ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2007, Vol. 52, No. 1, pp. 7–9. © Pleiades Publishing, Inc., 2007.
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Synthesis and Properties of Palladium(I) Carbonyl Chlorides

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Received November 21, 2005

Abstract—Palladium(I) carbonyl chloride $(PdCOCl)_n$ has been synthesized by the effect of CO on $PdCl_2$ in the presence of trace water. Anionic palladium(I) carbonyl chloride has been synthesized during treatment of ethanol-based or acetone-based solutions of H_2PdCl_4 containing small amounts of water; it has been isolated from the solution as the salt $Cs_2[Pd_2(CO)_2Cl_4]$. IR-spectra, X-ray diffraction patterns, and thermogravimetry data on synthesized palladium(I) carbonyl complexes are presented.

DOI: 10.1134/S0036023607010020

Palladium carbonyl chloride was first prepared by the effect of CO on a suspension of $PdCl_2$ in absolute methanol or via passing dry CO over $PdCl_2$ [1]:

$$PdCl_2 + CO \longrightarrow PdCOCl_2. \qquad (1)$$

Reaction (1) is catalyzed by methanol or ethanol vapor; its kinetics are presented in [2].

Lemon-colored $PdCOCl_2$ is very sensitive to water and decomposes very rapidly under its effect:

$$PdCOCl_2 + H_2O \longrightarrow Pd + CO_2 + 2HCl. \qquad (2)$$

Reaction (2) includes the steps of reduction of palladium(II) to palladium(0) with the formation of lower carbonyl chlorides:

$$Pd(II) \longrightarrow Pd(II, I) \longrightarrow Pd(I) \longrightarrow Pd(I, 0) \longrightarrow Pd(0).$$

By dosing the amount of water, one can stop reaction (2) at one of the intermediate steps, and lower palladium carbonyl chloride can be obtained. For example, polymeric palladium(I) carbonyl chloride $(PdCOCl)_n$ was obtained under the effect of moist air or nitrogen on a suspension of palladium(II) carbonyl chloride in methanol containing 0.25 mol % water [3].

Palladium(I, 0) carbonyl chloride $Pd_2(CO)_2Cl$ was previously obtained under the effect of CO on the solution of the $Pd(C_6H_5CN)_2Cl_2$ compound in chloroform [4].

We obtained olive-colored polymeric palladium(I) carbonyl chloride of composition $(PdCOCl)_n$ by the effect of moist CO on $PdCl_2$ under atmospheric pressure at room temperature:

$$2PdCl_2 + 3CO + H_2O = 2PdCOCl + CO_2 + 2HCl.$$

This product is stable in air for a relatively long period, but is rapidly decomposed by water:

$$2PdCOCl + H_2O = 2Pd + CO_2 + 2H_2O. \qquad (3)$$

Reaction (3) can be used to prepare a palladium powder.

The peaks of metal palladium and palladium dichloride are absent in the X-ray diffraction pattern of the resulting polymeric carbonyl chloride $(PdCOCl)_n$ (Fig. 1), and a strong band $\nu(CO) = 1950\ cm^{-1}$ is present in its IR spectrum (Fig. 2).

According to thermogravimetry data (Fig. 3), PdCOCl decomposes thermally in helium at 230°C, which is accompanied by an endotherm:

$$2PdCOCl = Pd + 2CO + PdCl_2. \qquad (4)$$

Thermolysis in air is also accompanied by an exotherm, which is due to the catalytic oxidation of CO on palladium:

$$2CO + O_2 = 2CO_2.$$

The occurrence of reaction (4) was confirmed analytically. When leaching the products of thermolysis of PdCOCl in water, it was found that 50% of palladium was in the form of metal and 50 % was in the form of dichloride.

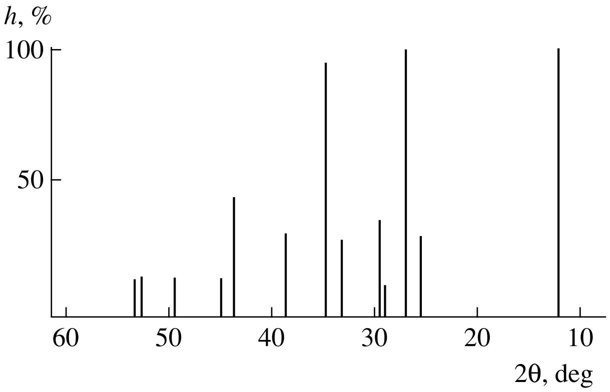

Fig. 1. X-ray diffraction pattern of a PdCOCl sample.

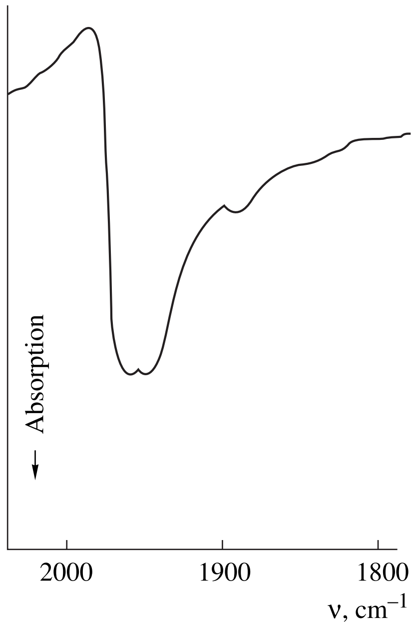

Fig. 2. IR spectrum of a PdCOCl sample.

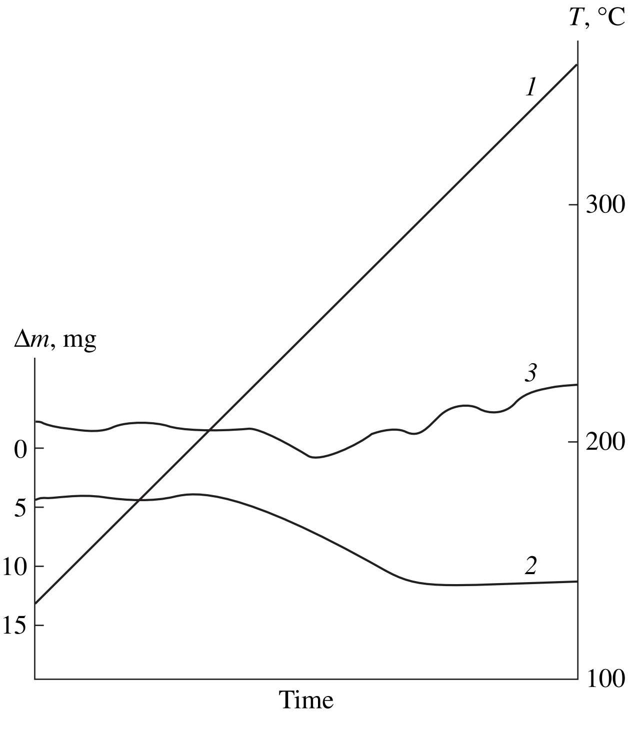

Fig. 3. Thermogravimetry pattern of the PdCOCl sample in helium. (*1*) *T*, °C; (*2*) Δ*m*, mg; and (*3*) DTA curve.

In the IR spectrum of the thermolysis products, no absorption in the region of CO groups is observed, while the band of the $PdCl_2$ compound is present.

According to Eq. (4), weight loss during thermolysis of PdCOCl should be 16.48%. For three PdCOCl samples average weight loss upon thermolysis is 16.62%.

Concentrated HCl dissolves PdCOCl to yield anionic carbonyl chloride:

$$2HCl = 2PdCOCl \longrightarrow H_2[Pd_2(CO)_2Cl_4].$$

We isolated the anionic form of palladium(I) carbonyl chloride as the salt $Cs_2[Pd_2(CO)_2Cl_4]$ when water–alcohol and water–acetone solutions of $PdCl_2$ in concentrated HCl were treated with carbon monoxide under vigorous stirring at room temperature. For the systems R–H_2O–HCl–$H_2[PdCl_4]$, where R is ethanol, propanol-1, butanol-2, acetone, or ethyl methyl ketone, the color rapidly changes from orange, which is characteristic of the chloropalladium(I) complex, through yellow to muddy green and palladium black segregates. In order for palladium black to segregate, a certain minimal amount of water should be present in the solution and the acidity should be low.

The change of solution color is associated with the change of both the ligand surrounding of the palladium atom and the degree of its oxidation.

Using 95% ethanol and concentrated HCl in the volume ratio 4 : 1 with the palladium(II) content 83 g/L and passing CO for 25 min, we obtained a yellow solution. When a solution of CsCl in concentrated HCl was added to this solution, a straw-colored precipitate appeared immediately. The product was separated by filtration using a glass filter, washed with ethanol and acetone, and air-dried at 130°C.

Elemental analysis showed that the product corresponds to the formula $Cs_2[Pd_2(CO)_2Cl_4]$. Bands $\nu(CO) = 1916\ cm^{-1}$(s) and $\nu(CO) = 1873\ cm^{-1}$ (w) appeared in its IR spectrum (Fig. 4).

By increasing the water content and the duration of CO treatment, we isolated cesium salts of other compositions with differing IR spectra, for example, the product of gross formula $Cs_6[Pd_5(CO)_4Cl_{12}]$, whose spectrum involved bands $\nu(CO) = 1966\ cm^{-1}$ (s), $\nu(CO) = 1916\ cm^{-1}$ (s), and $\nu(CO) = 1871\ cm^{-1}$ (m). No detailed investigation of these products was carried out. However, we may assume that a mixed (Pd(I) + Pd(II)) carbonylchloride anion is formed in this case.

After carbonylation of alcohol solutions, cesium chloride quantitatively precipitated palladium. The residual concentration of palladium was less than 0.03 mg/L.

Reduction $Pd(II) \longrightarrow Pd(I)$ in the system acetone–HCl–$H_2[PdCl_4]$–CO proceeds rather rapidly, which manifests itself in the change in color and a decrease in the oxidation–reduction potential. As the potential attains 180–170 mV with respect to the silver/silver chloride electrode, pouring of a solution of CsCl in concentrated HCl causes immediate formation of a straw-colored precipitate of the composition $Cs_2[Pd_2(CO)_2Cl_4]$, whose IR spectrum involves the bands $\nu(CO) = 1916\ cm^{-1}$ (s) and $\nu(CO) = 1873\ cm^{-1}$ (w).

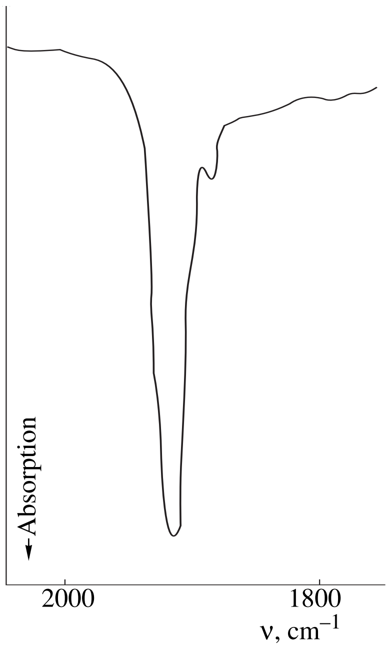

Fig. 4. IR spectrum of the $Cs_2[Pd_2(CO)_2Cl_4]$ complex.

Being heated, the $Cs_2[Pd_2(CO)_2Cl_4]$ complex melts with decomposition:

$$Cs_2[Pd_2(CO)_2Cl_4] \xrightarrow{T,\,°C} Pd + 2CO + Cs_2[PdCl_4]. \quad (5)$$

Reaction (5) starts at 478 K and proceeds at the highest rate at 528 K (Fig. 5). Weight loss is 8.28%, while the theoretical value is 8.53%. The occurrence of reaction (5) is confirmed by the X-ray diffraction pattern, which showed palladium and $Cs_2[PdCl_4]$.

In water, $Cs_2[Pd_2(CO)_2Cl_4]$ experiences rapid hydrolytic redox decomposition:

$$\begin{aligned} Cs_2[Pd_2(CO)_2Cl_4] + H_2O &= 2Pd \\ + 2CsCl + 2HCl + CO + CO_2&. \end{aligned} \quad (6)$$

Preliminary investigations showed that reactions (3) and (6) can be used to obtain ultrafine palladium powders with specific surface areas less than 30 m^2/g and a bulk density less than 0.25 g/cm^3. In the presence of stabilizers, we can apparently expect the formation of palladium nanoparticles.

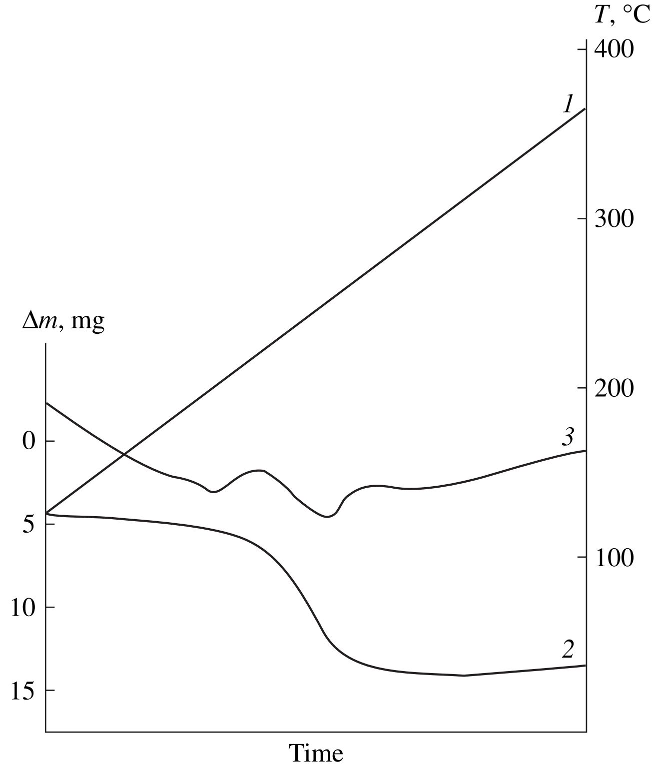

Fig. 5. Thermogravimetry pattern of the $Cs_2[Pd_2(CO)_2Cl_4]$ complex.

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