Journal of Organometallic Chemistry, 154 (1978) 13—19
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PENTAFLUOROPHENYLANTIMONY COMPOUNDS

A. OTERO and P. ROYO
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Murcia (Spain)

(Received January 3rd, 1978)

Summary

The chemical behaviour of $(C_6F_5)_3Sb$ (I), has been studied. Attempts to isolate transition-metal complexes of I were unsuccessful. Hydrolysis of I gives the binuclear $[(C_6F_5)_2Sb]_2O$ (II) and treatment of I with chlorine, thallic chloride or copper(II) chloride gives $(C_6F_5)_3SbCl_2$ (III). Reactions of III with $AgNO_3$, $AgClO_4$ and $NaOCH_3$ give disubstituted compounds of the type $(C_6F_5)_3SbX_2$ (IV, X = NO_3; V, X = ClO_4; VI, X = OCH_3). Reactions of III with sodium acetylacetonate and sodium oxinate gives the monosubstituted octahedral complexes $(C_6F_5)_3SbCl$-Acac (VII) and $(C_6F_5)_3SbClOx$ (VIII). Compounds VI—VIII are insoluble in water whereas compounds III—IV are hydrolysed to the binuclear derivatives $[(C_6F_5)_3SbX]_2O$ (IX, X = Cl; X, X = NO_3), and V similarly gives $\{[(C_6F_5)_3Sb]_2O\}$-$(ClO_4)_2$.

Introduction

Recently we described the preparation of novel pentafluorophenyl arsenic(V) derivatives by oxidation of $(C_6F_5)_3As$ [1]. Pentafluorophenyl antimony(V) compounds $(C_6F_5)_3SbX_2$ (X = Cl, Br) were obtained [2] by the same reaction. We describe the isolation of new compounds of antimony(III) and antimony(V), and discuss below their chemical behaviour and structure.

Results and discussion

(a) Coordinating capacity of $(C_6F_5)_3Sb$

$(C_6F_5)_3Sb$, prepared as previously described [3], does not react with anhydrous nickel(II) halides in ethanol, nor does it stabilize the nickel(I) complex when solutions in ethanol of nickel(II) chloride are reduced with $NaBH_4$ in its presence.

The reaction of $(C_6F_5)_3Sb$ with $AgClO_4$ in benzene gives unchanged starting material, whereas under the same conditions $(C_6F_5)_3As$ forms fairly stable neutral and cationic complexes [1].

(b) Hydrolysis of $(C_6F_5)_3Sb$

Addition of water to solutions of $(C_6F_5)_3Sb$ causes cleavage of one of the C—Sb bonds, and a subsequent condensation gives the binuclear oxo bridge derivative:

$$2(C_6F_5)_3Sb + H_2O \rightarrow 2\ C_6F_5H + (C_6F_5)_2SbOSb(C_6F_5)_2 \qquad (1)$$

(c) Oxidation of $(C_6F_5)_3Sb$

Addition of a CCl_4 solution of chlorine or bromine to solutions of $(C_6F_5)_3Sb$ is known to give bis-haloorganoantimony(V) compounds [2]. We have prepared $(C_6F_5)_3SbCl_2$ (III), not only by direct reaction with chlorine but also by using $TlCl_3$ and $CuCl_2$ as oxidants, according to eq. 2 and 3.

$$(C_6F_5)_3Sb + TlCl_3 \xrightarrow{\text{Ethyl ether}} (C_6F_5)_3SbCl_2 + TlCl\downarrow \qquad (2)$$

$$(C_6F_5)_3Sb + 2\ CuCl_2 \xrightarrow{\text{Acetone}} (C_6F_5)_3SbCl_2 + 2\ CuCl\downarrow \qquad (3)$$

Bromine also reacts similarly when the solution is kept in the cold, but above room temperature the dibromide decomposes slowly to regenerate the free halogen. In contrast, iodine does not react with compound I even in the cold.

Similar reactions of chlorine, bromine and iodine with $(C_6F_5)_3Bi$ give only unidentified decomposition products.

(d) Substitution reactions of $(C_6F_5)_3SbCl_2$

When benzene solutions of silver salts such as $AgNO_3$ or $AgClO_4$ are added to solutions of III, AgCl separates immediately. The disubstituted organoantimony(V) compounds can be isolated from the solution (eq. 4). In contrast, $(C_6F_5)_3$-$AsCl_2$ gives monosubstituted products [1]. This difference in behaviour may be attributed to the greater tendency of antimony to expand its coordination sphere, and to the lower element—chlorine bond energy. However, whereas $(C_6F_5)_3AsCl_2$ gives $(C_6F_5)_3AsCl(OR)$ on treatment with alcohols [1], III is recovered unchanged from its solutions in methanol or ethanol. This suggests that equilibrium 5 lies far over to the left. However, addition of $NaOCH_3$ gives the disubstituted compound VI (Table 1).

$$(C_6F_5)_3SbCl_2 + 2\ AgX \rightarrow (C_6F_5)_3SbX_2 + 2\ AgCl \qquad (4)$$

$$(X = NO_3,\ ClO_4)$$

$$(C_6F_5)_3SbCl_2 + 2\ ROH \rightleftharpoons (C_6F_5)_3Sb(OR)_2 + 2\ HCl \qquad (5)$$

When sodium salts of bidentate anionic ligands such as acetylacetonate and oxinate are used, one of the chlorine atoms is replaced to give the hexacoordinate complexes VII and VIII (Table 1).

(e) Hydrolysis of pentafluorophenyl antimony(V) compounds

Addition of water to solutions of compounds III—V causes cleavage of only one of the Sb—X bonds. Simultaneous condensation occurs, to give the binuclear oxo bridge compound (eq. 6).

$$2(C_6F_5)_3SbX_2 + H_2O \rightarrow (C_6F_5)_3XSbOSbX(C_6F_5)_3 + 2\ HX \qquad (6)$$

$$(X = Cl,\ NO_3)$$

TABLE 1

ANALYTICAL DATA FOR PENTAFLUOROPHENYLANTIMONY COMPOUNDS

Compound	Molecular formula	Analysis (calcd. (found)) in %				
		C	Sb.	Cl	H	N
I	$C_{18}SbF_{15}$	34.70 (34.12)	19.55 (19.40)			
II	$C_{24}Sb_2F_{20}O$	31.05 (31.75)	26.25 (26.10)			
III	$C_{18}SbCl_2F_{15}$	31.13 (31.08)	17.54 (17.63)	10.22 (10.11)		
IV	$C_{18}SbF_{15}N_2O_6$	28.92 (29.86)	16.30 (16.45)			3.75 (3.01)
V	$C_{18}SbCl_2F_{15}O_8$	26.28 (26.15)	14.81 (14.92)	8.62 (8.70)		
VI	$C_{20}SbF_{15}H_6O_2$	35.05 (35.12)	17.78 (17.80)		0.87 (0.81)	
VII	$C_{23}SbClF_{15}H_7O_2$	36.41 (36.38)	16.07 (16.20)	4.68 (4.63)	0.10 (0.18)	
VIII	$C_{27}SbClF_{15}H_8NO$	40.40 (39.98)	15.17 (15.23)	4.41 (4.45)	0.78 (0.82)	1.72 (1.70)
IX	$C_{36}Sb_2Cl_2F_{30}O$	32.40 (31.98)	18.59 (18.61)	5.41 (5.40)		
X	$C_{36}Sb_2F_{30}N_2O_7$	31.18 (30.84)	17.57 (17.60)			2.02 (1.98)
XI	$C_{36}Sb_2Cl_2F_{30}O_9$	29.58 (29.32)	16.67 (16.70)	4.85 (4.81)		

When X = ClO_4, the same reaction gives the binuclear cationic compound containing tetracoordinate antimony atoms (eq. 7).

$$2(C_6F_5)_3Sb(ClO_4)_2 + H_2O \rightarrow [(C_6F_5)_3SbOSb(C_6F_5)_3](ClO_4)_2 + 2\ HClO_4 \qquad (7)$$

(f) Oxidizing properties of $(C_6F_5)_3SbCl_2$

Compound III behaves as a halogenating agent. Thus, on reaction with PPh_3AuCl, both chlorine atoms are transfixed:

$$(C_6F_5)_3SbCl_2 + PPh_3AuCl \rightarrow (C_6F_5)_3Sb + PPh_3AuCl_3 \qquad (8)$$

Compound III also oxidizes bromide and iodide ion in acetone to give free halogen.

$$(C_6F_5)_3SbCl_2 + 2\ X^- \rightarrow (C_6F_5)_3Sb + X_2 + 2\ Cl^- \qquad (9)$$

$$(X = Br, I)$$

This behaviour is consistent with the low stability of $(C_6F_5)_3SbBr_2$; this may be prepared by the inverse reaction [2], but its solutions in chloroform decompose slowly at room temperature with elimination of bromine. Reaction 9 with X = I is also consistent with complete lack of stability of the iodo compound.

TABLE 2

MELTING POINTS AND CONDUCTIVITIES OF PENTAFLUOROPHENYL ANTIMONY DERIVATIVES

Compound	M.p. (°C)	Λ (ohm^{-1} cm^2 mol^{-1}) [a]		
		Acetone	Nitromethane	Benzene
I	74	4.53		
II	142	1.26		
III	255	40.08	16.06	
IV	—			0.09
V	95	260.43	178.35	
VI	60	13.63	12.56	
VII	160	2.10		
VIII	200	3.70		
IX	105	38.32		
X	130	30.21	12.86	
XI	110	257.34	167.89	

[a] Measured in solution of 5×10^{-4} *M*.

(g) Conductivity

The antimony(III) derivatives are non-conductors in acetone. The conductivities of the $(C_6F_5)_3SbX_2$ species depend on the substituent. Dissociation increases as the coordinating capacity of X decreases. When X = OCH_3 the compound is a non-conductor in solvents such as acetone or nitromethane (see Table 2), but conductivity is observed for X = Cl. Conductivity measurements could not be made on the dinitrate because this compound is not soluble in polar solvents. It is a non-conductor in benzene. Finally, for X = ClO_4 the conductivity in polar solvents corresponds to a 2/1 electrolyte [4]. Similar behaviour is observed for compounds IX—XI of the type $(C_6F_5)_6Sb_2OX_2$. The conductivities found correspond to partial dissociation for compounds in which X = Cl, NO_3. Hexacoordinate complexes VII—VIII are non conductors in acetone.

(h) IR Spectroscopy

All isolated compounds show IR absorptions characteristic of the C_6F_5 group [5,6]. The IR spectrum of compound I has been previously described [2]. Compound II shows the IR absorptions found for compound I, but also has an additional absorption at 870—790 s cm^{-1}, which must be assigned to the ν(Sb—O—Sb) vibration. We propose a structure containing two pyramidal antimony(III) atoms bonded through an oxygen bridge. In accordance with structures of other organoantimony(V) compounds [7,8], we propose a trigonal bipyramidal structure for compounds III—VI of the type $(C_6F_5)_3SbX_2$.

A decision between three possible isomers can be reached from IR spectroscopy. The ν_{sym}(C—Sb) vibration for the *trans*-X isomer with the three C_6F_5 groups occupying equatorial positions should be IR inactive, and moreover should give a unique ν(X—Sb) absorption. The two remaining isomers should give an IR active ν_{sym}(C—Sb) absorption corresponding to the *t*-mode which must be located in the region 300—250 cm^{-1} [2] and one of them has to show two different ν(X—Sb) absorptions. All the isolated pentacoordinate compounds show IR spectra in which the absorption ν_{sym}(C—Sb) is absent, and we conclude that all

TABLE 3

RELEVANT IR ABSORPTIONS OF THE ANIONS IN R_3SbX_2 [a] AND R_3SbClX [a] COMPOUNDS (CM^{-1})

$R_3Sb(NO_3)_2$	$R_3Sb(ClO_4)_2$	$R_3Sb(OCH_3)_2$	$R_3SbClAcac$	$R_3SbClOx$	Assignments
c	c	500—530w	460w	540m	ν(Sb—O)
1450—1500 [b]					$\nu_{as}(NO_2)$ [d]
c					$\nu_s(NO_2)$ [d]
1010—1040 [b]					ν_s(NO) [d]
c					$\delta(NO_3)$ [d]
	1140s [b]				ν_1 [e]
	925vw				ν_2 [e]
	625m [b]				ν_3 [e]
	1010—1020vs [b]				ν_4 [e]
	635m				ν_5 [e]
		2920m			ν(C—H)
				415w	ν(Sb—N)
			1535—1540s		ν(C—O)
			1535—1540s		ν(C—C)

[a] R = C_6F_5. [b] Overlapped by C_6F_5 absorptions. [c] Absent. [d] Referred to the monodentate NO_3 modes. [e] Referred to the ClO_4 modes [11].

compounds have a bipyramidal structure with the three C_6F_5 groups in the equatorial plane. Compound III shows an absorption at 330 s cm^{-1} which must be assigned to the ν(Cl—Sb) vibration. These data permit the assignment of a *trans*-Cl bipyramidal structure to compound III.

The same structure is probably also present in compounds IV—VI, since as the ν_{sym}(C—Sb) is absent, the ν(Sb—O) vibrations cannot be assigned. The presence of NO_3 or ClO_4 groups is consistent with the IR spectra (see Table 3). It is noteworthy that compound V exists as covalent pentacoordinate molecules in the solid, but it is completely dissociated in polar solvents, as shown by the conductivity measurements.

The ν_{sym}(C—Sb) absorption is also absent in spectra of compounds IX and X. They show an absorption at 720—630 s cm^{-1} which can be assigned to the ν(Sb—O—Sb) vibration. Compound IX has the ν(Cl—Sb) vibration at 310 cm^{-1}. Thus, a trigonal bipyramidal structure containing an oxygen bridge can be proposed for these two complexes.

Compound XI, which is ionic in solution, also contains the free ClO_4 anion in the solid. It shows an absorption at 730—650 s cm^{-1}, which can be assigned to the ν(Sb—O—Sb) vibration. All the remaining absorptions are similar to those observed for compound I. Thus, it is possible to propose the existence in the solid of a binuclear cation containing tetrahedral antimony atoms. Structure cannot be suggested for compounds VII and VIII containing a bidentate anionic ligand on the basis of IR data only.

Experimental

The IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer (over the range 4000—250 cm^{-1}) using Nujol mulls between CsI plates and KBr pellets. Conductivities were measured with a Phillips PW 9501/01 conductimeter. C, H, N analyses were made with a Perkin—Elmer 240 microanalyzer. Antimony was determined according to ref. 9 and chlorine was determined according to ref. 10. $(C_6F_5)_3Sb$(I) was obtained as described in ref. 3.

$[(C_6F_5)_2Sb]_2O$ (II)

The addition of a few ml of water to a solution of I (1 g, 1.60 mmol) in petroleum ether produces a muddy suspension. After stirring at room temperature for a few minutes, evaporation of the solvent gives II as a crystalline solid, which is filtered off and dried over $CaCl_2$. Yield 80%.

$(C_6F_5)_2SbCl_2$ (III)

(a) Oxidation with chlorine. 6.25 ml of a 0.5 *N* solution of Cl_2 in CCl_4 (0.114 g, 1.606 mmol) are slowly added to a solution of I in petroleum ether (1 g, 1.605 mmol). The solution is stirred at room temperature for 24 h under dry N_2 and III is obtained as crystals by concentration and cooling of the solution. It is recrystallized from petroleum ether. Yield 78%.

(b) with $TlCl_3$. Ethyl ether (40 ml) is added to a solid mixture of $(C_6F_5)_3Sb$ (1 g, 1.605 mmol) and $TlCl_3$ (0.50 g, 1.606 mmol). After stirring at room temperature for 48 h, TlCl is filtered off and solution is evaporated to dryness under vacuo. The residue is recrystallized from petroleum ether to give III. Yield 70%.

(c) With $CuCl_2$. I (1 g, 1.605 mmol) is added to a solution of $CuCl_2 \cdot 2\,H_2O$ (0.274 g, 1.605 mmol) in acetone (100 ml). After stirring at room temperature for 1 h, CuCl is filtered off and the solution is evaporated to dryness. The residue is recrystallized as in (b). Yield 80%.

$(C_6F_5)_3SbX_2$, $X = NO_3$, ClO_4, OCH_3 (IV—VI)

A solution of III (1 g, 1.44 mmol) in benzene (50 ml) is added to a solution of $AgNO_3$ (0.489 g, 2.880 mmol) or $AgClO_4$ (0.600 g, 2.899 mmol) in benzene. After stirring under reflux for 2 h, AgCl is filtered off. Compounds IV and V are obtained as white crystalline solids by evaporation and cooling. Yield 40 and 48% respectively.

Compound VI is similarly obtained by addition of sodium methoxide (0.466 g, 8.640 mmol) to a solution of III (1.500 g, 2.160 mmol) in methanol (150 ml). After stirring at room temperature for 4 h the solution is evaporated to dryness. The addition of a few drops of water to the solution of the residue in methanol produces VI as a crystalline solid. Yield 48%.

$(C_6F_5)_3SbCl(O—L)$ ((O—L) = acac, oxinate) (VII—VIII)

NaAcac (0.351 g, 2.882 mmol) or NaOxinate (0.481 g, 2.882 mmol) are added to a solution of III (2 g, 2.882 mmol) in chloroform. The suspension is stirred under reflux for 5 h and the remaining insoluble solid is eliminated by filtration. The filtrate (colorless for VII and yellow for VIII) is evaporated to dryness under vacuo. The residue is recrystallized from chloroform by addition of a few drops of cyclohexane to give colorless crystals of VII (yield 54%) or yellow crystals of VIII (yield 68%).

$[(C_6F_5)_3SbCl]_2O$ (IX)

A solution of III (2 g, 2.880 mmol) in hot aqueous ethanol is stirred at room temperature for 1 h. Evaporation of the solvent gives IX as a crystalline solid, which is filtered off and dried under vacuo. Yield 42%.

$[(C_6F_5)_3Sb(NO_3)]_2O$ (X)

A suspension of V in water is stirred for 1 h at room temperature. Compound X is obtained in 43% yield by filtration and is dried over $CaCl_2$.

$[(C_6F_5)_3Sb]_2O(ClO_4)_2$ (XI)

(a) With $AgClO_4$. A solution of IX (3.158 g, 2.411 mmol) in ethanol is added dropwise to a solution of $AgClO_4$ (1 g, 4.822 mmol) in benzene. After stirring for 2 h at room temperature AgCl is filtered off. The solution is evaporated to dryness and the residue is recrystallized from acetone to give white crystals of XI. Yield 58%.

(b) With water. A solution of V in aqueous acetone is stirred for 1 h at room temperature. Subsequent concentration of the solution gives XI, which is filtered off and dried over $CaCl_2$. Yield 76.5%.

Acknowledgement

We greatly appreciate the award of a Research Fellowship (to A.O.) by the Ministerio de Educación y Ciencia (Spain).

References

1 A. Otero and P. Royo, J. Organometal. Chem., 149 (1978) 315.
2 B.A. Nevett and A. Perry, Spectrochim. Acta A, 31 (1975) 101.
3 M. Fild, O. Glemser and G. Christoph, Angew. Chem., 76 (1964) 953.
4 W.J. Ceary, Coord. Chem. Rev., 7 (1971) 81.
5 D.A. Long and D. Steele, Spectrochim. Acta, 19 (1963) 1955.
6 I.J. Hyams, E.P. Lippincott and R.T. Bailey, Spectrochim. Acta, 22 (1966) 695.
7 A.F. Wells, Z. Krist. A, 99 (1938) 367.
8 T.N. Polynova and M.A. Porai-Koshits, J. Struct. Chem. (USSR) (Engl. Transl.), 86 (1964) 209.
9 E. Schulek and Wofstadt, Z. Analyt. Chem., 108 (1937) 400.
10 D.C. White, Microchim. Acta, (1961) 449.
11 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley—Interscience, New York, 1970.