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Palladium Complexes [Ph$_3$PCH$_2$C(O)Me][PdCDmso-*S*)] and [Ph$_4$Sb(Dmso-*O*)][PdBr$_3$(Dmso-*S*)]: Synthesis and Structures

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Abstract—Ionic palladium complexes with mononuclear anions [Ph$_3$PCH$_2$C(O)Me][PdCl$_3$(Dmso-*S*)] (**I**) and [Ph$_4$Sb(Dmso-*O*)][PdBr$_3$(Dmso-*S*)] (**II**) are synthesized from tetraorganylphosphonium or tetraorganylstibonium halide and palladium dihalide in the presence of hydrochloric or hydrobromic acid. The structures of complexes **I** and **II** are determined by X-ray diffraction (XRD) (CIF files CCDC nos. 1907718 (**I**) and 1979208 (**II**)). The complexes contain tetrahedral tetraorganylphosphonium or tetraorganylstibonium cations and square anions [PdHal$_3$(Dmso-*S*)]$^-$. According to the XRD data, the phosphorus and antimony atoms in the cations have a slightly distorted tetrahedral coordination with the CPC (105.76(7)°–110.31(7)°) and CSbC (100.03(16)°–117.62(15)°) bond angles slightly differed from the theoretical value and close P–C (1.7903(15)–1.8037(16) Å) and Sb–C (2.061(5)–2.100(4) Å) bond lengths. The P–C$_{\mathrm{Alk}}$ bonds are longer (1.8037(16) Å) than the P–C$_{\mathrm{Ph}}$ bonds. In the square planar anions [PdHal$_3$(Dmso-*S*)]$^-$, the Pd–Cl and Pd–Br bond lengths vary in ranges of 2.2918(7)–2.3012(8) and 2.371(3)–2.403(2) Å, respectively, and the S–Pd distances (2.2492(6) and 2.237(2) Å) are less than the sum of covalent radii of palladium and sulfur atoms (2.44 Å). The *cis*-ClPdCl (89.88(3)°) and *cis*-BrPdBr (88.93(4)°, 89.59(4)°) angles do not almost differ from the theoretical value (90°). The *trans*-ClPdCl and *trans*-SPdCl angles are comparable and equal to 178.15(2)° and 178.714(19)°. The corresponding values for complex **II** are 174.22(3)° and 177.53(4)°. The deviations of the palladium atom from the Cl$_3$S and Br$_3$S planes are insignificant (0.019 and 0.033 Å). The structural organization in the crystals of the complexes is formed by interionic contacts S=O···H–C (2.56–2.72 Å (**I**) and 2.44–2.62 Å (**II**)), Pd–Cl···H–C (2.83–2.93 Å), and Br···H (2.86–3.04 Å).

Keywords: palladium complexes, acetonyltriphenylphosphonium cation, tetraphenyltriphenylstibonium cation, dimethyl sulfoxide, *S*-dimethylsulfoxidotrihalopalladate anion, synthesis, structure, XRD studies

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INTRODUCTION

The coordination chemistry of palladium complexes is interesting due to their efficient applications in catalysis [1–10] and wide use in reactions of organic and organoelement synthesis [11–15]. Structural features of the coordination palladium compounds are actively studied at present. Numerous structurally characterized halogen-containing ionic palladium complexes are mainly presented by mononuclear [PdHal$_4$]$^{2-}$ and, to a less extent, binuclear [Pd$_2$Hal$_6$]$^{2-}$ anions [16]. The influence of solvents on the design of the Pd-containing anions and mutual transformations of the anions into each other in various solvents were reported [17]. The synthesis of the palladium complexes with the S-coordinated dimethyl sulfoxide molecule in the mononuclear [PdHal$_3$(Dmso-*S*)]$^-$ anions has previously been reported [18–28], but there are only few bromine-containing derivatives among them.

The study of the synthesis and structural features of the earlier unknown ionic palladium complexes [Ph$_3$P-CH$_2$C(O)Me][PdCl$_3$(Dmso-*S*)] and [Ph$_4$Sb(Dmso-*O*)]-[PdBr$_3$(Dmso-*S*)] was continued in this work.

EXPERIMENTAL

Tetraphenylstibonium bromide was synthesized according to a described procedure [29]. Acetonyltriphenylphosphonium chloride (Alfa Aesar), palladium dichloride and dibromide (ABCR), a 48% solution of hydrobromic acid (Sigma Aldrich), and dimethyl sulfoxide and hydrochloric acid (reagent grade) were used.

Acetonyltriphenylphosphonium *S*-dimethylsulfoxidotrichloropalladate (I) was synthesized using a known procedure [18] from palladium dichloride (0.100 g, 0.56 mmol) and acetonyltriphenylphosphonium chloride (0.400 g, 1.13 mmol) in the presence of hydrochloric acid followed by the recrystallization of the dried precipitate from dimethyl sulfoxide.

Complex **I**: brown crystals, T_{decomp} = 135°C. The yield was 82%. IR (ν, cm^{-1}): 3059, 3013, 3003, 2959, 2911, 2866, 1713, 1585, 1485, 1439, 1414, 1354, 1315, 1298, 1153, 1119, 1028, 995, 920, 845, 750, 721, 691, 515, 503, 488, 432, 424.

For $C_{23}H_{26}O_2PSCl_3Pd$

Anal. calcd., %	C, 45.26	H, 4.26
Found, %	C, 45.22	H, 4.30

***O*-Dimethylsulfoxidotetraphenylstibonium *S*-dimethylsulfoxidotribromopalladate (II)** was synthesized similarly from palladium dibromide (0.100 g, 0.38 mmol) and tetraphenylstibonium bromide (0.39 g, 0.76 mmol).

Complex **II**: brown crystals, $T_{\text{decomp}} = 110°C$. The yield was 74%. IR (ν, cm^{-1}): 3072, 3053, 3045, 3024, 2997, 2911, 2854, 1478, 1434, 1399, 1335, 1294, 1184, 1179, 1163, 1157, 1111, 1072, 1023, 996, 951, 916, 891, 458. Found, %: C, 36.00; H, 3.29. $C_{28}H_{32}O_2S_2SbBr_3Pd$. Calculated, %: C, 36.06; H, 3.43.

The IR spectra of the compounds were recorded on a Shimadzu IR Affinity-1S FT-IR spectrometer in a range of 4000–400 cm^{-1} (KBr pellets).

XRD was carried out on a D8 QUEST four-circle diffractometer (Bruker) with a graphite monochromator at 293 K. Data were collected and edited, unit cell parameters were refined, an absorption correction was applied, and the structures were determined and refined using the available software [30–32]. The structures of complexes **I** and **II** were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1907718 (**I**) and 1979208 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Compound **I**: brown crystals, monoclinic crystal system, space group $P2_1/c$, $a = 14.204(4)$, $b = 9.827(3)$, $c = 19.722(6)$ Å; $\alpha = \gamma = 90.00°$, $\beta = 110.850(12)°$, $V = 2572.6(13)$ Å^3, $Z = 4$, $\rho_{\text{calc}} = 1.576$ g/cm^3; $\mu = 1.194$ mm^{-1}, $F(000) = 1232.0$. The number of measured reflections was 146030, the number of independent reflections was 20362 ($R_{\text{int}} = 0.0504$), and the number of refinement parameters was 283: $R_1 = 0.0473$, $wR_2 = 0.0937$.

Compound **II**: brown crystals, monoclinic crystal system, space group $P2_12_12_1$, $a = 9.308(10)$, $b = 15.707(16)$, $c = 21.65(3)$ Å; $\alpha = \gamma = 90.00°$, $\beta = 90.90°$, $V = 3165(6)$ Å^3, $Z = 8$, $\rho_{\text{calc}} = 1.957$ g/cm^3; $\mu = 5.366$ mm^{-1}, $F(000) = 1800.0$. The number of measured reflections was 52839, the number of independent reflections was 8521 ($R_{\text{int}} = 0.0479$), and the number of refinement parameters was 338: $R_1 = 0.0311$, $wR_2 = 0.0593$.

RESULTS AND DISCUSSION

For the synthesis of the ionic palladium complexes, a solution of alkyltriphenylphosphonium or tetraphenylstibonium was poured to a solution of palladium dihalide in hydrohalic acid. A brown precipitate was formed and recrystallized from dimethyl sulfoxide after filtration and drying.

In the first case, after the solvent was evaporated, acetonyltriphenylphosphonium *S*-dimethylsulfoxidotrichloropalladate $[Ph_3PCH_2C(O)Me]^+[PdCl_3(Dmso\text{-}S)]^-$ was obtained as brown crystals

$$2[Ph_3PCH_2C(O)Me]Cl + PdCl_2 \xrightarrow{1.\ H_2O/HCl} [Ph_3PCH_2C(O)Me]_2[PdCl_4],$$

$$[Ph_3PCH_2C(O)Me]_2[PdCl_4] \xrightarrow{2.\ Dmso} [Ph_3PCH_2C(O)Me]^+[PdCl_3(Dmso\text{-}S)] + [Ph_3PCH_2C(O)Me]Cl.$$

(I)

O-Dimethylsulfoxidotetraphenylstibonium *S*-dimethylsulfoxidotribromopalladate was synthesized similarly

$$Ph_4SbBr\_ + PdBr_2 \xrightarrow{\substack{1.\ H_2O/HBr\\ 2.\ Dmso}} [Ph_4Sb(Dmso\text{-}O)]^+[PdBr_3(Dmso\text{-}S)]^-.$$

(II)

Compounds **I** and **II** are brown crystalline substances resistant to air moisture and oxygen, highly soluble in acetonitrile, chloroform, and tetrahydrofuran, and insoluble in aliphatic hydrocarbons.

The IR spectra of complexes **I** and **II** exhibit intense absorption bands in ranges of 1439 and 995 cm^{-1}, as well as in ranges of 1434 and 996 cm^{-1}, which are characteristic of stretching vibrations of the $P{-}C_{Ph}$ and $Sb{-}C_{Ph}$ bonds, respectively [33]. The observed shift of the absorption bands of the S=O bond (1119 and 1111 cm^{-1}) to the short-wavelength range compared to unbound dimethyl sulfoxide (1055 cm^{-1}) is characteristic of similar complexes with S-coordinated dimethyl sulfoxide [34].

According to the XRD data, the crystals of the complexes consist of tetrahedral acetonyltriphenylphosphonium cations, trigonal bipyramidal (*O*-dimethylsulfoxido)tetraphenylstibonium cations, and mononuclear square $[PdHal_3(Dmso\text{-}S)]^-$ anions (Figs. 1, 2).

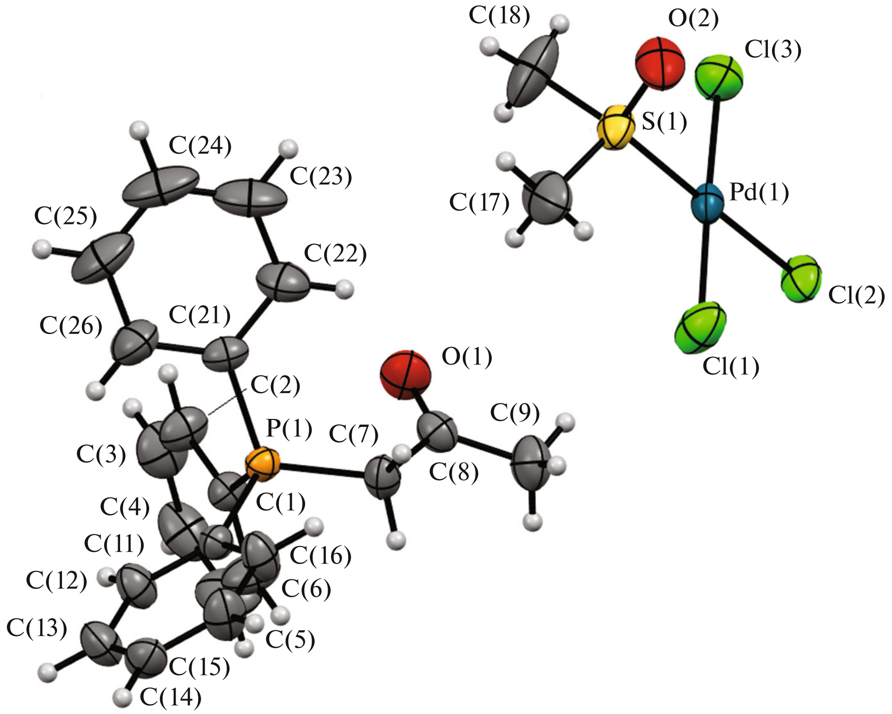

Fig. 1. General view of compound **I**.

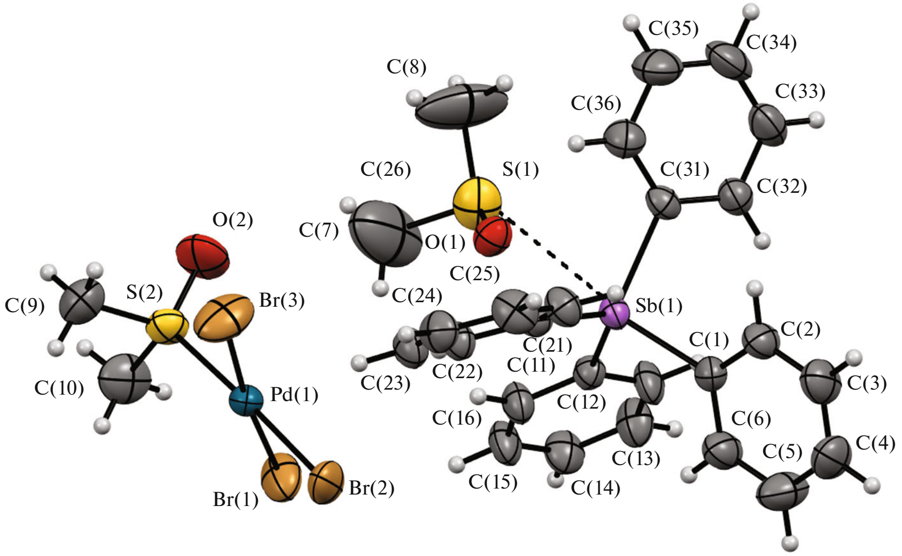

Fig. 2. General view of compound **II**.

The phosphorus atom in the cation of complex **I** has a slightly distorted tetrahedral coordination with the CPC bond angles (105.76(7)°–113.03(8)°), which slightly differ from the theoretical value, and close P–C bond lengths. The P–C_{Alk} distance (1.8037(16) Å) is longer than the P–C_{Ph} bond length (1.7903(15)–1.7981(15) Å). In the square planar [$PdCl_3$(Dmso-*S*)]$^-$ anions, the Pd–Cl bond lengths range from 2.2918(7) to 2.3012(8) Å, and the S–Pd distance (2.2492(6) Å) is less than the sum of covalent radii of palladium and sulfur atoms (2.44 Å [35]). The *cis*-ClPdCl angles (89.88(3)°) do not almost differ from the theoretical value (90°). The *trans*-ClPdCl and *trans*-SPdCl angles are comparable and equal to 178.15(2)° and 178.714(3)°, respectively. In the cation of complex **II**, the dimethyl sulfoxide molecule is coordinated to the antimony atom (O···Sb 2.617 Å) via the oxygen atom, and the antimony atom has the trigonal bipyramidal coordination (axial angle CSbO 178.42°). The CSbC bond angles range from 100.03(16)° to 117.62(15)°, and the Sb–C bond lengths are 2.061(5)–2.100(4) Å. In the square planar $[PdBr_3(Dmso\text{-}S)]^-$ anions, the Pd–Br bond lengths range from 2.371(3) to 2.4033(18) Å, and the S–Pd distance (2.237(2) Å) is less than the sum of covalent radii of palladium and sulfur atoms (2.44 Å [35]). The *cis*-BrPdBr angles (88.93(3)° and 89.59(4)°) differ slightly from the theoretical value (90°), and the *trans*-BrPdBr and *trans*-SPdBr angles are comparable and equal to 174.22(3)° and 177.53(4)°, respectively. In the anions of complexes **I** and **II**, the deviation of the palladium atom from the Hal_3S plane is 0.019 and 0.033 Å, respectively, and the minimum value is observed in compound **I**. The structural organization in the crystals of the complexes is formed by interionic contacts O···H (2.56–2.72 Å (**I**) and 2.44–2.62 Å (**II**), which is close to the sum of van der Waals radii of oxygen and hydrogen atoms (2.7 Å)). The crystals of compounds **I** and **II** also contain shortened Cl···H (2.83–2.93 Å) and Br···H (2.86–3.04 Å) distances, which is close to the sum of van der Waals radii of chlorine, hydrogen (3.0 Å) and bromine, hydrogen (3.1 Å) atoms [36].

Thus, the ionic palladium complexes with the square mononuclear anions $[PdHal_3(Dmso\text{-}S)]^-$ (Hal = Cl, Br) were synthesized from acetonyltriphenylphosphonium and tetraphenylstibonium halides and palladium dihalide in the presence of hydrohalic acid. The structures of the complexes were proved by XRD.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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