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Synthesis and Physicochemical Properties of Bis[1,3-bis(diphenylphosphino)propane]palladium(II) Trifluoroacetate

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Abstract – Bis[1,3-bis(diphenylphosphino)propane]palladium(II) trifluoroacetate was synthesized by the interaction of palladium(II) trifluoroacetate with 1,3-bis(diphenylphosphino)propane (in excess) in dichloromethane solution. The complex was characterized by elemental analysis, electrospray mass-spectrometry, and infrared and X-ray photoelectron spectroscopy data.

The necessity of the production of new types of environmentally safe polymeric materials has stimulated intensive investigation on catalytic co-polymerization of olefines and carbon(II) oxide in the last few years. The highest activity in such processes was observed for catalytic systems based on palladium(II) salts with weakly coordinated anions modified by 1,3-bis(diarylphosphino)propanes $R_3P(CH_2)_3PR_3$ (R – aryl radical) [1 - 3]. Similar systems based on palladium or other Group VIII metals exhibit high catalytic activity in a number of other commercially important processes [4 - 6], and this fact stimulated the elaboration of industrial production technologies for the above-mentioned ligands [7].

In this connection, the investigation of the compounds that arise in the systems under discussion is of great interest. Some complexes with the general formula $Pd(Dppp)X_2$ [Dppp is 1,3-bis(diphenylphosphino)propane], which contain one diphosphine ligand for each palladium atom, were reported previously [8 - 10]. In this paper, we describe the preparation of $[Pd(Dppp)_2](CF_3COO)_2$ (**I**) and present the results of its investigation by means of infrared (IR) and X-ray photoelectron spectroscopy (XPS) and electrospray mass spectrometry (ESMS).

The preparation of palladium(II) trifluoroacetate and 1,3-bis(diphenylphosphino)propane was described in [11, 12]. The solvents for the synthesis (benzene and dichloromethane) were distilled from P_2O_5 before use.

The preparation of I. Palladium(II) trifluoroacetate (0.35 g) was added to a solution of 1.3 g (3.15 mmol) of Dppp in 30 ml of dichloromethane in an inert atmosphere. The reaction mixture was magnetically stirred for 30 min, until the palladium salt dissolved. The yellow solution that resulted was filtered and allowed to stand for 72 h. The white precipitate formed was filtered off, washed with benzene, and vacuum dried. Compound **I** was obtained in the form of white fine crystals (the yield was 0.65 g, or 53%).

For $C_{58}H_{52}P_4F_6O_4$ Pd anal. calcd. (%): C, 60.19; H, 4.53; F, 9.85; P, 10.70; Pd, 9.69.

Found (%): C, 60.26; H, 4.47; F, 10.32; P, 10.7; Pd, 9.03.

The IR spectra were recorded on Specord 75IR or UR-20 spectrometers over the range 400 - 4000 cm^{-1}. The samples for IR investigation were prepared as pressed discs with KBr or as nujol mulls.

The XPS spectra were recorded using a VIEE-15 instrument employing the Mg anode ($h\nu$ = 1253.6 eV). The resolution of the analyzer, measured as the full width at the half maximum of the $Au4f_{7/2}$ peak from metallic gold, was 1.60 eV over a full energetic range. The pressure in the spectrometer chamber was not more than 2×10^{-6} mm Hg. The spectra were calibrated against the C1*s* peak (285.0 eV). The samples were prepared for XPS investigation by applying them as a thin layer on an Al support coated with a thin oxide film (20 - 40 Å) [13]. The atomic ratio of elements was determined from the integral intensities of photoelectron lines using a photoionization cross section from Scofield's table [14].

Mass-spectral investigation was performed on a time-of-flight mass-spectrometer (mass-reflectron type) with the extraction of dissolved ions under the atmospheric pressure described in [15, 16]. The methanol solution of **I** was injected at a flow rate of 2 μl min^{-1} into the ion source via a metallic capillary with an inner diameter of 0.1 mm. The application of about 2 kV voltage to the capillary in the oxygen flow leads to a fine electrospray

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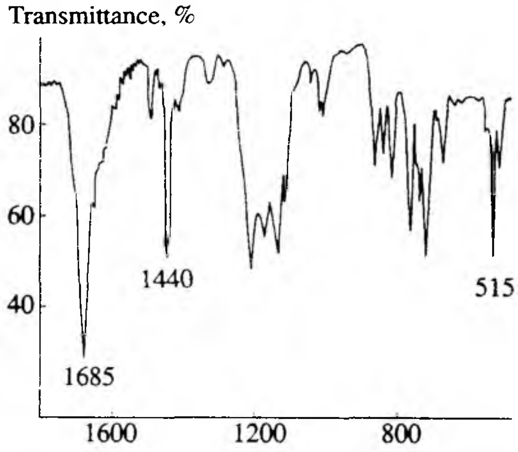

Fig. 1. IR spectrum of compound I, $[Pd(Dppp)_2](CF_3COO)_2$.

of the analyzed solution; the final stage of the process is the field evaporation of the ions contained in the liquid. A portion of the ions arrive at the mass analyzer via vacuum interface. The application of ΔV voltage in the area of the first stage of differential pumping allows the controllable fragmentation of the ions to be implemented.

RESULTS AND DISCUSSION

The interaction of palladium(II) trifluoroacretate with an excess of Dppp in dichloromethane in an inert atmosphere produces a colorless fine-crystal precipitate stable in air, the elemental analysis for which corresponds to the formula $[Pd(Dppp)_2](CF_3COO)_2$. The obtained compound **I** is insoluble in alifatic hydrocarbons, slightly soluble in aromatics and chlorohydrocarbons, and soluble in alcohols. Taking into account the poor solubility of the compound obtained in nonpolar solvents and the characteristic property of Pd(II) having coordination number 4 [17], we proposed that compound **I** possesses ionic structure with trifluoroacetate ions in the outer coordination sphere.

The IR spectrum of **I** in the region 400 - 4000 cm^{-1} presents a superposition of the spectra of the trifluoroacetate ion and the coordinated phosphine ligand Dppp. The most intensive IR absorbtion band in the spectrum of **I** is that at 1685 cm^{-1} (Fig. 1), which may be assigned to an antisymmetric stretching vibration of the carboxylate group. This band is markedly narrower than that in the platinum(II) trifluoroacetate spectrum. In our opinion, this indicates the equivalency of both trifluoroacetate ions in the compound under study. We failed to assign the band corresponding to the symmetric stretching vibrations of COO groups and more precisely define the type of bonding of the anions because of the band's low intensity and the presence of phosphine ligand absorbtion bands in the region 1300 - 1500 cm^{-1}. It should be noted that the ν^{as}_{COO} for **I** coincides closely with that for ionic sodium and potassium trifluoroacetates [18].

The most intensive IR bands of coordinated Dppp (1440 and 515 cm^{-1}) are also sufficiently narrow (Fig. 1). The assignment of these bands may be easily made by comparing the spectra of **I** and the calibration compound $[Pd(Dppp)Cl_2]$. The small line width and coincidence of positions for a number of Dppp bands in the spectra of these compounds indicate their similar conformation and their coordination modes (chelate cycle and Pd–P bonds) of both Dppp ligands in **I**.

The positive-ion mass-spectrum of a methanol solution of **I** is shown in Fig. 2. The main peak ($m/z = 465$ for ^{106}Pd isotope) corresponds to the $[Pd(Dppp)_2]^{2+}$ cation in mass and isotope composition (Fig. 2). There are peaks with $m/z = 335$, 595, and 1043 in the spectrum in addition to the main peak. The peak second in intensity ($m/z = 1043$, $\approx 10\%$ of the main peak intensity) is due to the single charged $[Pd(Dppp)(CF_3COO)]^+$ ion, and two other peaks ($m/z = 335$ and 595) arise as a result of collisional fragmentation of $[Pd(Dppp)_2]^{2+}$ ions. Actually, the enhancement of the voltage in the first stage of differential pumping leads to an increase of the peak intensities for the peaks with $m/z = 595$ and 335 and, simultaneously, to a decrease of the intensity for the peak with $m/z = 465$ (Fig. 3). According to these data, we propose that the decomposition of $[Pd(Dppp)_2]^{2+}$ ion may be schematized as follows:

$$[Pd(Dppp)_2]^{2+} \longrightarrow Pd(Dppp)Ph]^+ + [Dppp\text{–}Ph]^+.$$
$$465 \qquad\qquad 595 \qquad\qquad 335$$

In principle, the above reaction may be one of the steps of the $[Pd(Dppp)_2(CF_3COO)]^+$ ion decomposition. The nature of other peaks (for example, with $m/z = 301$, Fig. 2) is not clear yet, but their intensities are not high (less than 1% of the main peak intensity).

We also found the $[Pd(Dppp)_2]^{2+}$ ion in the PdX_2–Dppp–CF_3COOH homogeneous system, which is a catalyst for ethylene and CO copolymerization [1]. The role of this coordinately saturated ion in the catalytic system is not clear. We will publish a report on this catalytic system investigation later.

The binding energies (in eV) and atomic ratios [P/Pd] for compound **I** and the standard samples according to the XPS investigation are given below:

Compound	$Pd3d_{5/2}$	$F1s$	$P2p$	$[P/Pd]^{XPS}_{at}$
$[Pd(Dppp)_2](CF_3COO)_2$	338.6	688.0	131.7	4.4
$Pd(CF_3COO)_2$	338.8	688.2		
$[Pd(Dppp)Cl_2]$	338.0		131.5	2.5
Pd (metal)	335.5			

The main peak position $Pd3d_{5/2}$ ($E_b = 338.6$ eV) shows that the palladium in **I** is divalent. In some syntheses, in addition to the peak mentioned above, a product forms whose XPS spectrum shows the $Pd3d_{5/2}$ peak with $E_b = 336.3$ eV, 5 - 15% of the main peak intensity. The reduction of Pd(II) to Pd(0) appears to take place, but it is not caused by X-ray irradiation of the sample in the course of XPS spectrum recording because

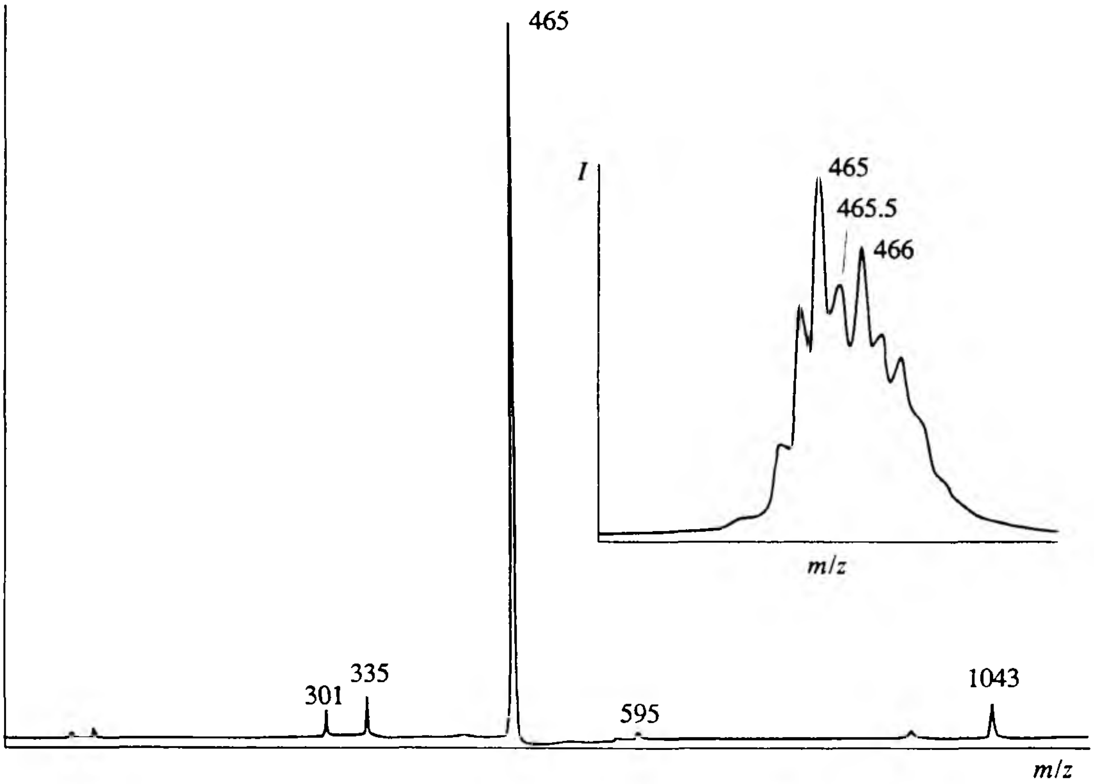

Fig. 2. Positive-ion mass-spectrum of a methanol solution of compound **I**, recorded at $\Delta U = 180$ V. The inset is the mass spectrum in the region of the $[Pd(Dppp)_2]^{2+}$ ion ($m/z = 465$), extended along the x-axis.

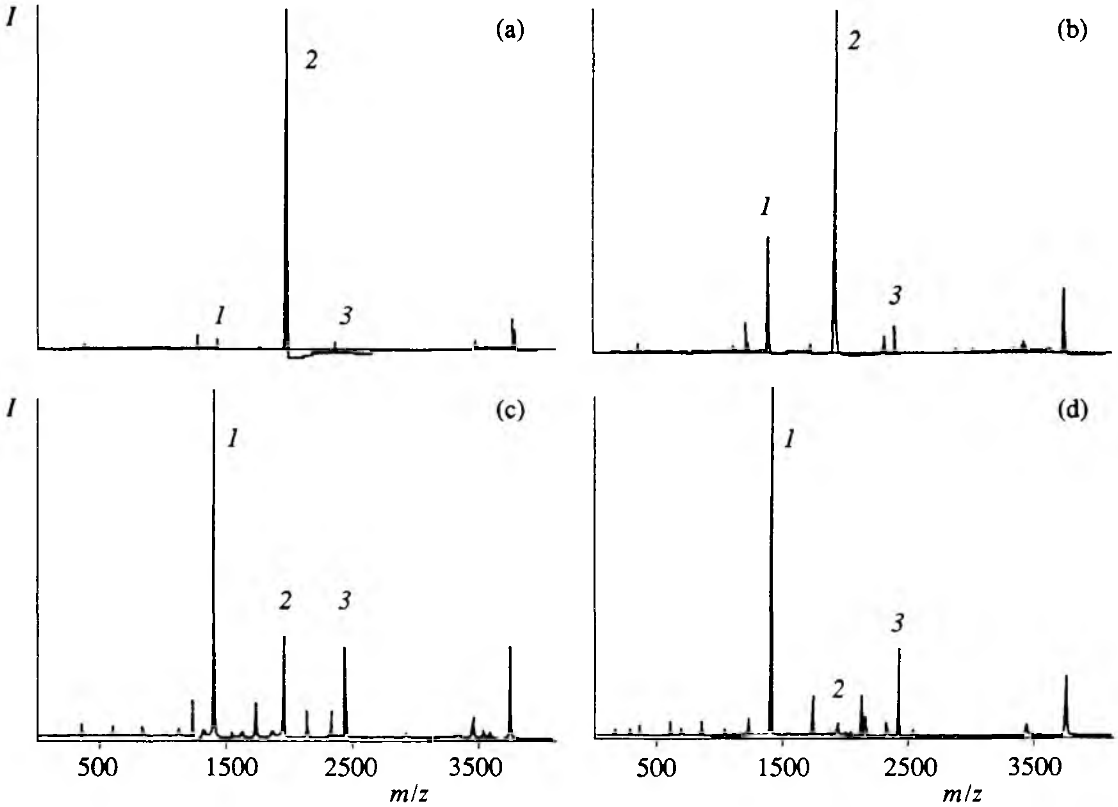

Fig. 3. Positive-ion mass-spectra of compound **I**, recorded at ΔU = (a) 180, (b) 200, (c) 220, and (d) 240 V. The peaks labeled as *1*, *2* and *3* correspond to the ions with m/z = 335, 465, and 595, respectively.

dependence of the Pd3*d* line shape on the time of exposure was not observed. It is noteworthy that such a dependence was not observed for the initial palladium(II) trifluoroacetate. One may assume that the Pd(0) compound arises upon complex synthesis as a result of phosphine oxidation by traces of oxygen, as was described recently for triphenylphospine [19]. A comparison of the spectra of the specimens of **I** containing Pd(0) and those that do not contain Pd(0) leads one to think that the palladium(0) complex in **I** may be $[Pd(Dppp)_2]$. The complex $[Pd(Dppp)_2]$ obviously cannot appear in the mass spectrum by the described way of recording.

Quantitatively, the [P/Pd] ratios calculated in the standard manner give somewhat overstated values. However, in general, the measured values correctly display the composition of the compound $[Pd(Dppp)_2](CF_3COO)_2$ under the assumption that the error of determination for the ratio of the elements is systematic.

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