Synthesis and catalytic activity of carbonyl palladium clusters

Ilya I. Moiseev

N.S.Kurnakov Institute of General and Inorganic Chemistry
USSR Academy of Sciences, Moscow 117907, USSR

Abstract – Palladium carbonyl acetate (PCA), a tetranuclear
cluster with a planar nearly rectangular metal skeleton, and
related clusters were synthesized. Clusters with planar
square or tetrahedral Pd metal cores were prepared by
reacting PCA with Na[CpMo(CO)$_3$] or 1,10-phenanthroline (Phen) ,
respectively. Palladium carbonyl hydrides of type
[PdPhen(CO)H(OAc)]$_n$, where n = 2 or 4, were synthesized and
shown to be catalysts for hydrogenation and olygomerization
of alkenes and alkynes. Anionic octanuclear cluster
Na$_2${Pd$_4$[CpMo(CO)$_3$]$_4$} containing Pd-Mo bonds provides
dehydration of alcohols evidently via a carbene mechanism.
Products of decarbonylation of Pd phenantroline carbonyl
clusters were shown to be active catalysts for oxidative
acetoxylation and alcoxylation of unsaturated hydrocarbons.

INTRODUCTION

Palladium (II) complexes have been known for a long time to be the catalysts
for many oxidative reactions (ref.1–3). Up to 1975, when our study was
launched some of these reactions have been suggested to be really catalyzed
by polynuclear compounds of palladium in oxidative states lower than (+2).
In search for such catalytically active compounds or their models we have
turned to the methods of metal-carbonyl chemistry as a useful tool for the
synthesis of polynuclear compounds. The methods of the synthesis of
carbonyl Pd complexes with phosphine ligands are well known now (ref.4–11).
However, phosphine, arsine and related ligands are readily oxidized.
Bearing in mind the search of materials for oxidative catalysis, we have
chosen α,α'-bipyridine (Bipy), 1,10-phenanthroline (Phen), and related hard-
oxidizable compounds as stabilizing ligands. Necessary CO ligands were ass-
umed to be removed in either event at the final steps of the synthesis. Our
study have resulted in a series of polynuclear Pd compounds including
so-called giant Pd clusters (ref.12). In the course of this study we have
obtained a number of low-molecular carbonyl palladium clusters. Their
chemistry is the subject of the paper.

PALLADIUM CARBONYL ACETATE CHEMISTRY

When solutions of palladium (II) carboxylate Pd(OCOR)$_2$ (R = Me, Et or Ph)
are contacted with CO, reduction of Pd (II) to Pd metal usually occurs.
In glacial acetic acid containing alkali metal acetates, reduction of
Pd(OAc)$_2$ with CO results in formation of palladium metal, acetic anhydride,
and CO$_2$ (ref.13):

$$Pd(OAc)_2 + CO \longrightarrow Pd + (Ac)_2O + CO_2 \qquad (1)$$
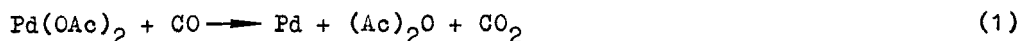
In carboxylic acids or (carboxylic acid+benzene) mixtures as solvents, in
the abscence of alkali metal acetates, we obtained relatively stable
complexes of stoichiometry RCOO•Pd•CO•nRCOOH where n = 0.5 or 0. Thus,
carbonylation (1 atm of CO) of Pd(OAc)$_2$ in glacial acetic acid at 50°C
gave AcO•Pd•CO•0.5AcOH (1). Crystals of 1 lose 0.5 mol of acetic acid per
1 g.-atom of palladium when kept for about 10 days in vacuo over KOH at
20°C forming palladium carbonyl acetate (PCA) AcO•Pd•CO (2).IR spectra of the
complexes show two strong absorption bands in C-O stretching region at 1934

and 1975 cm^{-1} for 1 and 1940 and 1975 cm^{-1} for 2 in addition to frequencies
corresponding to the bidentate coordinated acetate ligands (ref.13).
According to X-ray analysis data, crystals of 1 consist of tetranuclear
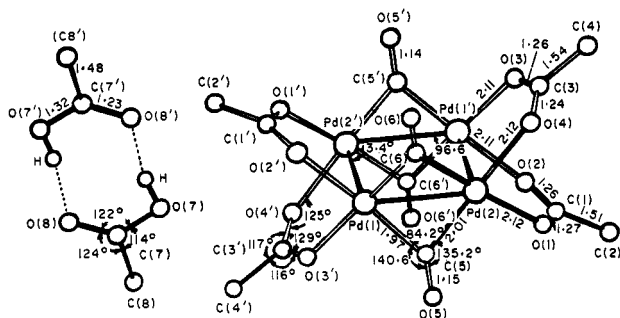clusters $Pd_4(CO)_4(OAc)_4$ and hydrogen-bonded dimeric molecules of AcOH
(Fig.1).

Fig.1. Structure of $Pd_4(CO)_4(OAc)_4$.
•2 AcOH.

The Pd_4 framework of the
cluster is nearly
rectangular, with almost
right angles (83.4° and
96.6°). Acetate-bridged
Pd-Pd distances (2.909 Å)
are longer, and the CO-
bridged ones (2.663 Å) are
shorter than the shortest
Pd-Pd distance (2.751 Å)
in Pd metal (ref.13).
Reaction of palladium (II)
propionate with CO gave
a PCA analogue, palladium
carbonyl propionate
$Pd_4(CO)_4(OCOEt)_4$. Similarly,
palladium carbonyl benzoate
$Pd_4(CO)_4(OCOPh)_4$ was
prepared by reacting
palladium (II) benzoate
with CO in (benzoic acid +
+ benzene) solution . The
similarities in CO and COO
regions of IR spectra, the
chemical compositions and
chemical behavior of these
complexes and corresponding
properties of PCA suggest
that all of them contain tetranuclear Pd cluster the same as PCA.
Therefore, PCA synthesis depicted by eq.2

$$4 \ Pd(OAc)_2 + 8 \ CO \longrightarrow Pd_4(CO)_4(OAc)_4 + 2 \ (Ac)_2O + 4 \ CO_2 \qquad (2)$$
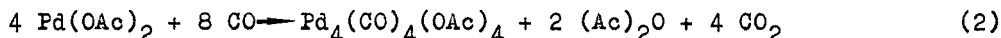
offers a general way to palladium (I) carbonyl carboxylates.

Kinetic study showed that the rates of PCA accumulation at 40°C obey a
total second-order equation (ref.14):

$$w = k_{PCA}\left[Pd(II)\right]\left[CO\right]$$

In AcOH solutions, in the   absence of alkali metal acetate, at 25–40°C
palladium (II) acetate is a trimer $Pd_3(OAc)_6$ and dissociates slowly. The
observed first-order dependence on both Pd(II) and CO concentrations suggests that
CO is coordinated with trinuclear palladium (II) acetate at the first stage
of the reaction. Reduction of $Pd(OAc)_2$ with CO was studied also in anhydrous
us benzene to elucidate possible ways of further reactions of trinuclear
carbonyl palladium (II) intermediate complex. Addition of benzene to AcOH
solutions was found to give no retardation the PCA formation from $Pd(OAc)_2$
and CO. Volumetric experiments at 60°C showed that benzene solutions of
$Pd(OAc)_2$ absorb nearly 2 moles of CO per 1 g.-atom of Pd. CO_2 appears in
gaseous phase along with CO absorption though no precipitation of Pd metal
occured. After treatment with CO, a light brown residue was isolated, IR
spectrum of which showed a band at 1810 cm^{-1} ascribed to acyl group bonded
to palladium (II) atom. Further evedence for intermediate formation of
acyl-palladium (II) complex was provided by trapping of this complex with
H_2O, ethanol, dihydrogen, and sodium acetate to give acetic acid, ethyl
acetate, acetaldehyde, and acetic anhydride, respectively.
The stoichiometric and kinetic data led to conclusion that the reaction of
trinuclear carbonyl palladium (II) complex includes CO insertion into Pd-OAc
bond followed by CO_2 elimination resulting in formation of acylic palladium
(II) complex $Pd_3(\mu\text{-}OAc)_4(OAc)COCH_3$.

The coordinated OAc groups in PCA are rather readily replaced by other
carboxylic anions by reactions of the corresponding acid with PCA. Thus,
PCA was recrystallized from trifluoroacetic acid to give a crystalline
complex $Pd_4(CO)_4(OCOCF_3)_4$. Complexes $Pd_4(CO)_4(OCOCCl_3)_4$ and
$Pd_4(CO)_4(OCOCH_2Cl)_4$ were obtained by recrystallization of PCA from benzene
solutions containing CCl_3COOH and $CH_2ClCOOH$, respectively , see eq. 3.

$$Pd_4(CO)_4(OAc)_4 + RCOOH \longrightarrow Pd_4(CO)_4(OCOR)_4 + AcOH \qquad (3)$$
$$R = CF_3, \ CCl_3, \ CH_2Cl.$$
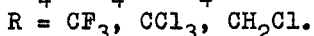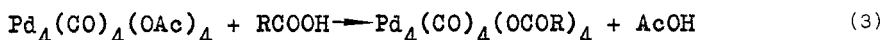
The similarities in IR spectra, chemical behaviour, and stoichiometry of these compounds with the related data of PCA suggest that all the complexes are analogous to PCA.

The anionic octanuclear cluster $Na_2\{Pd_4[CpMo(CO)_3]_4\}$·2 THF ($\underline{3}$) was obtained by reaction of PCA with $Na[CpMo(CO)_3]$ in THF (ref.15). X-ray diffraction data showed that the structural unit of the complex $\underline{3}$ contains the centrosymmetric anion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$ (Fig.2), two sodium cations, and two THF molecules. The cluster $\underline{3}$ has a square planar configuration with

Fig.2. Structure of $Pd_4[CpMo(CO)_3]_4^{2-}$ cluster dianion.

Pd-Pd distances 2.675-2.691(2) Å. Each of the Mo atoms is connected with two Pd atoms [Pd-Mo 2.723-2.741(2) Å], all the metal atoms lying in the same plane.
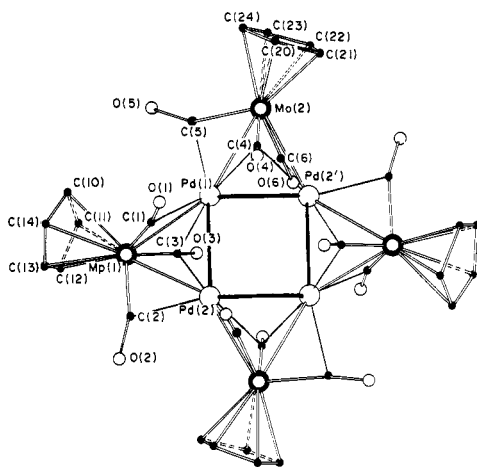Neutral molecular clusters $[Pt_2M_2W_4(\mu\text{-CR})(\mu_3\text{-CR})_3(\mu\text{-CO})$·$(CO)_7(\eta\text{-Cp})_4]$·$CH_2Cl_2$, where $M = Pt$, Ni; $R = C_6H_4Me\text{-}4$, with metal core similar to that of $\underline{3}$ were synthesized recently (ref.16).
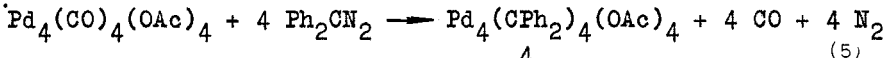The three carbonyl ligands attached to each Mo atoms approach Pd, one of them in a triply bridging mode, $\mu_3\text{-CO}$, Pd-C 2.22-2.45(2) Å, and two others are doubly bridging ligands, $\mu\text{-CO}$, Pd-C 2.34-2.36 Å. IR spectrum of $\underline{3}$ displays bands at 2000, 1945, 1900, 1870, and 1830 cm^{-1} corresponding to coordinated CO ligands. The environment of each Mo and Pd atom is

similar to that in the known cluster $Pd_2Mo_2(Cp)_2(\mu\text{-CO})_4(\mu_3\text{-CO})_2(PEt_3)_2$ (ref.8). Formation of cluster $\underline{3}$ from PCA is accompanied by displacement of OAc ligands by $CpMo(CO)_3^-$ anions and by elimination of some carbonyl ligands. Moreover, the reaction is not restricted to ligand substitution processes. Assuming that Mo atoms retain their zero oxidation state as in initial $Na[CpMo(CO)_3]$, the observed reaction may be formally described as reduction of $Pd(+1)$ to $Pd(+1/2)$, according to eq. 4.

$$Pd_4(CO)_4(OAc)_4 + 6 \ Na[CpMo(CO)_3] \longrightarrow Na_2[Pd_4Mo_4Cp_4(\mu\text{-CO})_8(\mu_3\text{-CO})_4] +$$
$$+ [CpMo(CO)_3]_2 + 4 \ NaOAc + 4 \ CO$$
$$(4)$$
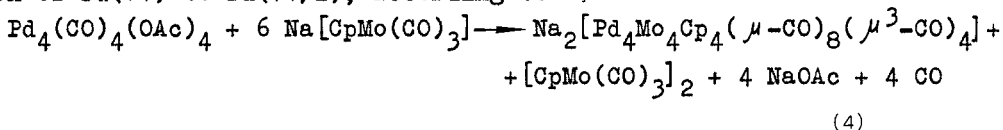
Reaction of PCA with diphenyldiazomethane in benzene solutions resulted in the substitution of CO groups with carbene ligands (ref.17) as described by eq. 5.
$$Pd_4(CO)_4(OAc)_4 + 4 \ Ph_2CN_2 \longrightarrow Pd_4(CPh_2)_4(OAc)_4 + 4 \ CO + 4 \ N_2$$
$$\underset{\underline{4}}{} \qquad (5)$$
Hydrogenation of diphenylcarbene palladium acetate $\underline{4}$ proceeds through the cleavage of Pd-C bonds yielding diphenylmethane and Pd metal as described by eq. 6.
$$Pd_4(CPh_2)_4(OAc)_4 + 6 \ H_2 \longrightarrow 4 \ Ph_2CH_2 + 4 \ AcOH + 4 \ Pd \qquad (6)$$
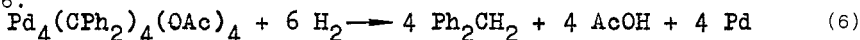
In contrast to hydrogenation of $\underline{4}$, reaction of PCA with H_2 gives no CO hydrogenation products under similar conditions:

$$Pd_4(CO)_4(OAc)_4 + 2 \ H_2 \longrightarrow 4 \ Pd + 4 \ CO + 4 \ AcOH \qquad (7)$$
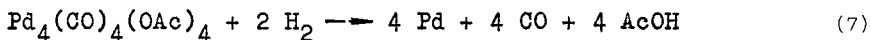
By analogy with CO, free carbene species or carbene donors were expected to reduce Pd(II) complexes resulting in Pd carbene complexes similar to PCA. However, our attempt to perform such a reaction with $Pd(OAc)_2$ and Ph_2CN_2 in

benzene solution showed that diphenyldiazomethane decomposed yielding N_2 and benzophenone azine as the main products. The reaction also gives rise to an orange palladium complex isolated from reaction mixture. ^{1}H NMR and IR spectra, elemental analysis data, and molecular weight measurements permit to regard this complex as a tetranuclear one containing four bridging acetate groups and two tentatively triply palladated benzophenone azine molecules as ligands (ref.18). Upon heating in AcOH as a proton-donor solvent, this compound transformed into the complex $Pd_3(OAc)_4(Ph_2(C_6H_4)_2-C_2N_2)$ (5). According to X-ray data, the molecule of complex 5 contains a bent chain of three Pd atoms bridged with four acetate ligands. The terminal Pd atoms of the chain are bonded to the double ortho-palladated benzophenone azine molecules forming two palladocycles. The Pd-N bonds, 1.98-1.99(1) Å in length, are situated at the Pd_3 plane while the Pd-C bonds of 1.96-1.97 Å are perpendicular to 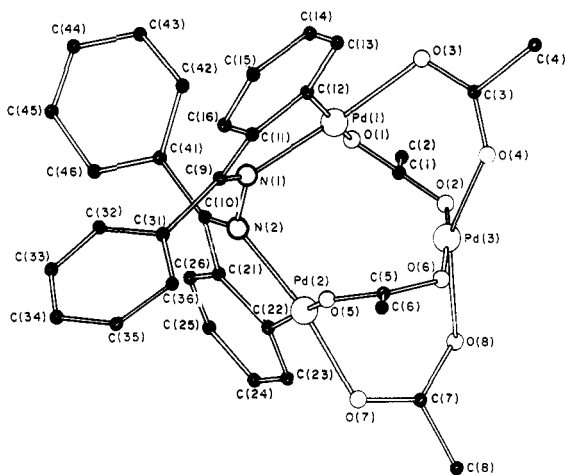t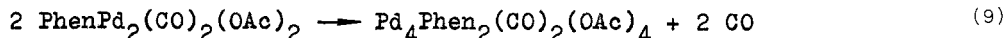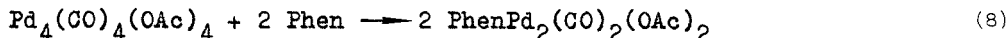he plane (Fig.3). Geometry of $Pd(C_6H_4)(CPh)N-N$ fragment is similar to that of mononuclear complex $ClBrPd(C_6H_4)(CMe)N-NHPh$ (ref. 19).

Reactions between PCA and bidentate N-ligands such as Phen, Bipy and their analogs led to a number of complexes depending on temperature and Pd:ligand ratio. Addition of Phen to PCA in AcOH solutions initiates at 25-90°C reversible CO evolution. Volumetric data for this reaction at 25°C and Phen:Pd $\approx$ 2:1 are in good agreement with eq. 8-9 supposing PCA to be split into binuclear species $PhenPd(CO)_2(OAc)_2$ in AcOH solutions containing Phen. Under this assumption, the experimental data were found to be described by eq. 10 with equilibrium constant $K = (1.2\pm0.1)\cdot10^{-4}$ mol/l at 25°C (ref.20):

Fig.3. Structure of $Pd_3(\mu\text{-}OAc)_4 \cdot \mu^4\text{-}C_6H_4(Ph)C=N-N=C(Ph)C_6H_4$.

$$Pd_4(CO)_4(OAc)_4 + 2 \text{ Phen} \longrightarrow 2 \text{ } PhenPd_2(CO)_2(OAc)_2 \qquad (8)$$

$$2 \text{ } PhenPd_2(CO)_2(OAc)_2 \longrightarrow Pd_4Phen_2(CO)_2(OAc)_4 + 2 \text{ } CO \qquad (9)$$

$$K = [Pd_4Phen_2(CO)_2(OAc)_4][CO]^2 / [PhenPd_2(CO)_2(OAc)_2]^2 \qquad (10)$$

Further CO loss observed at higher temperatures is asuumed to be decarboxylation of complex $Pd_4Phen_2(CO)_2(OAc)_4$. Volumetric data at 90°C correspond to reversible loss of 1 mole of CO per 4 Pd atoms, in accord with eq.6.

$$Pd_4Phen_2(CO)_2(OAc)_4 \longrightarrow Pd_4Phen_2(CO)(OAc)_4 + CO \qquad (11)$$
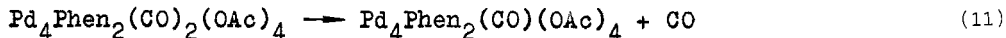
The last CO molecule can be removed only irreversibly by heating solutions of $Pd_4Phen_2(CO)(OAc)_4$ in AcOH in O_2 atmosphere at 90°C as depicted by eq.7

$$Pd_4Phen_2(CO)(OAc)_4 + O_2 \longrightarrow Pd_4Phen_2(OAc)_x + Pd(OAc)_2 + $$
$$+ PdPhen(OAc)_2 + CO_2 \qquad (12)$$
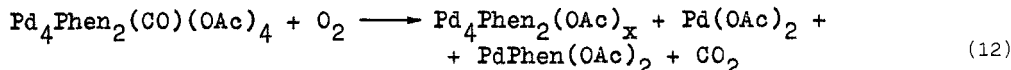
Disproportionation and partial oxidation of Pd atoms contained in the starting $Pd_4Phen_2(CO)(OAc)_4$ complex give rise to Pd(II) complexes $Pd(OAc)_2$ and $PhenPd(OAc)_2$, and to compound of the composition $Phen_2Pd_4(OAc)_x$, x = 1-3, the last being stable under conditions of oxidative decarbonylation.

By reacting PCA with Phen at a ratio Phen:Pd = 1:1 in AcOH solutions in Ar atmosphere, complex $Pd_4(CO)_2Phen_4(OAc)_4$ was prepared in accord with eq. 13 (ref.21) .

$$Pd_4(CO)_4(OAc)_4 + 4 \text{ Phen} \longrightarrow Pd_4(CO)_2Phen_4(OAc)_4 + 2 \text{ CO} \tag{13}$$
$$\underset{\underline{6}}{}$$
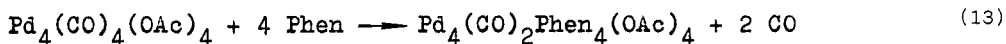
IR spectrum of $\underline{6}$ shows a strong band at 1800 cm^{-1} corresponding to the bridging CO group stretching mode. X-ray analysis data showed that $\underline{6}$ contained a nearly tetrahedral cluster of palladium atoms (Fig.4).
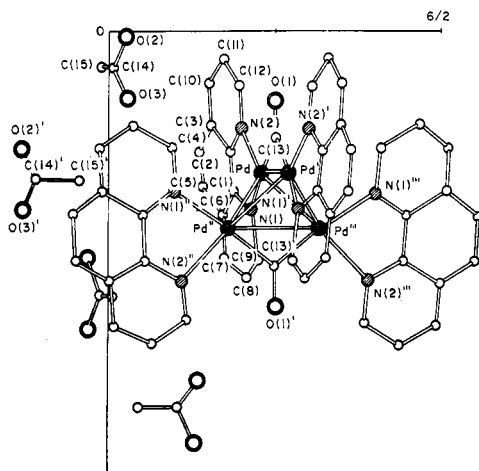

Fig.4. Structure of $[Pd_4(CO)_2Phen_4](OAc)_4$

Two edges of the tetrahedron with CO bridges are slightly longer (2.809(6) Å) than the non-bridged ones (2.718(6) Å). Both distances are noticeably longer than the shortest Pd-Pd distance in Pd metal. As comparison with PCA geometry (Fig.1) shows, formation of complex $\underline{6}$ from PCA is accompanied by shortening of AcO-bridged bonds and lengthening of CO-bridged ones. All OAc ligands of PCA molecule are displaced to the outer sphere when tetra-cation $Pd_4(CO)_2Phen_4{}^{4+}$ is formed. On the basis of these data, the first step of the reaction of PCA with Phen was proposed (ref.21) to be substitution of OAc ligands by Phen molecules to split PCA cluster into two complex di-cations $PhenPd(CO)_2PdPhen^{2+}$, as depicted by eq. 14.

$$Pd_4(CO)_4(OAc)_4 + 4 \text{ Phen} \longrightarrow 2 \text{ PhenPd(CO)}_2PdPhen^{2+} + 4 \text{ OAc}^- \tag{14}$$
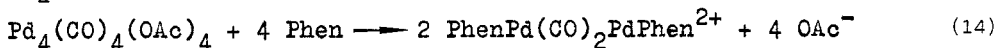
The next CO ligand was supposed to be eliminated from the cationic intermediate to form complex di-cation $\underline{7}$:

$$PhenPd(CO)_2PdPhen^{2+} \longrightarrow PhenPd(CO)PdPhen^{2+} + CO \tag{15}$$
$$\underset{\underline{7}}{}$$
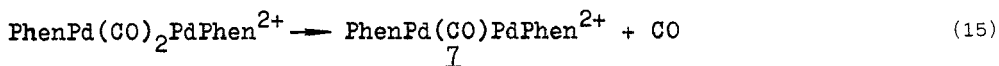
Tetrahedral cluster $\underline{6}$ is conceivably formed by dimerization of coordinatively unsaturated species $\underline{7}$. The shortest distance between the axes of PhenPd(CO)PdPhen groups in cluster $\underline{6}$ (see Fig.4) was found to be equal to ca.1.8 Å (ref.21). At this distance, overlapping between the two PhenPd(CO)PdPhen group orbitals might be effective enough to contribute into the core stabilization of cluster $\underline{6}$. By treating with CO solutions of $Pd(OAc)_2$ and Phen (Pd:Phen = 1:1) in AcOH at 20°C complex $Pd_4(CO)_4Phen_4 \cdot (OAc)_4$ ($\underline{8}$) characterized by elemental analysis data, molecular weight and IR spectrum was obtained, as shown by eq. 16.

$$4 \text{ Pd(OAc)}_2 + 4 \text{ Phen} + 4 \text{ CO} \longrightarrow Pd_4(CO)_4Phen_4(OAc)_4 + 4 \text{ CO}_2 \tag{16}$$
$$\underset{\underline{8}}{}$$
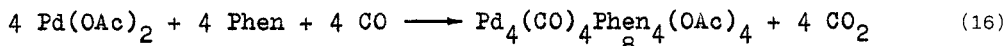
In a tetrahedron, six edges are available which could be occupied by CO ligands. In fact, along with the complex $\underline{8}$ some higher carbonyl complexes are seemingly formed as by-products of carbonylation of $Pd(OAc)_2$ under the conditions of reaction 10. Another side reaction might be a reductive carbonylation resulting in carbonyl hydrides. Thus, a complex of a tentative composition $[PdPhen(CO)H(OAc)]_n$ was obtained by carbonylation of complex $\underline{8}$ in AcOH solution at 50°C. IR and ^{1}H NMR spectra show a band at 1700 cm^{-1} (bridging CO group) and a singlet at -15.3 ppm (H atom in a bridging position), respectively. Molecular weight of the compound in ethanol solution was found to correspond to n = 4 (M.W.found 1420, M.W. calc. for $[PdPhen(CO)H(OAc)]_4$ is equal to 1498). This value seems to be a lower limit of the molecular weight since conductivity of the complex in ethanol and

other polar solvents corresponds to one of a weak electrolyte. Nevertheless, the data suggest the complex may be formulated as $Pd_4Phen_4(CO)_4H_4(OAc)_4$ (9), its formation being depicted as follows:

$$Pd_4Phen_4(CO)_4 (OAc)_4 + 2 CO + 4 AcOH \longrightarrow Pd_4Phen_4(CO)_4H_4 (OAc)_4 +$$
$$+ 2 CO_2 + Ac_2O \qquad (17)$$
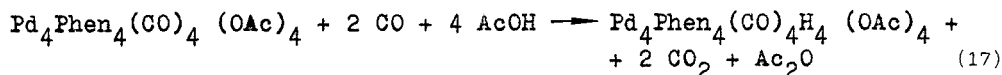
The amounts of CO consumed and CO_2 formed are in accord with eq.11. Another way to complex 9 could be hydrogenation of complex 8. At the exposition of solutions of 8 in AcOH under H_2 at 20-50°C, 2 moles of H_2 per mole of complex 8 were absorbed. IR and ^1H NMR spectra of the complex obtained reveal a band at 1790 cm^{-1} and singlet at -15.3 ppm, respectively, coinciding with those for complex 9 (ref.22). The elemental analysis data could be brought into accord with the formula $[PdPhen(CO)H(OAc)]_n$ coinciding with that of complex 9. However, the molecular weight data correspond to n = 2 in the above formula (M.W.found 800, M.W.calc. for $[Pd Phen(CO)H(OAc)]_2$ is equal to 749). Therefore, this complex may be formulated as $Pd_2Phen_2(CO)_2H_2 \cdot (OAc)_2$ (10).

Complexes related to 9 and 10 were prepared by hydrogenation of AcOH solutions containing $Pd(OAc)_2$ and Phen (Phen:Pd ratio 1:1) and following carbonylation of the solution (ref.22). The product of hydrogenation was found to be a polynuclear hydride complex of composition $[Pd_4PhenH_4(OAc)_2]_n$ (11) where n 100 (ref.23). A carbonyl hydride substance, possibly a mixture of complexes, of average composition $Pd_4Phen_3(CO)_4H(OAc)_3$ (12) was obtained by carbonylation of complex 11. ^1H NMR and IR spectra of complex 12 are similar to those for complexes 9 and 10.

CATALYTIC REACTIONS

PCA has been shown to be an intermediate compound in the reductive carbonylation of $Pd(OAc)_2$ in AcOH solutions containing NaOAc, as a result Ac_2O and Pd metal were formed (see eq.1). This reaction being combined with reoxidation step

$$Pd + Ox + 2 AcOH \longrightarrow Pd(OAc)_2 + Red \qquad (18)$$
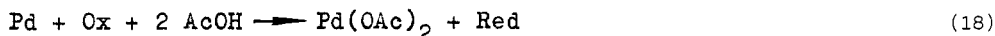
(Ox is an oxidant, Red is a reduced form of the Ox) could be used to produce carboxylic acid anhydride under mild conditions as depicted by eq. 19.

$$AcOH + CO + Ox \longrightarrow (Ac)_2O + CO_2 + Red \qquad (19)$$
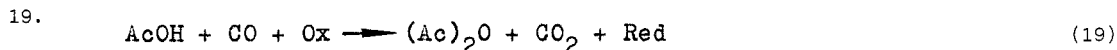
Dehydration of AcOH is usually performed at high temperatures (500-600°C) because of thermodynamic restrictions:

$$2 AcOH \longrightarrow (Ac)_2O + H_2O, \quad \Delta G^o_{298} = +12 \text{ kcal/mole} \qquad (20)$$
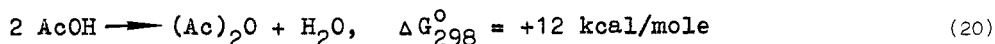
Reaction (12) inherently includes oxidation of carbon monoxide (eq.14):

$$CO + Ox \longrightarrow CO_2 + Red \qquad (21)$$
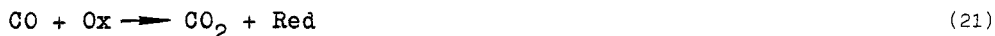
as a complementary exoenergetic reaction. In the case of $Ox = O_2$ and Red = H_2O, the thermodynamics of reaction 21 is characterized by $\Delta G_{298} = -61$ kcal/mole. So overall process 19, as a sum of reactions 20 and 21, is characterized by $\Delta G^o_{298} = -49$ kcal/mole permitting the reaction at room temperature. However, in the case of $Ox = O_2$, water should be removed from reaction mixture effectively because CO oxidation

$$CO + 1/2 O_2 \longrightarrow CO_2$$
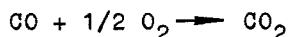
dominates in AcOH-water solution .
PCA was found to be inert towards alkenes and was decomposed in H_2 atmosphere. Acetylene is polymerized in AcOH solutions of PCA and converts into vinylacetate with a small yield. No oxidation of alkenes or arenes was observed in the presence of PCA in AcOH or alcohol solutions. However, addition of Phen to PCA solution results in formation of an active catalyst arising from PCA decarbonylation by the action of Phen and O_2 (see eq. 9,11, 12). Thus, propylene and 2-methylpropene were oxidized at 20°C and 1 atm in methanol solutions which initially contained Phen and PCA at a ratio Phen: Pd = 1:1. Selective formation of allylmethyl and methallylmethyl ethers was observed under these conditions (ref.24).

The catalyst of this reaction seems to be a complex of type $Pd_4Phen_2(OAc)_x$ (see eq.12). In contrast with this complex, palladium (II) compounds are known to provide catalytic oxidation of alkenes and alcohols into acetals and ketals (ref.2). The same complex was found to be a catalyst for oxidative acetoxylation of alkylarenes (ref.25) and alkenes (ref.26). It is noteworthy that alkylarenes undergo oxidative substitution into aromatic ring in the presence of Pd (II) compounds instead of side-chain substitution. In the presence of Pd (II) complexes alkenes are mainly converted into vinyl esters (ref.1,2), carbonyl compounds being the main products in the reaction mixtures containing more than 1% of water. In contrary to that, no water influence was observed in the presence of $Pd_4Phen_2(OAc)_x$.

Contrary to expectations, complexes 9 and 10 do not catalyze isomerisation of 1-alkenes in spite of the presence of coordinated hydrogen. Both IR band at 1790 cm^{-1} and singlet at -15.3 ppm in ^1H NMR spectrum disappeared after addition of unsaturated compounds to the solutions of the complexes in AcOH or alcohols. Saturation of the solution with ethylene gives rise to ethyl acetate, propionic aldehyde, and diethyl ketone in amounts commensurable with those of the complex used. The reaction may be pictured as the insertion of alkene molecule into Pd-H bond followed by carbonylation of the Pd-alkyl bond formed. The $Pd-COC_2H_5$ fragment arised seemingly undergoes insertion of the second C_2H_4 molecule and/or hydrogenolysis by the coordinated hydrogen to give rise to diethyl ketone and propionic aldehyde, correspondingly. Ethyl acetate is assumed to be formed as a result of AcOH attack on Pd-Et bond formed initially. The final Pd compounds, which might contain C_2H_4 and Phen molecules as stabilizing ligands, were found to be active in oligomerization of ethylene into butenes and hexenes. The complexes provide also catalytic hydrogenation of alkenes and alkynes under H_2 atmosphere at 25-50°C. The reaction is neither fast nor selective. Thus, hydrogenation of phenylacetylene at 50°C and 1 atm of H_2 in the presence of 9 or 10 as the starting compounds for catalyst formation was found to give styrene in 35-50% yield and ethylbenzene, 10-20%, after 24 h. No hydroformylation nor alkoxycarbonylation occured in the presence of Pd phenanthroline carbonyl hydrides.

Pd,Mo-cluster 3 was found to be a catalyst for alcohol oxidation. Thus, methanol is converted into methyl formate, oxidation of ethanole gives rise to diethyl acetal, and that of benzyl alcohol results in benzaldehyde formation at 60-80°C and 1 atm of O_2. The starting complex was destroyed under reaction conditions and the observed catalytical activity was due to the products of oxidation of the starting cluster 3. Dehydration of alcohols in the presence of Pd,Mo-cluster was found to proceed at 60-80°C under Ar atmosphere or in vacuo (ref.27). No ethers were found in the reaction mixture. In the case of methanol and ethanol the main product of dehydration is white wax-like substance. trans-Stilbene was obtained by dehydration of benzyl alcohol. Dehydration of alcohols under essentially non-acidic conditions is rather unexpected. No less unusual feature of the reaction is the dehydration of methanol and benzyl alcohol under mild conditions, despite of the abscence of H-atom at β-position to hydroxyl groups in their molecules. All the facts mentioned suggest to involve carbene species in the reaction. The first step of the reaction appears to be oxidative addition of alcohol molecule to Mo-Pd bond. The complex containing both Mo-coordinated hydroxyl anion and Pd 6-bonded alkyl group is formed at this step. Proton transfer from the alkyl group to the coordinated hydroxyl results in formation of complex containing coordinated water molecule and carbene ligand, which gives rise to organic products. In the course of the reaction the starting complex may be partially decarbonylated, so it is unclear whether the reaction is catalyzed by cluster 3 or by products of its transformations. It is doubtless that the presence of Pd-Mo bond in the catalyst molecule is necessary. Neither PCA nor $Na[CpMo(CO)_3]$ are active in the reaction under consideration.
It is obviously that hydrogenolysis of the intermediates containing coordinated alkyl group or carbene ligand would lead to corresponding alkane. Our attempts to carry out hydrogenation of benzyl alcohol in the presence of Pd,Mo-cluster failed, however, because of instability of the complex under H_2. Nevertheless, toluene in amount commensurable with that of cluster 3 was found by H_2 treatment of the solution of 3 in benzyl alcohol after preliminary exposition under Ar for 30-40 days at 80°C.

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