Low-valence palladium complexes: stoichiometric reactions and catalysis

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New data on the structure and reactivity of palladium clusters are surveyed. The mechanisms of stoichiometric and catalytic reactions of the palladium cluster complexes with alkenes, alcohols, aldehydes, formic acid, CO, and phenol are discussed.

Key words: palladium, clusters, catalytic activity.

The achievements of the last decade in catalysis of redox reactions (the oxidation of alkenes to carbonyl compounds, acetals and ketals, the oxidative acetoxylation of alkenes and alkylarenes, the reduction of the multiple bonds of alkynes and alkenes, *etc.*) are considerably due to development of the chemistry of polynuclear, including cluster, complexes of transition metals.

The data on synthesis and the studies of the reactivity of palladium cluster compounds, including low-molecular clusters and colloidal metal, which played a significant role for elucidation of mechanism and for development of a series of catalytic processes, *e.g.*, the industrial processes of ethylene oxidation to acetaldehyde and vinyl acetate, of propene to allyl acetate, and reactions involving carbon monoxide, are surveyed in this review.

Giant palladium clusters

The structure and physicochemical properties of giant palladium clusters

Giant palladium clusters discovered in 1985 are intermediates between conventional molecular clusters and dispersed particles of a bulk metal.[1,2] A typical molecule of the giant cluster consists of a dense-packed metal nucleus (561 atoms of the metal in the idealized formula) and a ligand shell containing both ligands coordinated with the metal nucleus (*e.g.*, *o*-phenanthroline (phen) or α,α′-bipyridyl (bipy)) and outer-sphere anions (OAc^-, PF_6^-, CF_3COO^-) (Fig. 1).[1–5]

The structure of the giant palladium clusters has been studied in detail using scanning tunnel microscopy (STM),[6] high (atomic) resolution electron microscopy (HREM),[7–11] and electron energy loss spectroscopy (EELS) techniques.[12] The results obtained made it possible to evaluate the shape and size of both metallic nucleus (the HREM data) and the whole cluster together with the ligand shell (the STM data). Three types of packing of Pd atoms in the metallic nuclei of giant clusters have been found: (1) face-centered cubic; (2) icosahedral; (3) dense packing without ordering in arrangement of the metal atoms in the nucleus.[9]

It has been found recently that giant palladium clusters display an unusual temperature dependence of their magnetic properties and heat capacity near absolute zero (0.01—1.00 K): the magnetic succeptibility passes through a maximum at 1 K, and the dependence of heat capacity on temperature, especially in high magnetic fields, is abnormal in character.[13] Both characteristics differ sharply from those observed for bulk Pd metal. These size quantum effects for small metal particles have previously been predicted theoretically, but their experimental observation became possible only when the well-characterized uniform cluster particles with a narrow unimodal size distribution such as the giant palla-

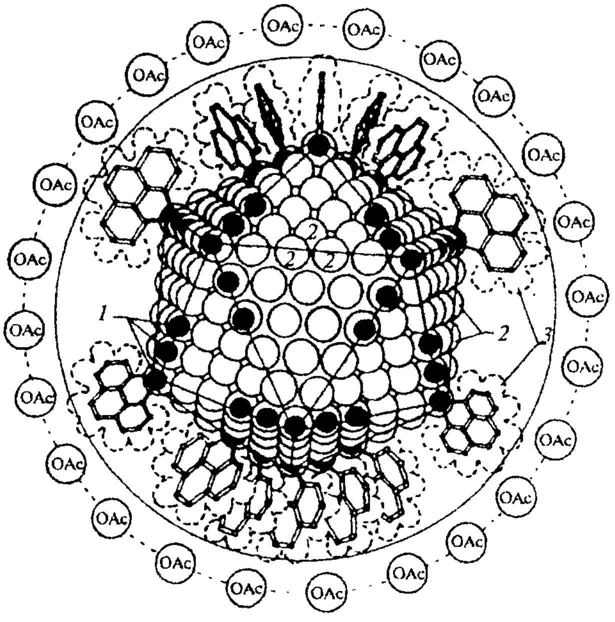

Fig. 1. Idealized structure of the giant palladium cluster: *1*, Pd atom bounded to phen molecule; *2*, non-coordinated Pd atom; *3*, phen molecule in a coordination sphere of the cluster.

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dium clusters were synthesized. Thus, in the genetic sequence "mononuclear complex—oligonuclear cluster—giant cluster—colloidal metal—bulk metal", the giant Pd_{561} clusters are those species which retain the properties of molecular clusters but already exhibit the main features inherent to the metallic state of a substance.

Reactions catalyzed by giant palladium clusters

Alkene oxidation. The giant palladium clusters with idealized formulas $Pd_{561}(phen)_{60}(OAc)_{180}$ (**1**) and $Pd_{561}(phen)_{60}O_{60}(PF_6)_{60}$ (**2**) catalyze efficiently the oxidative acetoxylation of alkenes and alkylarenes with 95—98% selectivity (reactions (1)—(3)) under mild conditions (293—363 K, 0.1 MPa).

$$CH_2{=}CH_2 + 1/2\ O_2 + AcOH \longrightarrow CH_2{=}CHOAc + H_2O \quad (1)$$

$$CH_2{=}CHMe + 1/2\ O_2 + AcOH \longrightarrow$$
$$\longrightarrow CH_2{=}CHCH_2OAc + H_2O \quad (2)$$

$$PhMe + 1/2\ O_2 + AcOH \longrightarrow PhCH_2OAc + H_2O \quad (3)$$

Unlike industrial heterogeneous catalysts which operate only at significantly higher temperatures,[14,15] giant clusters do not promote undesired side reactions of substrates and are insensitive to water formed during reaction.[16,17] The kinetic study of reactions (1) and (2) showed that their rates (r_0) obey an equation of the Michaelis—Menten type[16,18]:

$$r_0 = k[\text{clust}]\frac{[C_2H_4][O_2][AcOH]}{(K_I+[C_2H_4])(K_{II}+[O_2])(K_{III}+[AcOH])},$$

where k is the rate constant, and K_I, K_{II}, K_{III} are the Michaelis constants for ethylene, oxygen, and acetic acid, respectively.

Based on of these data combined with the values of kinetic isotope effects obtained and the kinetics of the inhibition by ligands of various nature, the mechanism of reactions (1)—(3) has been proposed (Scheme 1).[16] In accordance with this scheme, the metal core of the giant cluster operates as an "electron mediator".

The effect of promotion of alkene oxidation by acids, which is uncommon for palladium catalysts, was found for catalysis by the giant Pd clusters. Unlike catalysts based on Pd^{2+} complexes, whose activity drops with increasing acidity of the solution[18] and is suppressed in the presence of bulky donor ligands of the PPh_3 and phen types,[19] the alkene oxidation in aqueous solutions of giant clusters **1** and **2** is practically insensitive to excess ligands of the PPh_3 and phen types and occurs only in the presence of strong acids (*e.g.*, $HClO_4$, H_2SO_4).[20]

Ethylene is successively oxidized to acetaldehyde and acetic acid (Eq. (4)), and propylene is oxidized to allyl alcohol, acrolein, and acrylic acid (Eq. (5))[20].

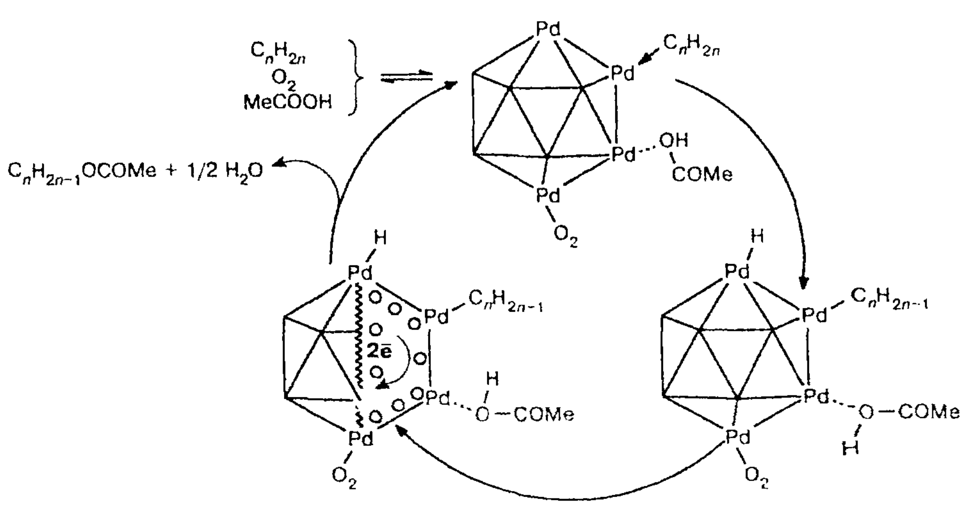
$$C_2H_4 + O_2 \longrightarrow MeCHO \longrightarrow MeCOOH \quad (4)$$

$$C_3H_6 + O_2 \longrightarrow CH_2{=}CHCH_2OH \longrightarrow$$
$$\longrightarrow CH_2{=}CHCHO \longrightarrow CH_2{=}CHCOOH \quad (5)$$

In the case of propylene, acetone was the only reaction product in the aqueous solutions of Pd^{2+},[19] whereas only traces of acetone were formed on catalysis by clusters **1** and **2**.[20] In alcoholic (MeOH, EtOH) solutions of the giant clusters containing 1.6 mol L^{-1} of H_2SO_4, the main products of propylene oxidation were acrylic acid and its ester.[20]

The oxidation of alcohols and aldehydes. In the presence of giant clusters **1** and **2**, normal aliphatic alcohols are readily oxidized forming aldehydes and esters whose alcoholic and acidic components contain

Scheme 1



the same carbon skeleton as the starting alcohol.[16,21,22] The secondary alcohols are oxidized to ketones. The carbonyl compounds formed are transformed by excess alcohol to acetals and ketals, and the acetal formation is also catalyzed by the giant palladium clusters.[23]

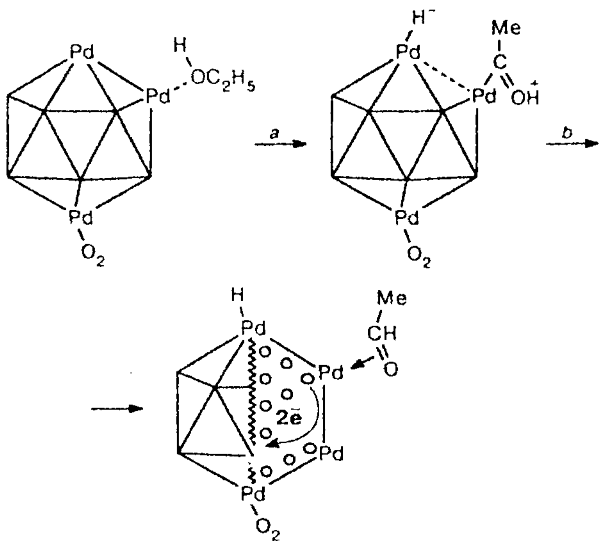
The kinetic study[21] showed that the oxidation of methanol to methyl formate obeys the following equation

$$r_0 = k[\text{clust}][\text{MeOH}]\frac{[O_2]}{K+[O_2]},$$

where k is the rate constant, and K is the Michaelis constant.

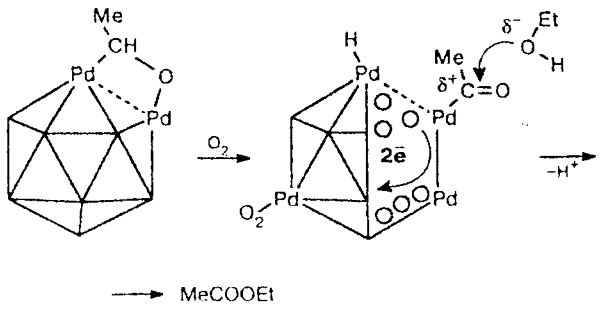
Based on these data and the values of the kinetic isotope effects obtained, the following reaction mechanism has been proposed[21] (Scheme 2, *a* is a slow step, *b* is a fast step).

Scheme 2



The further transformations of the primary reaction products occur according to Scheme 3.[24]

Scheme 3



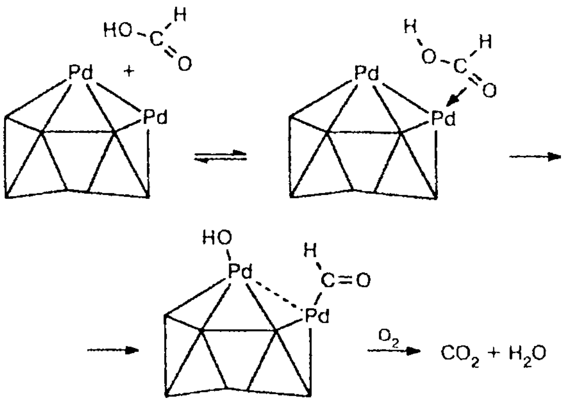
When ethanol is oxidized in nonaqueous solvents (MeCN, EtOH, acetone), acetic anhydride is formed along with the products mentioned as a result of the attack of the AcOH molecule or AcO^- anion on the coordinated acyl group $Me^+C{=}O$.[24]

Reactions involving formic acid. *Oxidation of formic acid.* Giant clusters **1** and **2** catalyze efficiently the oxidation of formic acid in the presence of dioxygen.[25]

$$HCOOH + 1/2\ O_2 = CO_2 + H_2O$$

The kinetics of this reaction has been studied in detail, and its mechanism has been proposed (Scheme 4), which involves the coordination of the HCOOH molecule accompanied by the rupture of the C—O bond as the rate-determining step.

Scheme 4



Hydrogenation of the multiple bonds by formic acid. Platinum metals and their complexes are widely used in catalysis of hydrogenation of the multiple bonds (N=O, C=C, C=O) with H_2 and other hydrogen donors such as cyclohexene, isopropyl alcohol, ascorbic, and formic acids.[26,27] Unlike the majority of substrates, nitriles are hardly reduced by both dihydrogen and other hydrogen donors.[27,28]

It has been found[29] that in the presence of giant cluster **1** nitriles are readily hydrogenated at 20 °C, when formic acid is used as the donor of H atoms (reactions (6) and (7), Table 1).

$$2\ MeC{\equiv}N + 4\ HCOOH \longrightarrow Et_2NH + 4\ CO_2 + NH_3 \quad (6)$$

$$3\ MeC{\equiv}N + 6\ HCOOH \longrightarrow Et_3N + 6\ CO_2 + 2\ NH_3 \quad (7)$$

The reduction of acrylonitrile with formic acid catalyzed by cluster **1** in a solution of methanol results in primary amine in a yield of 30%. The C=C bond is primarily hydrogenated to form propionitrile which is further hydrogenated to *n*-propylamine.

$$CH_2{=}CHC{\equiv}N + HCOOH \xrightarrow[-CO_2]{} MeCH_2C{\equiv}N \longrightarrow$$

$$\xrightarrow[-2\ CO_2]{2\ HCOOH} Pr^nNH_2$$

Table 1. The reduction of the compounds with multiple bonds by formic acid in the presence of giant cluster **1**[a]

Substrate	Conversion of substrate (%)	Reaction products	Yield[b] (mol.%)	TN[c]
MeC≡N	90	Et_2NH	20	1500
		Et_3N	80	
CH_2=CHC≡N	100	$Pr^n NH_2$	30	600
		Pr^n_2NH	10	
		Pr^n_3N	45	
		$MeCH_2CH(OMe)_2$	15	
PhC≡N	95	$PhCH_2NH_2$	45	1200
		$(PhCH_2)_2NH$	45	
		PhMe	10	
$PhNO_2$	100	$PhNH_2$	100	3160
PhN=O	100	$PhNH_2$	100	3030
PhC(Me)=O	90	$PhCH_2(OH)Me$	65	2500
		$PhCH_2Me$	35	
PhCH=O	100	PhMe	50	1530
		$PhCH(OMe)_2$	50	
PhCH=CH_2	100	$PhCH_2Me$	100	2840

[a] Reaction conditions: [**1**] = 2.5 g L^{-1} ($3.1 \cdot 10^{-5}$ mol L^{-1}), T = 20 °C, 1 atm Ar, $[\text{substrate}]_0$ = 0.17—0.20 mol L^{-1} in a solution of MeOH; $[\text{substrate}]_0 : [HCOOH]_0 = 1 : 2$, duration of reaction 2 h.

[b] Per reacted substrate.

[c] TN is the turnover number of the catalyst (moles of substrate consumed for 1 h per 1 mole of cluster **1**).

The hydrogenation of benzonitrile by HCOOH leads to the formation of benzylamine and dibenzylamine. Simultaneously, metathesis of primary amines to secondary and tertiary amines readily occurs.[29]

$$MeCN + Et_2NH \longrightarrow \underset{(85\%)}{EtNMe_2} + \underset{(5\%)}{Et_2NH} + \underset{(10\%)}{Et_3N}$$

The reaction proceeds according to Scheme 5.

In solutions of giant cluster Pd_{561}, nitrobenzene, nitrosobenzene, and phenylhydroxylamine are readily reduced by formic acid to afford aniline.[29]

$$PhNO_2 + 3\ HCOOH \longrightarrow PhNH_2 + 3\ CO_2 + 2\ H_2O$$

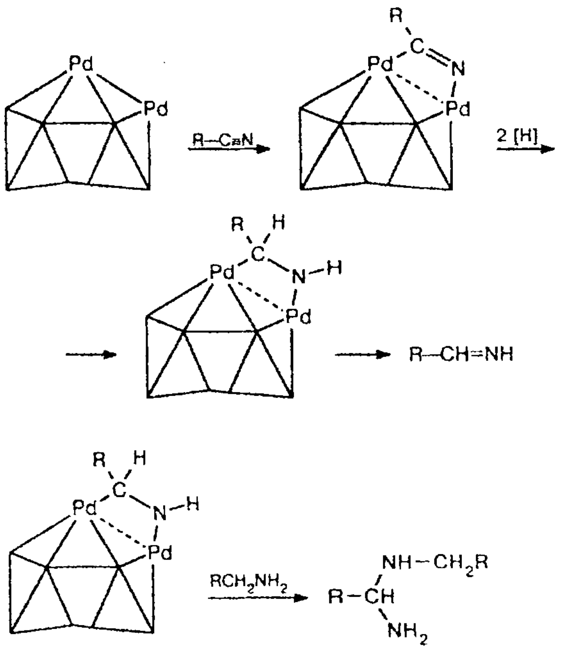
$$PhNO + 2\ HCOOH \longrightarrow PhNH_2 + 2\ CO_2 + H_2O$$

$$PhNHOH + HCOOH \longrightarrow PhNH_2 + CO_2 + H_2O$$

When nitroarenes are reduced in acetonitrile, the products of metathesis of the corresponding amines are formed in significant amounts.[29]

$$PhNO_2 + MeCN \longrightarrow \underset{(8\%)}{PhNH_2} + \underset{(90\%)}{PhNHEt} + \underset{(2\%)}{PhNEt_2}$$

Scheme 5



In this catalytic system, the C=O and C=C bonds attached to the benzene ring are readily hydrogenated (see Table 1).[29]

Reactions involving CO. The giant palladium clusters catalyze efficiently oxidation of CO by both dioxygen and other oxidants, *e.g.*, nitrobenzene. In the presence of small amounts of water (2—5 wt.%), nitrobenzene is smoothly reduced to aniline, whereas in the absence of H_2O or at a small content of it (≤1—2 wt.%), the reaction catalyzed with cluster **1** results in the formation of phenylisocyanate.[30]

$$PhNO_2 + 3\ CO + H_2O \longrightarrow PhNH_2 + 3\ CO_2$$

$$PhNO_2 + 3\ CO \longrightarrow PhNCO + 2\ CO_2$$

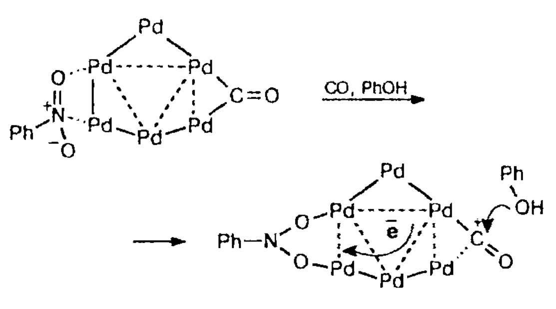
When this reaction is performed in phenol, the oxidative carbonylation of phenol to diphenyl carbonate was found to occur simultaneously with the reduction of nitrobenzene:

$$2\ PhOH + CO + Ox \longrightarrow Ph_2CO_3 + Red,$$

where Ox = $PhNO_2$, Red = PhNCO or $PhNH_2$ (3 h, 140 atm, 150 °C, yield equal to 200 moles per mole of the cluster).[30] In this reaction, the giant cluster molecule operates as the catalyst that conjugates two redox processes: the reduction of the nitro compound and the oxidative carbonylation of phenol (Scheme 6).

Reactions involving aldehydes. Giant clusters are not strong acids or bases. Nevertheless, it was observed that clusters **1** and **2** are capable of catalyzing the reactions

Scheme 6



typical of acid-base catalysis, *e.g.*, the acetalization of carbonyl compounds by alcohols in neutral solutions (20—50 °C) mentioned above.[23]

$$\mathrm{MeCHO + 2\,EtOH \longrightarrow MeCH(OEt)_2 + H_2O} \qquad (8)$$

Reaction (8) was found to be catalyzed by both clusters **1** and **2** and palladium blacks.[23,31]

It was observed recently that in solutions containing giant palladium clusters, the oxidative destruction of acetaldehyde accompanied by the rupture of the C—C bond occurs smoothly under comparatively mild conditions (1 atm, 60 °C).

$$\mathrm{MeCHO + 1/2\,O_2 \longrightarrow CH_4 + CO_2}$$

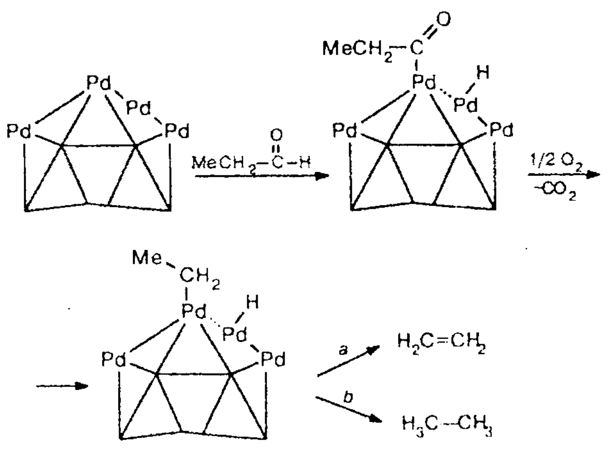
In the case of homologs of acetaldehyde, CO_2, H_2O, and alkene are formed along with small amounts of the corresponding alkane.[23]

$$\mathrm{MeCH_2CHO + O_2 \longrightarrow CH_2{=}CH_2 + CO_2 + H_2O}$$

$$\mathrm{MeCH_2CH_2CHO + O_2 \longrightarrow CH_2{=}CHMe + CO_2 + H_2O}$$

$$\mathrm{Me_2CHCHO + O_2 \longrightarrow CH_2{=}CHMe + CO_2 + H_2O}$$

Scheme 7



The key stages of the proposed mechanism are presented in Scheme 7 [31] (*a* is β-elimination (—H) and *b* is alkyl—H recombination).

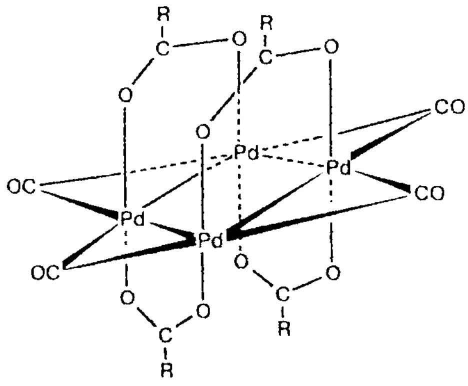
Palladium(I) carbonylcarboxylate clusters

The study of the reactions of the carbonylacetate cluster $Pd_4(CO)_4(OAc)_4$ (**3**)[33] has shown that the coordinated acetate groups are readily replaced by other carboxylates during reaction with the corresponding acids:

$$\underset{\mathbf{3}}{\mathrm{Pd_4(CO)_4(OAc)_4}} + 4\,\mathrm{RCOOH} \longrightarrow \mathrm{Pd_4(CO)_4(RCOO)_4} + 4\,\mathrm{AcOH},$$

$$\mathrm{R = CD_3,\ Et,\ Ph,\ CF_3,\ CCl_3,\ CH_2Cl.}$$

A comparison of the structural data obtained by single-crystal X-ray diffraction study of cluster **3** and those obtained by EXAFS for the other carbonylcarboxylates allows one to conclude that all these compounds are similar in structure: a flat metal skeleton (rectangle, square, or rhombic) with the bridging carboxylate and carbonyl ligands coordinated to its sides.[34]



Along with isomerization of the metallic framework, isomers with different mutual arrangements of the ligands can exist: either in pairs, as in cluster **3** structurally characterized by X-ray diffraction analysis, or a uniform distribution of the same ligands in some other clusters.

The reaction of cluster **3** with complex $NaCpMo(CO)_3$ in THF affords the anionic octanuclear cluster $Na_2\{Pd_4[CpMo(CO)_3]_4\} \cdot 2THF$ (**4**).[35,36]

According to the single-crystal X-ray structural data for cluster **4** (Fig. 2),[36] its structural unit consists of the centrosymmetric anion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$, two Na^+ cations, and two THF molecules. The Pd atoms are located in the vertices of the square (Pd—Pd is 2.675—2.691 Å). Each Mo atom forms a nearly equilateral triangle with two Pd atoms (Pd—Mo is 2.723—2.741 Å), and all metal atoms are in the same plane. The metal—metal distances observed correspond to the ordinary

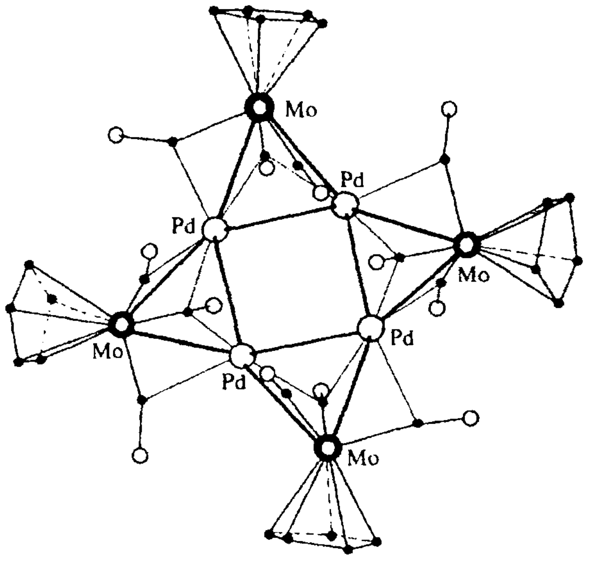


Fig. 2. The molecular structure of cluster **4** based on the data of single-crystal X-ray study.[36]

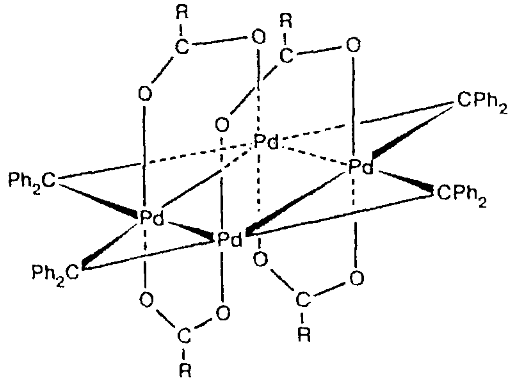
bonds. Three carbonyl ligands are bound to each Mo atoms: one of these carbonyls is a μ^3-bridge on the Pd_2Mo face and the two others are bridges at the Pd—Mo bonds.

During the formation of the octanuclear cluster, not only substitution of the acetate ligands for the $CpMo(CO)_3^-$ anions occurs but also the displacement of the CO molecules takes place. The vacancies in the coordination sphere of the Pd atom that become free are occupied by the bridging CO molecules coordinated to the Mo atom. This process is not limited by the ligand substitution: during the reaction, the Pd^{1+} atoms are reduced, due likely to the one-electron oxidation of the $CpMo(CO)_3^-$ anions. If one assumes that the Mo atoms entering the complex retain the zero oxidation state, then the transformation observed can be treated as the reduction of Pd^{1+} to $Pd^{0.5+}$. The $[CpMo(CO)_3]_2$ dimer formed due to the one-electron oxidation of $CpMo(CO)_3^-$ was found in the reaction products. The cluster obtained is the first example of the compound in which eight metal atoms with the metal—metal bonds are arranged in the same plane.

The reaction of cluster **3** with diphenyldiazomethane, which is capable of generating *in situ* diphenylcarbene species, results in the displacement of the CO groups and the formation of complex **5** containing diphenylcarbene as a ligand.

$Pd_4(CO)_4(OAc)_4 + Ph_2CN_2 \longrightarrow$
3
$\longrightarrow Pd_4(CPh_2)_4(OAc)_4 + 4\ CO + 4\ N_2$
5

According to the EXAFS data, the coordination environment of each Pd atom in molecule **5** includes two metal atoms at a distance of 2.67 Å, one metal atom at the a distance of 3.65 Å as well as two light atoms at distances of 1.86, 2.03, and 3.25 Å from each Pd atom; this is in good agreement with the structure presented below.[37–39]



The reactivities of the coordinated carbonyl and diphenylcarbene ligands were compared using the carbonylacetate (**3**) and carbeneacetate(**5**) clusters as examples. It was found that during thermolysis of the clusters in the absence of oxygen, the inner-sphere oxidation of the neutral ligands occurs to form CO_2 and Ph_2CO, respectively. The reaction involves the transfer of the O atom from the carboxylate group to the carbonyl or diphenylcarbene ligand, *i.e.*, the acetate group operates as an oxygen donor (an oxidant).[40–42]

$Pd_4Q_4(OAc)_4 \longrightarrow Pd + Q{=}O + Ac_2$

$Q = CO, CPh_2$

During thermolysis of a solution of cluster **3** in benzene or toluene, most of the CO_2 that is formed, as one could expect, due to the oxidation of the coordinated CO, is incorporated into the arylcarboxylic acid.

$Pd_4(CO)_4(OAc)_4 + Ar{-}H \longrightarrow Pd + ArCOOH + \ldots$
3

$Ar = Ph, MeC_6H_4$

One can assume that the formation of arylcarboxylic acids involves the oxidative addition of benzene or toluene to the palladium cluster framework along with the oxidation of the coordinated CO. The CO_2 formed is inserted into the C—H bond of the solvent molecule without leaving the coordination sphere of the cluster, forming the corresponding carboxylic acids.

The coordinated carbon monoxide in the transition metal complexes is known to be oxidized by the outer-sphere oxidants, *e.g.*, trimethylamine *N*-oxide, or by other compounds containing the N=O group.[43,44]

$$R_3N{=}O + L_nM(CO)_m \longrightarrow R_3N + CO_2 + L_nM(CO)_{m-1}$$

The study of the reactions of cluster **3** with nitrobenzene, nitrosobenzene, azoxybenzene, phenylhydroxylamine, and trimethylamine *N*-oxide showed that among all compounds containing the NO group, only nitrosobenzene and phenylhydroxylamine are capable of oxidizing the coordinated carbon monoxide under mild conditions, analogously to trimethylamine *N*-oxide.

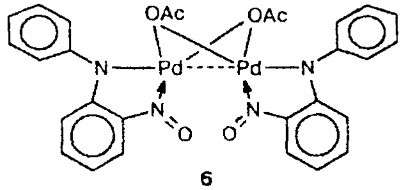
$$\underset{\mathbf{3}}{Pd_4(CO)_4(OAc)_4} + Me_3NO \longrightarrow$$
$$\longrightarrow Pd + CO_2 + Me_3N + Ac_2 + \ldots$$

$$\underset{\mathbf{3}}{Pd_4(CO)_4(OAc)_4} + PhNHOH \longrightarrow$$
$$\longrightarrow Pd + CO_2 + PhNH_2 + Ac_2 + Ac_2O + \ldots$$

$$\underset{\mathbf{3}}{Pd_4(CO)_4(OAc)_4} + PhNO \longrightarrow$$
$$\longrightarrow \underset{\mathbf{6}}{\overline{Pd_2(\mu\text{-}OAc)_2(Ph{-}N}{-}C_6H_4{-}NO)_2} + CO_2 +$$
$$+ PhN(O){=}NPh$$

In these reactions, the carboxylate ligands of cluster **3** compete with the NO-containing compounds in the oxidation of the coordinated CO, forming diacetyl or acetic anhydride.[45]

In the reaction of cluster **3** with PhNO, a complex of composition $Pd_2(\mu\text{-}OAc)_2(Ph{-}N{-}C_6H_4{-}NO)_2$ (**6**) is formed along with the organic products of transformation of the NO-containing compound (azoxybenzene, azobenzene, and aniline). According to the single-crystal X-ray structural analysis of complex **6**, two Pd atoms with a distance of 2.8 Å between them are bound through two acetate bridging ligands.[46] In addition, a new ligand, phenyl-*o*-nitrosophenylamide, is coordinated to each metal atom by two N atoms.



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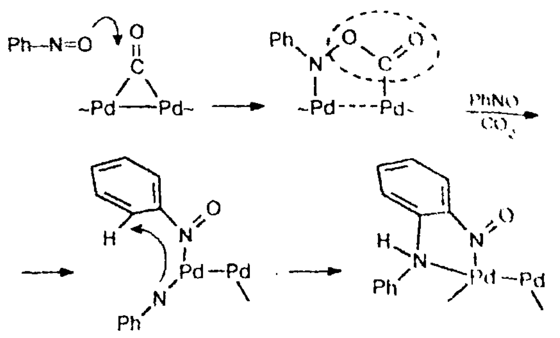
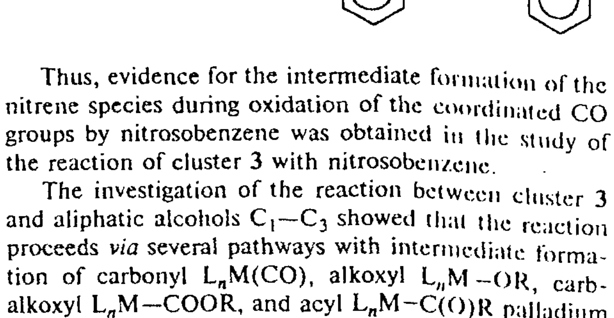
One can assume that the formation of the amide ligand involves the coordination of the nitrobenzene molecule, the insertion of CO into the Pd—O bond followed by the elimination of CO_2, and the reaction of the nitrene species formed with the second nitrobenzene molecule (the insertion of nitrene into the *ortho*-position of the phenyl ring) according to Scheme 8.

Scheme 8



The deprotonation of phenyl-*o*-nitrosophenylamine results in the amide found.

In the system **3**—nitrobenzene, reactions involving labile nitrene species occur to form the following compounds:

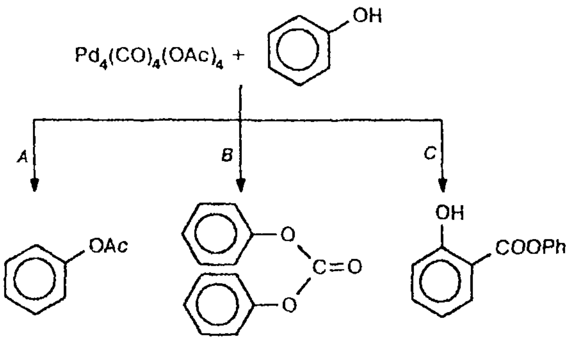


Thus, evidence for the intermediate formation of the nitrene species during oxidation of the coordinated CO groups by nitrosobenzene was obtained in the study of the reaction of cluster **3** with nitrosobenzene.

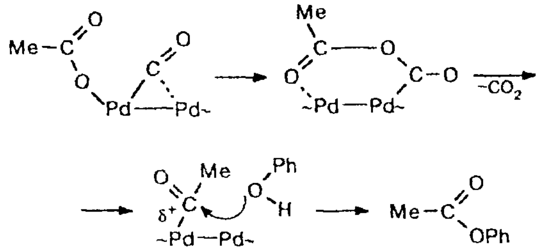
The investigation of the reaction between cluster **3** and aliphatic alcohols C_1—C_3 showed that the reaction proceeds *via* several pathways with intermediate formation of carbonyl $L_nM(CO)$, alkoxyl $L_nM{-}OR$, carbalkoxyl $L_nM{-}COOR$, and acyl $L_nM{-}C(O)R$ palladium compounds.[57,58] When cluster **3** reacts with ethanol, both diethyl carbonate and carbonyl compounds, acetaldehyde and its acetal, are formed. Diisopropyl carbonate, acetone, and its ketal are the reaction products in the case of isopropyl alcohol. The reaction of cluster **3** with methanol affords only methyl acetate.

When cluster **3** reacts with phenol, transformations through three pathways are observed which lead to phenyl acetate, diphenyl carbonate, and phenyl salicylate (Scheme 9, pathways *A*, *B*, and *C*, respectively).

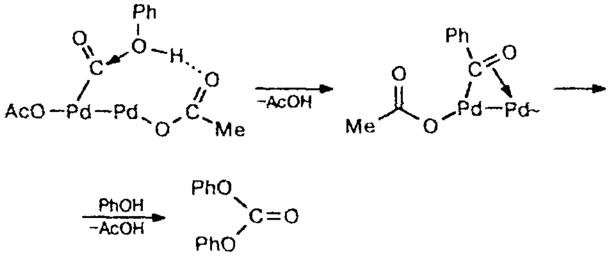
Scheme 9



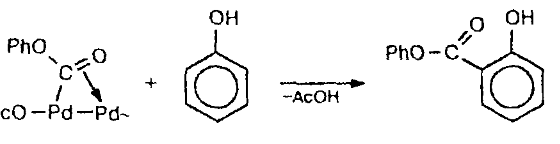
The esterification of the OAc$^-$ anion *via* pathway *A* likely involves the insertion of the CO group into the >Pd—OAc bond to form the unstable intermediate >Pd—C(O)OAc, the elimination of CO_2, and attack of the phenol molecule on the acetyl ligand formed.



The formation of diphenyl carbonate *via* pathway *B* seems to be the result of the nucleophilic attack of the PhOH molecule on the carbonyl ligand.



Salicyl ester appears as the result of the attack of the coordinated group PhOC(O)— on the aromatic ring of the phenol molecule.



Thus, both giant and low-molecular palladium clusters exhibit high and diverse reactivity in stoichiometric and catalytic reactions involving organic compounds and carbon monoxide. The study of these reactions makes it possible to obtain useful information on the mechanisms of the key stages of important industrial processes catalyzed by palladium and its complexes.

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