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Phenylation of Antimony(V) Organic Compounds with Pentaphenylantimony. The Structure of Tetraphenylantimony Chloride

V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, T. P. Platonova, O. P. Zadachina, and A. V. Gerasimenko

Blagoveshchensk State Pedagogical University, ul. Lenina 104, Blagoveshchensk, 675000 Russia
Institute of Chemistry, Far East Division, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 109, Vladivostok, 690022 Russia

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Abstract—Tetraphenylantimony chloride and bromide were synthesized through the reaction of pentaphenylantimony with diphenylantimony trichloride or tribromide taken at a molar ratio of 2 : 1 in toluene. When the initial compounds were taken at a molar ratio of 1 : 1, triphenylantimony dichloride or dibromide was formed. The phenylation of triphenylantimony sulfate with pentaphenylantimony yielded tetraphenylantimony sulfate. According to the X-ray diffraction data, the antimony atom in the tetraphenylantimony chloride molecule has a distorted trigonal bipyramidal configuration with the chlorine atom in the axial position. The Sb–Cl distance is equal to 2.686(1) and Sb–C distances are equal to 2.113(4) and 2.165(4) Å (av. 2.130 Å).

Pentaphenylantimony is known to phenylate triphenylantimony dihalides to give tetraphenylantimony halides [1, 2]; however, reactions of pentaphenylanitimony with diphenylantimony trihalides were not described in the literature. As a continuation of our studies on phenylating properties of pentaphenylantimony, its reactions with diphenylantimony trichloride and tribromide, triphenylantimony sulfate, and acetylacetonatotriphenylantimony chloride were investigated.

RESULTS AND DISCUSSION

It was established that the reactions of pentaphenylantimony with diphenylantimony trichloride (taken at a molar ratio of 2 : 1 and 1 : 1) in toluene at room temperature are accompanied by the redistribution of radicals between the antimony atoms to give tetraphenylantimony chloride or tetraphenylantimony chloride and triphenylantimony dichloride, respectively, in high yields:

$$2Ph_5Sb + Ph_2SbCl_3 \longrightarrow 3Ph_4SbCl,$$

$$Ph_5Sb + Ph_2SbCl_3 \longrightarrow Ph_4SbCl + Ph_3SbCl_2.$$

For these reactions to be complete, the reaction mixture should be heated at 90–100°C for a short time.

Reactions of pentaphenylantimony with diphenylantimony tribromide follow the same route.

When pentaphenylantimony reacts with triphenylantimony sulfate, the phenyl ligands also migrate from one antimony atom to another one. Although triphenylantimony sulfate is poorly soluble in toluene, at 90–100°C, this reaction virtually terminates in 6 h.

$$Ph_5Sb + Ph_3SbSO_4 \longrightarrow (Ph_4Sb)_2SO_4.$$

The reaction of acetylacetonatotriphenylantimony with pentaphenylantimony in toluene at room temperature is also accompanied by the exchange of the ligands between the antimony atoms:

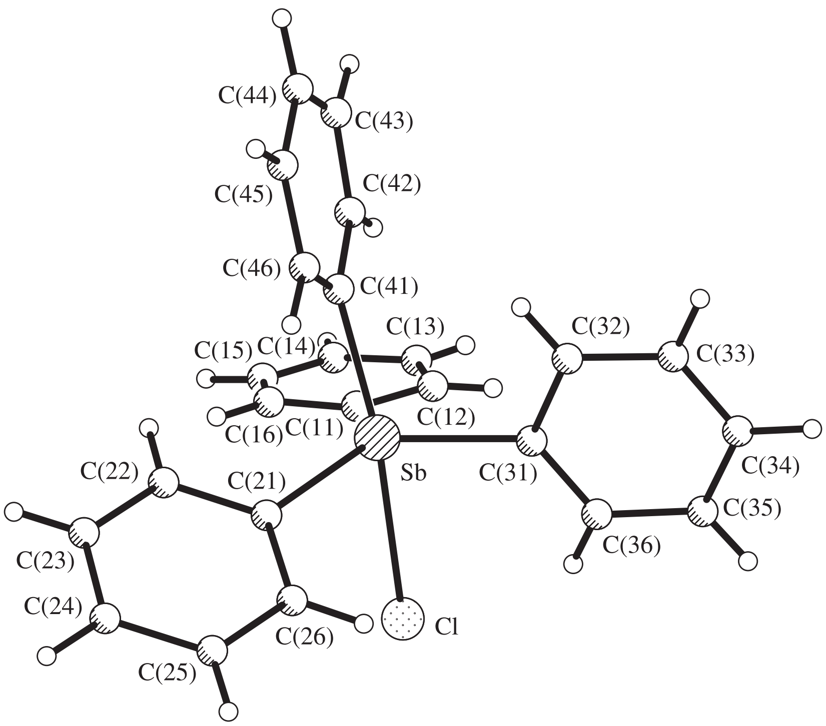
$$Ph_5Sb + Ph_3SbCl(Acac) \longrightarrow Ph_4SbCl + Ph_4Sb(Acac),$$

where Acac is the acetylacetone residue.

Melting points and IR spectra of the compounds synthesized via reactions of redistribution of radicals coincide with the analogous parameters of the known antimony compounds.

Thus, pentaphenylantimony can be used as the effective phenylating agent in reactions with antimony(V) derivatives.

The structure of tetraphenylantimony chloride (**I**) was determined in [3]; in this work, the structure of **I** was refined. According to X-ray diffraction data, the antimony atom in molecule **I** has a trigonal bipyramidal coordination with the axial Cl atom that is typical of antimony(V) compounds with the coordination number of 5 (see figure). The Sb–C_{eq} and Sb–C_{ax} bond lengths are equal to 2.113(4), 2.117(4), 2.126(4), and 2.165(4) Å, respectively. The Sb atom extends from the equatorial plane toward the axial phenyl group, as a result of which the C_{eq}SbCl angles are less than the perfect angle of 90°, while the C_{eq}SbC_{ax} angles exceed 90°. The sum of the equatorial angles is equal to 357.2°, but their values are different (115.9(1)°, 117.8(1)°, and 123.5(2)°). The angles formed by the phenyl rings and the equato-



The structure of molecule **I**.

rial plane are equal to 6.5° (C(11)–C(16)), 35.2° (C(21)–C(26)), and 98.5° (C(31)–C(36)). The C(41)SbCl angle is equal to 173.6(1)°. A linear geometry of the Cl–Sb–C(41) fragment is violated due to shifting of the Sb–Cl bond toward the phenyl ring (C(11)–C(16)) lying virtually in the equatorial plane. Different values of the axial angles and deviations of the equatorial angles from the theoretical value of 120° can be explained by the effect of the molecular packing in crystal **I**.

As in some other antimony compounds with the general formula Ph_4SbX, the Sb–Cl distance (2.686(1) Å) in complex **I** exceeds the sum of the covalent radii of Sb and Cl atoms (2.40 Å [4]), thus indicating that this bond is a polar bond.

EXPERIMENTAL

Reaction of pentaphenylantimony with diphenylantimony trichloride. a) A mixture of 1.00 g of pentaphenylantimony and 0.39 g of diphenylantimony trichloride crystal hydrate in 15 ml of toluene was allowed to stand at 100°C for 1 h; the solvent was removed and the residue was recrystallized from water. The yield of crystals **I** was 1.30 g (95%), mp 202°C (202–210°C [5]). Tetraphentlantimony bromide was synthesized using the same procedure. The yield was 90%, mp 218°C (216–218°C [5]). b) A mixture of 1.00 g of pentaphenylantimony and 0.78 g of diphenylantimony trichloride crystal hydrate in 15 ml of toluene was allowed to stand at 100°C for 1 h; the solvent was removed and the residue was recrystallized from water. Crystals **I** were thus obtained in a yield of 0.84 g (91%), mp 198°C. The residue insoluble in water was dissolved in alcohol containing hydrogen chloride. After cooling an alcohol solution, 0.75 g (89%) of triphenylantimony dichloride (mp 143°C) was obtained. Tetraphenylantimony bromide (90%) and triphenylantimony dibromide (77%) were synthesized using the same procedure.

Reaction of pentaphenylantimony with triphenylantimony sulfate. A mixture of 1.00 g of pentaphenylantimony and 0.88 g of triphenylantimony sulfate in 15 ml of toluene was heated in a glass evacuated ampoule at 90–100°C for 6 h; the solvent was removed; the residue was dissolved in a hot water and the obtained solution was filtered off. After the solvent was evaporated, 1.60 g (85%) of tetraphenylantimony sulfate was obtained, mp 233°C (234–237°C [5]).

Reaction of pentaphenylantimony with acetylacetonatotriphenylantimony chloride. A mixture of 1.00 g of pentaphenylantimony and 0.96 g of acetylacetonatotriphenylantimony chloride in 10 ml of toluene was heated in a glass evacuated ampoule for 1 h. After cooling, the solvent was removed and the residue was recrystallized from a heptane–toluene (5 : 1) mixture; 0.87 g of tetraphenylantimony acetylacetonate was obtained, mp 209°C (decomposition) (209°C [6]). The residue was recrystallized from water; 0.81 g (88%) of crystals **I** was obtained, mp 198°C.

Table 1. Crystallographic parameters and results of refinement of structure **I**

Parameter	I
Empirical formula	$C_{24}H_{20}ClSb$
M	465.60
Crystal system	Monoclinic
T	293(2) K
Space group	$P2_1/n$
Unit cell parameters:	
a, Å	10.144(1)
b, Å	14.635(2)
c, Å	14.019(2)
β, deg	90.023(3)
V, Å^3	2081.1(2)
Z	4
ρ(calcd), g/cm^3	1.486
μ_{Mo}, mm^{-1}	1.458
F(000)	928
Crystal size, mm	Prism (0.15 × 0.14 × 0.12)
θ, deg	2.44–22.99
Range of indices	$-10 \leq h \leq 11$, $-12 \leq k \leq 16$, $-15 \leq l \leq 15$
Total number of reflections	9019
Independent reflections	2891 (R_{int} = 0.0421)
Reflections with $I > 2\sigma(I)$	2227
Number of refined parameters	235
GOOF	0.938
R-factors for $F^2 > 2\sigma(F^2)$	R_1 = 0.0255, wR_2 = 0.0557
R-factors for all reflections	R_1 = 0.0387, wR_2 = 0.0593

Table 2. Coordinates of atoms (×10^4) and their equivalent isotropic thermal parameters (×10^3) in structure **I**

Atom	x	y	z	U_{eq}, Å^2
Sb	8524(1)	1100(1)	7503(1)	46.9(1)
Cl	10994(1)	1701(1)	7217(1)	72.5(3)
C(1)	8323(4)	1481(3)	6053(3)	52(1)
C(2)	7959(5)	2352(4)	5831(3)	91(2)
C(3)	7733(6)	2588(5)	4893(4)	114(2)
C(4)	7883(5)	1949(5)	4197(4)	103(2)
C(5)	8268(5)	1090(4)	4410(3)	91(2)
C(6)	8478(5)	851(3)	5345(3)	71(1)
C(21)	9542(4)	–82(3)	7957(3)	48(1)
C(22)	9289(5)	–907(3)	7522(3)	65(1)
C(23)	9930(5)	–1683(3)	7821(4)	83(1)
C(24)	10776(5)	–1645(4)	8569(4)	87(2)
C(25)	11007(5)	–838(4)	9026(3)	83(2)
C(26)	10406(4)	–41(3)	8715(3)	65(1)
C(31)	8220(4)	2160(3)	8517(2)	51(1)
C(32)	7071(5)	2136(3)	9051(3)	66(1)
C(33)	6838(6)	2803(4)	9725(3)	84(2)
C(34)	7699(7)	3482(4)	9865(3)	84(2)
C(35)	8836(6)	3536(3)	9342(4)	90(2)
C(36)	9102(5)	2853(3)	8659(3)	73(1)
C(41)	6588(4)	489(3)	7631(3)	54(1)
C(42)	5573(5)	764(3)	7050(3)	73(1)
C(43)	4307(5)	436(5)	7188(5)	108(2)
C(44)	4079(6)	–213(5)	7870(5)	124(2)
C(45)	5072(6)	–498(5)	8451(5)	114(2)
C(46)	6318(5)	–145(3)	8325(4)	81(1)

Table 3. Selected bond lengths and angles in structure **I**

Bond	d, Å	Angle	ω, deg
Sb–C(21)	2.113(4)	C(21)SbC(11)	123.5(2)
Sb–C(11)	2.117(4)	C(21)SbC(31)	117.8(1)
Sb–C(31)	2.126(4)	C(11)SbC(31)	115.9(1)
Sb–C(41)	2.165(4)	C(21)SbC(41)	94.6(2)
Sb–Cl	2.686(1)	C(11)SbC(41)	95.8(2)
C(11)–C(12)	1.363(6)	C(31)SbC(41)	96.6(2)
C(11)–C(16)	1.364(5)	C(21)SbCl	81.8(1)
C(12)–C(13)	1.378(6)	C(11)SbCl	81.9(1)
C(13)–C(14)	1.360(7)	C(31)SbCl	89.8(1)
C(14)–C(15)	1.350(7)	C(41)SbCl	173.6(1)

IR spectra were recorded on a Hitachi-215 spectrophotometer (suspension in mineral oil between sodium chloride plates).

X-ray diffraction analysis of a naturally faceted single crystal was carried out on a SMART-1000 CCD diffractometer (MoK_α radiation, graphite monochromator). The data were collected in sets of 606, 450, and 235 scans at $\varphi = 0°$, 90°, and 180°, respectively; ω-scanning with a step of 0.3° and the step counting time of 10 s; the crystal–detector distance was 45 mm. Correction for absorption of X-rays by the sample was applied using equivalent reflections.

The structure was solved by direct methods and refined by the least-squares method in an anisotropic approximation for non-hydrogen atoms. The positions of the hydrogen atoms were determined geometrically and refined in the rider model. The data were collected and processed and the unit cell parameters were refined using the SMART and SAINT-*Plus* programs [7]. All the calculations for the determination and refinement of the structure were performed using the SHELXTL/PC programs [8].

Selected crystallographic data and the results of the structure refinement are presented in Table 1. The coordinates and thermal parameters of non-hydrogen atoms are given in Table 2, and the main bond lengths and angles are listed in Table 3.

REFERENCES

1. Sharutin, V.V., Senchurin, V.S., Sharutina, O.K., *et al.*, *Zh. Obshch. Khim.*, 1996, vol. 66, no. 10, p. 1755.
2. Sharutin, V.V., Sharutina, O.K., Egorova, I.V., and Panova, L.P., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 2, p. 345.
3. Lebedev, V.A., Bochkova, R.I., Kuz'min, E.A., *et al.*, *Dokl. Akad. Nauk SSSR*, 1981, vol. 260, no. 5, p. 1124.
4. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 11, p. 3015.
5. Kocheshkov, K.A., Skoldinov, A.P., and Zemlyanskii, N.N., *Metody elementoorganicheskoi khimii. Sur'ma, vismut* (Methods of Organoelement Chemistry. Antimony and Bismuth), Moscow: Nauka, 1976.
6. Sharutin, V.V., Sharutina, O.K., Zadachina, O.P., *et al.*, *Zh. Obshch. Khim.*, 2000, vol. 70, no. 5, p. 746.
7. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Madison, WI, USA: Bruker AXS Inc., 1998.
8. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data*, Madison, WI, USA, Bruker AXS Inc.: 1998.