the oxidant molecule via the metal skeleton of giant cluster (Scheme 4) enables nucleophilic attack of phenol to the coordinated CO molecule to form DPC simultaneously with reduction of nitrobenzene.

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<sup>2</sup> The reactions between PCA and phenol and its derivatives will be discussed elsewhere.



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