ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 9, pp. 1753–1757. © Pleiades Publishing, Ltd., 2010.
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Reactions of Triphenylbenzylphosphonium and Tetraphenylstibonium Chlorides with Potassium Tetrachloroplatinates in Dimethylsulfoxide

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Received November 10, 2009

Abstract—Platinum complexes $[Ph_3PhCH_2P]^+[(Me_2S{=}O)PtCl_3]^-$ **I** and *cis*-$Cl_2(Ph_3Sb)(Me_2S{=}O)Pt$ **II** were synthesized by reaction of triphenylbenzylphosphonium and tetraphenylstibonium chlorides with potassium tetrachloroplatinate in DMSO. Crystal **I** is formed by triphenylbenzylphosphonium tetrahedral cations [P–C$_{Ph}$ 1.791(4)–1.795(4) Å, P–C$_{Alk}$ 1.811(4) Å; CPC 107.57(18)°–111.46(17)°] and by square anions $[(Me_2S{=}O)PtCl_3]^-$ [Pt–Cl 2.3236(11), 2.2981(12), 2.2977(11) Å; Pt–S 2.1950(10) Å; *trans*-angles SPtCl 177.51(4)°, ClPtCl 178.74(4)°]. In a square-planar complex **II** [*trans*-angles SPtCl 178.01(6)°, ClPtSb 177.96(4)°] with central platinum atom the chlorine atoms [Pt–Cl 2.308(1), 2.350(1) Å], triphenylstibine [Pt–Sb 2.5118(4) Å] and dimethyl sulfoxide [Pt–S 2.195(1) Å] molecules are coordinated. Compound **II** is a first example of mixed ligand complex of platinum(II), where in the coordination sphere of central atom the tertiary stibine is present along with DMSO ligand.

DOI: 10.1134/S1070363210090057

Numerous thermodynamically and kinetically stable complexes of square symmetry are known, in which platinum shows the most characteristic degree of oxidation +2. The kinetic inertness of platinum complexes makes their suitable to experimental study of various types of isomerism and complex nature of *trans*- and *cis*-effects. From this point of view, study of reaction allowing the introduction of new ligands into the platinum atom coordination sphere are of interest. Platinum has a small affinity to oxygen ligands and it predominantly binds with amines, sulfides, and phosphines [1]. Platinum(II) complexes with tertiary stibines were not studied earlier.

Reaction of tetraphenylstibonium with potassium hexachloroplatinate was established to proceed through exchange mechanism to form ionic complex with octahedral anion $[Ph_4Sb]_2^+[PtCl_6]^{-2}$ [2]. In the present work the reactions of triphenylbenzylphosphonium and tetraphenylstibonium chlorides with potassium tetrachloroplatinates in DMSO have been examined and results of the study of reaction products structure are presented.

We found that reaction of tetraphenylbenzylphosphonium chloride with potassium tetrachloroplatinate in DMSO gives rise to ionic complex $[Ph_3PhCH_2P]^+\cdot[(Me_2S{=}O)PtCl_3]^-$ **I**. In this case the ligand exchange is observed in the anion.

$$\mathrm{Ph_3PhCH_2PCl + K_2[PtCl_4]}$$

$$\xrightarrow{\mathrm{Me_2S=O}} \mathrm{[Ph_3PhCH_2P]^+[Pt(Me_2S{=}O)Cl_3]^- + 2\,KCl.}$$

I

By X-ray analysis data, crystal **I** is formed by tetrahedral triphenylbenzylphosphonium cations and square anions of dimethylsulfoxidotrichloroplatinate $[(Me_2S{=}O)PtCl_3]^-$. Tetrahedral configuration of the cation is not virtually distorted: lengths of bonds P–C differ a little from each other [P–C$_{Ph}$ 1.791(4)–1.795(4) Å, P–C$_{Alk}$ 1.811(4) Å], bond angles CPC [107.57(18)°–111.46(17)°] almost not deviate from the theoretical value. In the anion DMSO molecule is coordinated to the central atom through sulfur (Fig. 1). Distances Pt–Cl^2 and Pt–Cl^4 coincide practically for *trans*-arranged chlorine atoms and are 2.2981(12) and 2.2977(11) Å. The bond Pt–Cl^1 [2.3236(11) Å] is labile, which is explained by the presence of *trans*-effect of the substituent Me$_2$S=O. The bond length of Pt–S equals

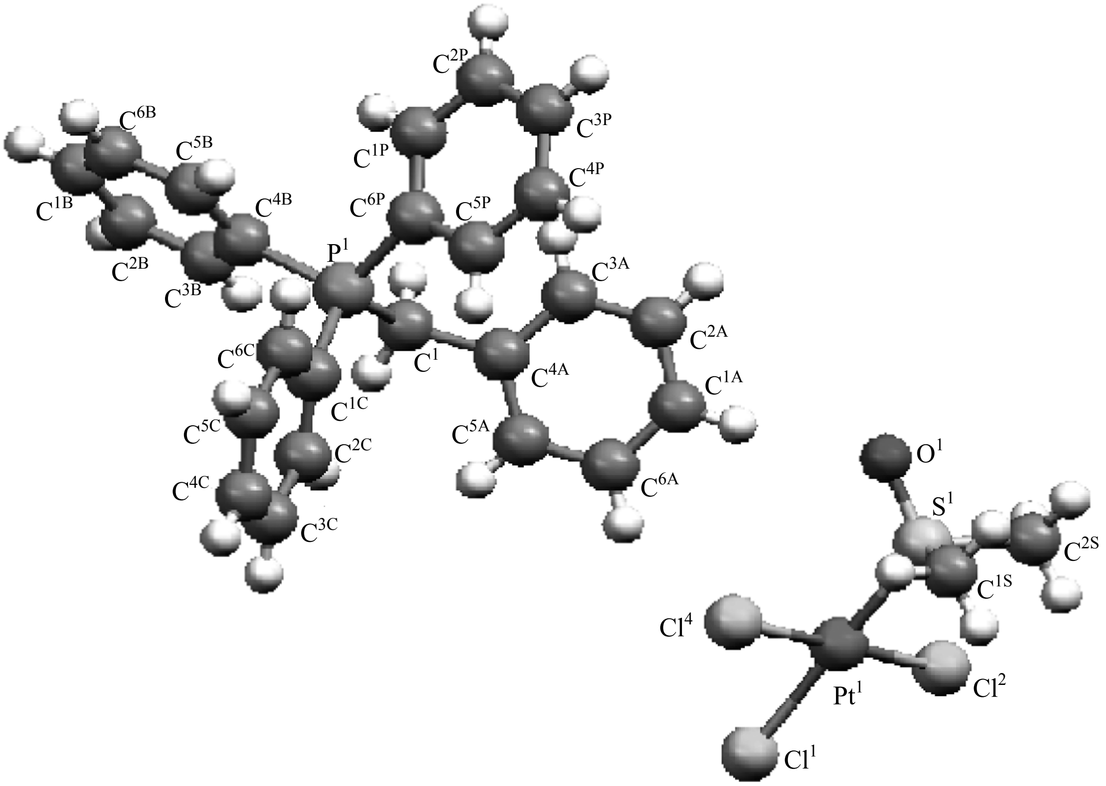

Fig. 1. Structure of complex **I**.

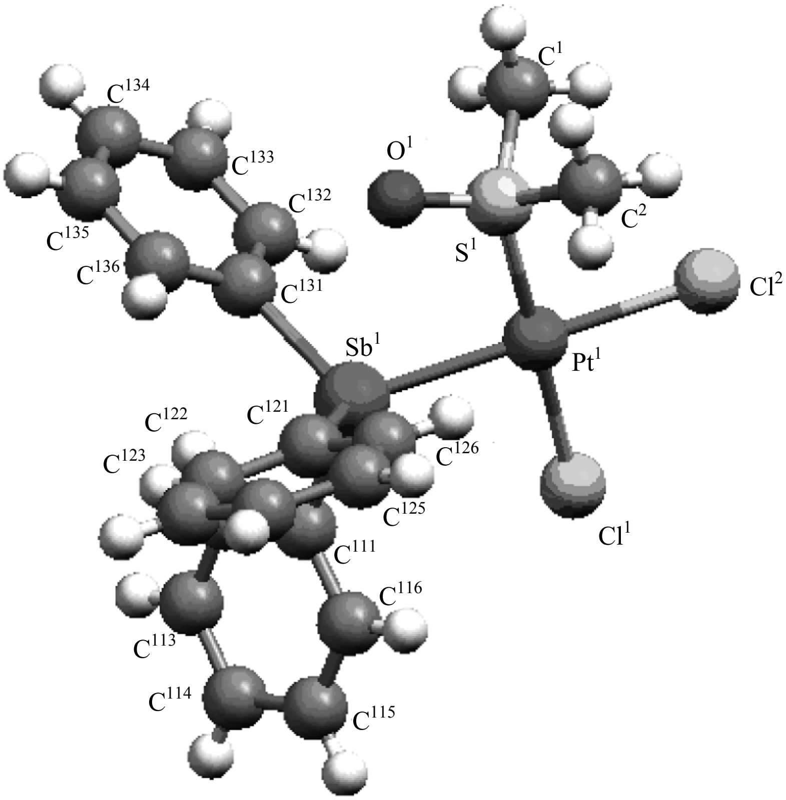

Fig. 2. Structure of complex **II**.

2.1950(10) Å. *trans*-Angles SPtCl[1] [177.51(4)°] and Cl[2]PtCl[4] [178.74(4)°] are close to 180°. The planar structure of anion is distorted: the sulfur atom is out-of-plane of [$PtCl_3$] by 0.13 Å. The oxygen atom of DMSO molecule participates in the formation of a hydrogen bond O···H–C (O···H 2.39 Å), where H is the *para* hydrogen atom of the phenyl ring of the benzyl substituent.

Reaction of tetraphenylstibonium chloride with potassium tetrachloroplatinate in DMSO occurs otherwise than the reaction of triphenylbenzylphosphonium chloride. On stirring the reaction mixture for several minutes the reddish brown crystals of potassium tetrachloroplatinate dissolved. The solution becomes yellow, the neutral mixed ligand complex of platinum(II) forms with triphenylstibine and DMSO molecule in the coordination sphere of the central atom of complex *cis*-$Cl_2(Ph_3Sb)(Me_2S{=}O)Pt$ **II**.

$$Ph_4SbCl + K_2[PtCl_4]$$

$$\rightarrow \underset{\mathbf{II}}{Cl_2(Ph_3Sb)(Me_2S{=}O)Pt} + PhCl + 2\,KCl$$

Solvent-free thermolysis of tetraphenylstibonium halides at 250°C is known to proceed as reductive elimination to give triphenylstibine and halobenzene [3]. As we established, reduction Sb(V) → Sb(III) occurs in the presence of platinum(II) salt at room temperature.

As follows from X-ray analysis data, complex **II** has a square-planar structure typical for Pt(II) [4]. Along with two chlorine ligands, coordination sphere of the central atom contains DMSO molecule coordinated through the sulfur atom, and triphenylstibine molecule. Chlorine atoms are in the *cis*-position relative to each other. *trans*-Angles Cl[1]PtS and Cl[2]PtSb are 178.01(6) and 177.96(4) respectively. Angles between *cis*-substituents SPtSb, SPtCl[1], SbPtCl[1], Cl[1]PtCl[2] equal 90.75(4), 90.24(6), 88.36(4), and 90.71(6)° respectively.

The bond length Pt–Sb is 2.5118(4) Å, the distance Pt–S [2.1954(15) Å] coincides with similar distance in complex **I**. Bond lengths Pt–Cl are unequal. The shorter bond Pt–Cl[1] [2.308(2) Å] corresponds to chlorine ligand having DMSO molecule as *trans*-molecule. Other distance Pt–Cl[2] equals 2.350(2) Å, that indicates stronger influence of triphenylstibine ligand in comparison with dimethyl sulfoxide ligand. A ligand with a strong *trans*-effect in the ligand exchange orients into the *trans*-position to itself a substituent with a weak effect as seen in the *cis*-structure of complex **II**. The confirmation of *trans*-effect rule is observed in complexes of Pt(II) of general formula *cis*-Cl_2L_2Pt, in which bond length Pt–Cl is somewhat smaller for DMSO platinum complex (2.133, 2.251 Å, L = DMSO [5]) and longer for similar platinum complexes with triarylstibine ligands (2.292 Å, L = Ar_3Sb [6]).

Table 1. Crystallographic data, experimental parameters and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
M	732.96	697.17
T, K	100.0(2)	120
Crystal system	Rhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a, Å	15.0075(3)	10.4372(4)
b, Å	18.3330(4)	10.7245(4)
c, Å	19.6894(4)	12.7531(4)
a, deg		65.1510(10)
β, deg		88.4410(10)
g, deg		61.9140(10)
V, Å^3	5417.19(19)	1116.54(7)
Z	8	2
ρ_{calc}, g cm^{-3}	1.797	2.074
μ, mm^{-1}	5.632	7.807
F(000)	2864	656
Crystal form (size, mm)	Fragment (0.26×0.13×0.08)	Plate (0.05×0.06×0.06)
Theta range for data collection, deg	2.04–31.48	1.7–27.5
Index ranges	$-21 \le h \le 13$, $-21 \le k \le 26$, $-21 \le l \le 26$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-16 \le l \le 10$
Reflections collected	7536	8531
Independent reflections	5255	4968
Variables refined	309	237
GOOF	1.014	0.992
R-indices on $F^2 > 2\sigma(F^2)$	R_1 0.0352, wR_2 0.0665	R_1 0.0328, wR_2 0.0543
R-indices (all data)	R_1 0.0679, wR_2 0.0756	R_1 0.0583, wR_2 0.0607
Residual electron density (min/max), e A^{-3}	–2.158/2.776	–0.829/1.129

EXPERIMENTAL

Reaction of triphenylbenzylphosphonium chloride with potassium tetrachloroplatinate. A mixture of

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for structures **I** and **II**

Atom	x	y	z	U_{eq}, Å^2	Atom	x	y	z	U_{eq}, Å^2
		I					**II**		
Pt^{1}	5058.89(9)	4572.76(9)	7309.35(8)	14.51(5)	Pt^{1}	5482.9(3)	9312.4(3)	3133.8(2)	20.86(7)
S^{1}	6004.9(6)	4451.5(6)	8152.1(5)	15.8(2)	Sb^{1}	7076.5(4)	10048.3(4)	1778.6(3)	20.14(10)
P^{1}	509.9(6)	3186.4(6)	10191.1(5)	8.5(2)	S^{1}	7467.8(16)	7279.6(18)	4494.7(13)	27.2(3)
Cl^{1}	4080.5(7)	4653.8(8)	6397.8(6)	31.5(3)	Cl^{1}	3419.4(16)	11507.9(18)	1709.2(13)	31.3(4)
Cl^{2}	5614.5(7)	5703.3(7)	7035.6(6)	28.2(3)	Cl^{2}	3957.4(18)	8611(2)	4351.3(14)	34.3(4)
Cl^{4}	4472.1(8)	3452.3(6)	7580.1(6)	28.4(3)	C^{1}	7571(7)	5471(7)	4758(6)	41.0(17)
C^{1P}	1264(2)	3289(2)	11468(2)	13.4(8)	C^{2}	7297(7)	7247(8)	5887(5)	38.7(17)
C^{4P}	2854(3)	2628(2)	11066(2)	17.9(9)	O^{1}	8903(4)	7163(5)	4286(4)	33.3(10)
C^{6P}	1349(2)	3004(2)	10815.7(19)	8.5(8)	C^{111}	6063(7)	11861(7)	4(5)	27.1(14)
C^{3P}	2766(3)	2915(2)	11716(2)	18.9(10)	C^{112}	6472(7)	11549(7)	–944(5)	29.5(14)
C^{5P}	2149(2)	2674(2)	10615(2)	14.7(9)	C^{113}	5861(7)	12748(8)	–2093(5)	34.8(16)
C^{2P}	1976(3)	3242(2)	11916(2)	16.7(9)	C^{114}	4848(7)	14272(7)	–2310(5)	36.0(16)
C^{4B}	–580(2)	3224(2)	10564.9(19)	9.4(8)	C^{115}	4419(7)	14607(7)	–1366(5)	31.5(15)
C^{2C}	348(2)	2592(2)	8895(2)	12.6(8)	C^{116}	5009(7)	13406(7)	–230(5)	29.2(14)
C^{1C}	508(2)	2461(2)	9579(2)	10.4(8)	C^{121}	8200(6)	10887(6)	2384(5)	22.1(12)
C^{6C}	557(2)	1743(2)	9821(2)	15.1(9)	C^{122}	9129(7)	11366(7)	1750(5)	29.9(15)
C^{4A}	1704(2)	4177(2)	9609(2)	10.5(8)	C^{123}	9836(7)	11928(8)	2178(7)	42.3(18)
C^{2B}	–2030(2)	3770(2)	10634(2)	16.5(9)	C^{124}	9594(7)	12049(8)	3213(6)	43.3(18)
C^{3B}	–1179(2)	3764(2)	10363(2)	14.7(9)	C^{125}	8665(7)	11616(7)	3826(6)	34.4(15)
C^{6A}	2820(3)	4225(3)	8732(2)	20.9(10)	C^{126}	7975(6)	11016(7)	3419(5)	26.6(14)
C^{5A}	1936(3)	4133(2)	8928(2)	16.7(9)	C^{131}	8698(6)	8116(6)	1523(5)	22.7(13)
C^{4C}	323(2)	1296(2)	8693(2)	18.6(9)	C^{132}	8212(7)	7254(7)	1262(5)	28.4(14)
C^{3A}	2355(3)	4340(2)	10084(2)	16.6(9)	C^{133}	9250(8)	5974(7)	1090(5)	36.8(17)
C^{3C}	261(2)	2004(2)	8452(2)	17.0(9)	C^{134}	10703(8)	5612(7)	1147(5)	37.9(18)
C^{5C}	461(2)	1167(2)	9375(2)	18.1(9)	C^{135}	11164(7)	6486(7)	1384(5)	36.0(16)
C^{6B}	–1700(2)	2705(2)	11289(2)	16.0(9)	C^{136}	10168(7)	7743(7)	1597(5)	31.1(15)
C^{2A}	3237(3)	4427(2)	9885(2)	18.6(10)					
C^{1B}	–2290(2)	3244(2)	11097(2)	17.4(9)					
C^{1A}	3471(3)	4359(2)	9212(2)	20.4(10)					
C^{1}	744(2)	4074(2)	9829(2)	11.2(8)					
C^{5B}	–841(2)	2694(2)	11024(2)	15.6(9)					
O^{1}	5638.5(19)	4413.4(19)	8842.4(15)	26.2(8)					
C^{1S}	6655(3)	3663(3)	8022(2)	26.7(11)					
C^{2S}	6856(3)	5118(3)	8157(3)	28.9(11)					

Table 3. Bond lengths and bond angles for structures **I** and **II**

Bond	d, Å	Angle	ω, deg
	I		
Pt^1–S^1	2.1950(10)	S^{1}Pt^{1}Cl^1	177.51(4)
Pt^1–Cl(1)	2.3236(11)	S^{1}Pt^{1}Cl^2	91.95(4)
Pt^1–Cl^2	2.2981(12)	S^{1}Pt^{1}Cl^4	88.97(4)
Pt^1–Cl^4	2.2977(11)	Cl^{2}Pt^{1}Cl^1	89.45(5)
S^1–O^1	1.468(3)	Cl^{4}Pt^{1}Cl^1	89.67(5)
S^1–C^{1S}	1.762(4)	Cl^{4}Pt^{1}Cl^2	178.74(4)
S^1–C^{2S}	1.768(4)	O^{1}S^{1}Pt^1	117.55(13)
P^1–C^{6P}	1.791(4)	O^{1}S^{1}C^{1S}	107.6(2)
P^1–C^{4B}	1.795(4)	O^{1}S^{1}C^{2S}	107.4(2)
P^1–C^{1C}	1.794(4)	C^{1S}S^{1}Pt^1	109.33(17)
P^1–C^1	1.811(4)	C^{1S}S^{1}C^{2S}	99.7(2)
	II		
Pt^1–Sb^1	2.5118(4)	S^{1}Pt^{1}Sb^1	90.75(4)
Pt^1–S^1	2.195(1)	S^{1}Pt^{1}Cl^1	178.01(6)
Pt^1–Cl^1	2.308(1)	S^{1}Pt^{1}Cl^2	90.24(6)
Pt^1–Cl^2	2.350(1)	Cl^{1}Pt^{1}Sb^1	88.36(4)
Sb^1–C^{111}	2.125(6)	Cl^{1}Pt^{1}Cl^2	90.71(6)
Sb^1–C^{121}	2.099(6)	Cl^{2}Pt^{1}Sb^1	177.96(4)
Sb^1–C^{131}	2.121(5)	C^{111}Sb^{1}Pt^1	119.2(2)
S^1–C^1	1.773(6)	C^{121}Sb^{1}Pt^1	112.8(1)
S^1–C^2	1.767(6)	C^{121}Sb^{1}C^{111}	102.0(2)
S^1–O^1	1.469(4)	C^{121}Sb^{1}C^{131}	107.4(2)
C^{111}–C^{112}	1.391(7)	C^{131}Sb^{1}Pt^1	112.6(1)
C^{111}–C^{116}	1.389(8)	C^{131}Sb^{1}C^{111}	101.4(2)
C^{112}–C^{113}	1.378(8)	C^{1}S^{1}Pt^1	110.0(2)
C^{113}–C^{114}	1.369(8)	C^{2}S^{1}Pt^1	110.8(2)
C^{114}–C^{115}	1.400(8)	C^{2}S^{1}C^1	101.8(3)
C^{115}–C^{116}	1.368(8)	O^{1}S^{1}Pt^1	117.0(2)
C^{121}–C^{122}	1.391(8)	O^{1}S^{1}C^1	109.0(3)
C^{121}–C^{126}	1.387(7)	O^{1}S^{1}C^2	107.1(3)

0.20 g of potassium tetrachloroplatinate, 0.19 g of triphenylbenzylphosphonium chloride, and 10 ml of DMSO was stirred at room temperature for 5 min. The solvent was slowly evaporated. Yield 0.33 g (94%), yellow crystals, mp 169°C. IR spectrum, ν, cm^{-1}: 3052, 3022, 2927, 2883, 1583, 1484, 1436, 1316, 1126, 1109, 1024, 920, 838, 789, 745, 715, 696, 582, 514, 497, 445. Found, %: C 43.76; H 3.69. $\mathrm{C_{27}H_{28}Cl_3OPPtS}$. Calculated, %: C 44.23; H 3.82.

Reaction of tetraphenylstibonium chloride with potassium tetrachloroplatinate was performed similarly with 0.20 g of potassium tetrachloroplatinate, 0.22 g of tetraphenylstibonium chloride, and 10 ml of DMSO. Yield 0.22 g (79%), yellow crystals, mp 138°C. IR spectrum, ν, cm^{-1}: 3068, 3003, 2913, 1578, 1480, 1436, 1332, 1309, 1293, 1182, 1159, 1133, 1068, 1021, 996, 978, 937, 917, 850, 734, 693, 460, 441. Found, %: C 41.49; H 3.76. $\mathrm{C_{20}H_{21}Cl_2OPtS}$. Calculated, %: C 41.74; H 3.65.

IR spectra were recorded on an IR Fourier-spectrometer 1201 from KBr pellets. X-Ray diffraction experiment was performed on an automatic four-circle diffractometer Bruker–Nonius X8Apex (two-coordinate CCD detector, MoK_α irradiation, λ = 0.71073 Å, graphite monochromator, φ-scanning). The extinction was accounted for empirically (SADABS) [7]. Hydrogen atoms positions were calculated geometrically and involved into refinement in the *rider* model. The structure was solved by the direct method and refined by means of full-matrix least-squares in an anisotropic approximation for non-hydrogen atoms (SHELX-97) [8].

The main crystallographic data are given in Tables 1–3.

ACKNOWLEDGMENTS

Authors are grateful E.V. Peresypkina for X-ray diffraction analysis of complexes **I** and **II**.

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