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Aryl Compounds of Pentavalent Antimony: Syntheses, Reactions, and Structures

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Abstract—The synthesis methods, some reactions, and specific features of the structures of aryl compounds of pentavalent antimony and examples of their possible use are systematized and described on the basis of an analysis of the works published since 2009 to the present time. Some earlier works are also reviewed due to this special significance. When discussing the synthesis methods, the main attention is given to the most efficient approaches to the syntheses of the aryl compounds, for example, the reactions of ligand redistribution, substitution, and oxidative addition. The formation of heterocyclic antimony compounds is considered. The data on the biological and catalytic activities of selected antimony derivatives are presented. The bibliography consists of 318 references.

Keywords: mono-, bi-, and polynuclear antimony(V) compounds, synthesis, oxidative addition reactions, catalytic, bacterial, and anticancer activity

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Contents

INTRODUCTION

An increasing interest in organic antimony compounds is mainly determined by a high potential of their application in the very diverse areas of practical activity: as drugs, biocides, fungicides, and reagents and components of catalytic systems during polymerization, in fine organic synthesis, as antioxidants, and others. In the organoantimony derivatives antimony exists in two main oxidation states, +3 and +5, and, correspondingly, forms organic compounds of antimony(III) and antimony(V). In many cases, the structures of the antimony(III) derivatives are oligomeric or polymeric, which impedes, to a certain and sometimes significant extent, their study and use, whereas the organic derivatives of antimony(V) assume a broader variety of structural types and, correspondingly, reactivity. From the viewpoint of toxicity, the antimony(V) compounds are less toxic than the antimony(III) organic derivatives. The basic research of the structures and properties of the organoantimony com-

pounds prompted the extension of possibilities of their applied use: the cases of the nontrivial chemical behavior were observed, for example, the reversible binding of oxygen with antimony(V) *o*-amidophenolates and catecholates, the capability of selective fixing halide anions by the mono- and binuclear organometallic antimony derivatives, a high reactivity of the organoantimony compounds in some important reactions of organic synthesis, a significant biochemical activity along with a fairly low toxicity, etc. These factors predetermine, to a considerable extent, interest in the synthesis of new aryl compounds of pentavalent antimony and the development of the corresponding synthesis methods.

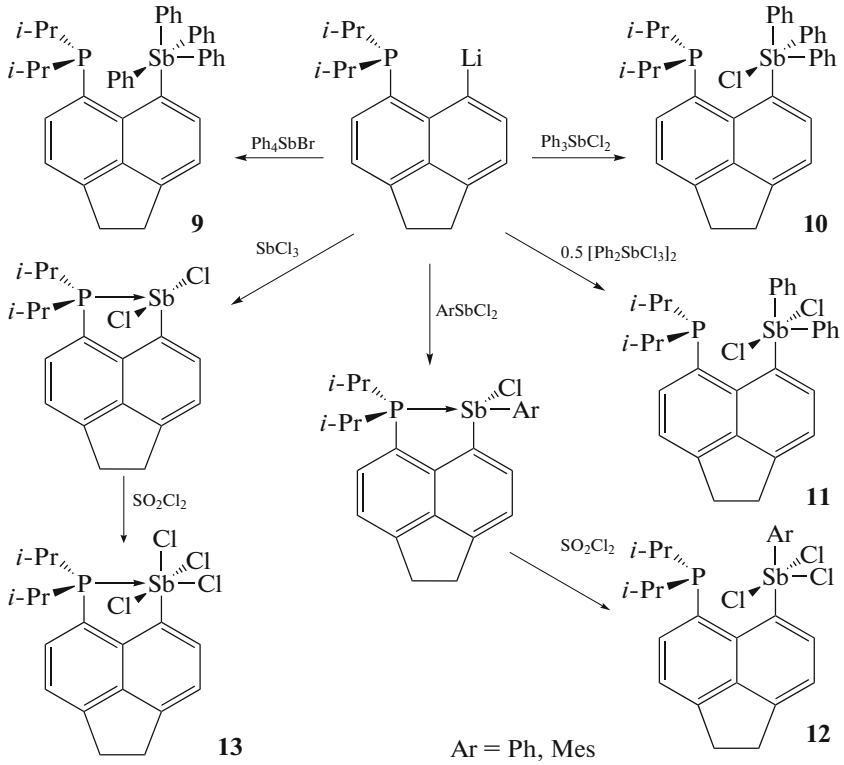
SYNTHESIS OF ANTIMONY PENTAARYL COMPOUNDS Ar_5Sb

The most efficient methods for the synthesis of the antimony pentaaryl derivatives are based on the reactions of antimony with organomagnesium or organolithium reagents. For example, the antimony pentaaryl compounds with *p*-methylphenyl and *p*-trifluoromethylphenyl substituents $Ar_nTol_{(5-n)}Sb$ ($n = 0$–5, Ar is *p*-$CF_3C_6H_4$, Tol is *p*-$CH_3C_6H_4$: Tol_5Sb (**1**), $ArTol_4Sb$ (**2**), Ar_2Tol_3Sb (**3**), Ar_3Tol_2Sb (**4**), Ar_4TolSb (**5**), and Ar_5Sb (**6**)) were synthesized from the corresponding triarylantimony dihalides or tetraarylantimony fluorides and the Grignard reagent or aryllithium in ether at −78°C [1]. Triarylantimony difluorides and tetraarylantimony fluorides were chosen as the initial compounds, because their reaction rates with the Grignard reagent or organolithium derivative are considerably higher than those for bromides. According to the X-ray diffraction analysis (XRD) data, the antimony atoms in compounds **2**–**6** have the trigonal bipyramidal environment, and the more electronegative *p*-trifluoromethylphenyl ligands in compounds **2**–**5** selectively occupy the axial positions. The ligand exchange reaction was found to occur in a deuterobenzene solution of a mixture of compounds **1** and **6** at 60°C, and all the six compounds **1**–**6** were detected in the equilibrium mixture by ^{13}C NMR spectroscopy, among which compound **3** was the most stable.

Another representative of the pentavalent antimony aryl derivatives, namely, penta(perchlorophenyl)antimony $(C_6Cl_5)_5Sb$ (**7**), was synthesized directly from antimony pentachloride and perchlorophenyllithium in a mixture of diethyl ether and hexane at −78°C in the yield up to 30% [2]. A low yield of the target product is due to the parallel reduction Sb(V) → Sb(III). According to the XRD data, the antimony atom in the molecule of compound **7** has a slightly distorted trigonal bipyramidal coordination mode.

At the molar ratio of perfluorophenyllithium to antimony equal to 4 : 1, the reaction ceases at the stage of formation of the corresponding tetraarylantimony monochloride $(C_6F_5)_4SbCl$ (**8**, 25%) [3].

The nonsymmetric antimony derivatives Ph_4ArSb (**9**) or $Ph_3ArSbCl$ (**10**) can be synthesized from aryllithium containing the *i*-Pr_2P group in the aryl substituent and triphenylantimony dichloride or tetraphenylantimony bromide (Scheme 1) [4].



Scheme 1.

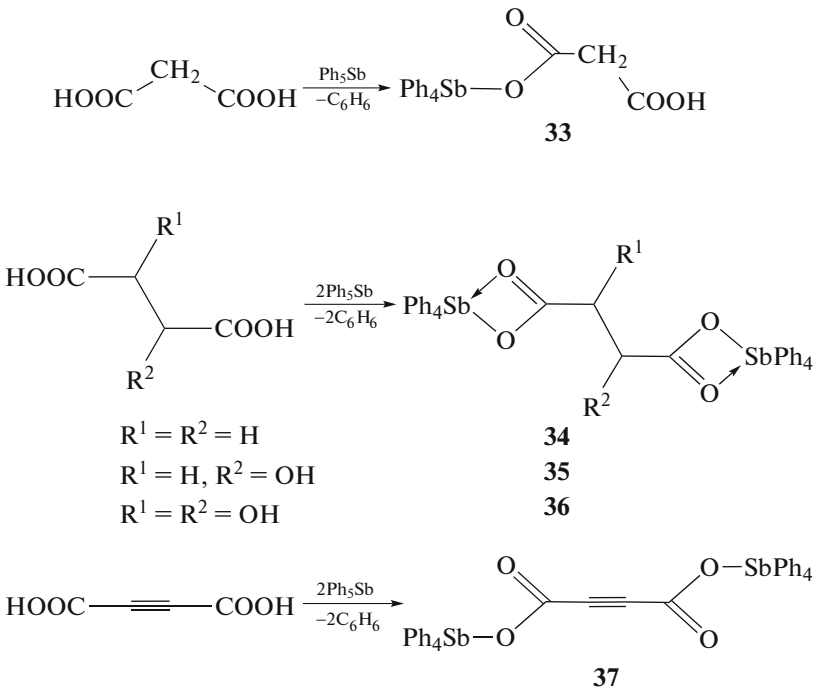
A series of organoantimony derivatives **9**–**13** containing the $Ph_{(4-n)}SbCl_n$ group was synthesized in the course of studying the reactions of the organolithium derivative of acenaphthene.

ANTIMONY DERIVATIVES Ar_4SbX AND THEIR REACTIONS

Synthesis of compounds Ar_4SbX by pentaarylantimony dearylation with acids. The efficient synthesis of the antimony derivatives with the general formula Ar_4SbX, where X is the electronegative ligand, are based on the reactions of pentaarylantimony with the compounds bearing the mobile hydrogen atom. In this case, the target product is synthesized in one step, and its isolation is not labor-consuming. A series of tetraphenylantimony aroxides $Ph_4(ArO)Sb$ was thus obtained in which Ar is 2-$NO_2C_6H_4$ (**14**) [5], 2,4,6-$Cl_3C_6H_2$ (**15**) [6], C_6H_7–C_6H_4 (4-cyclohexadienylphenyl) (**16**) [7], 2,6-Br_2-4-*t*-BuC_6H_2 (**17**) [7], 2,4-$(NO_2)_2C_6H_3$ (**18**) [7], 2,6-Br_2-4-$NO_2C_6H_2$ (**19**) [7], C_6F_5 (**20**) [8], C_6Cl_5 (**21**) [8], and 2,6-Br_2-4-MeC_6H_2 (**22**) [9]. Tetra-*p*-tolylantimony aroxides $Tol_4(ArO)Sb$, where Ar is C_6F_5, (**23**) [8], C_6Cl_5 (**24**) [8], 2,6-$Cl_2C_6H_3$ (**25**) [10], 2,4-$(NO_2)_2C_6H_3$ (**26**) [10], and 2,4,6-$(NO_2)_3C_6H_2$ (**27**) [10], were also synthesized using this method.

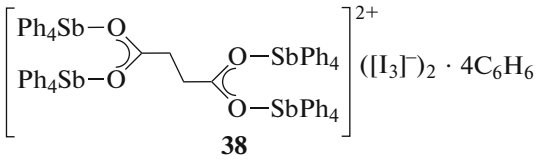
The reactions of pentaphenylantimony with such carboxylic acids as 1-adamantanecarboxylic (**28**) [11], *N*-benzoylglycinic (**29**) [12], phenylpropiolic (**30**) [13], 4-oxybenzoic (**31**) [14], and phthalic (**32**) [15] acids proceed similarly.

Acidic tetraphenylantimony malonate **33** was synthesized by the reaction of pentaphenylantimony and malonic acid taken in equimolar amounts in toluene (Scheme 2) [16]. At the same time, the reactions of dibasic carboxylic acids (succinic, malic, and tartaric) with pentaphenylantimony (2 mol) in toluene for 48 h afford binuclear antimony derivatives **34**–**36** in the yield up to 98% [17]. The product of the reaction of acetylenedicarboxylic acid with pentaphenylantimony (toluene, 24 h, 23°C, molar ratio 1 : 2) is bis(tetraphenyl)antimonyacetylene dicarboxylate **37** [18].



Scheme 2.

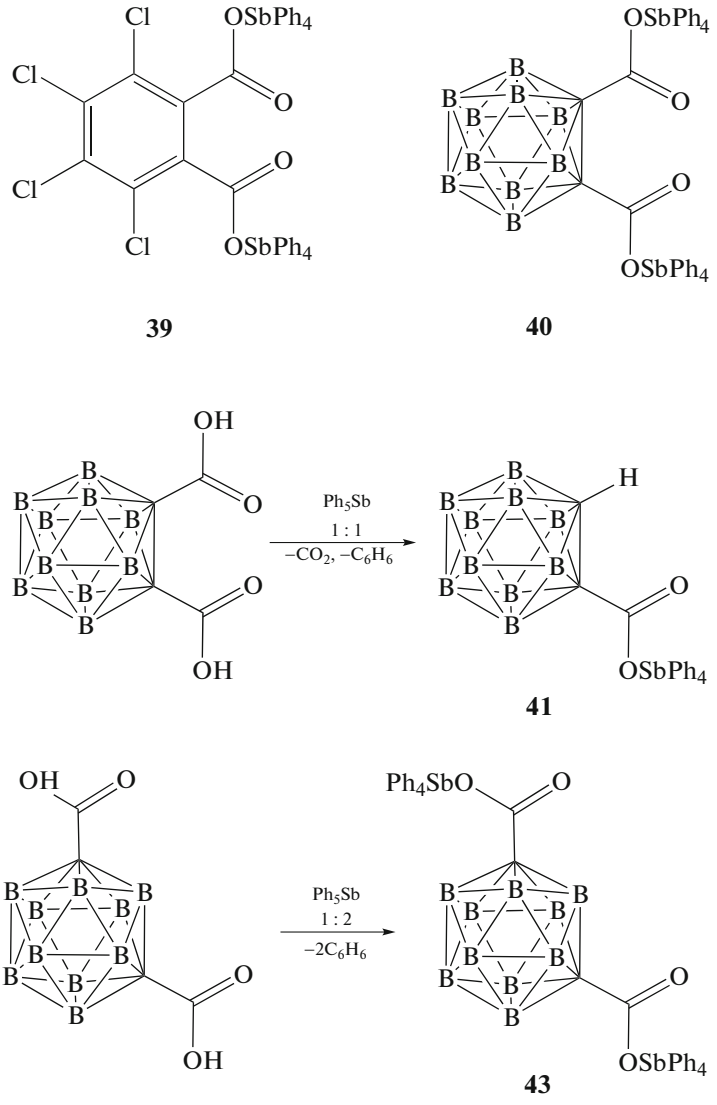
The reaction of bis(tetraphenylantimony) succinate with iodine in benzene should be mentioned affording [(μ_4-succinato)hexadecaphenyltetraantimony] triiodide solvate with benzene (**38**) in 72% yield (Scheme 3) [19].



Scheme 3.

The nonequivalent Sb(1) and Sb(2) atoms in the centrosymmetric cation of compound **38** have the trigonal bipyramidal coordination mode with the oxygen atoms in the axial positions (Sb(1,2)–O 2.347(4), 2.525(4), Sb(1,2)–C_{equiv} 2.109(7)–2.120(7) Å, 2.082(5)–2.106(7), Sb(1,2)–C_{ax} 2.158(7), 2.121(9) Å; angles OSb(1,2)C_{ax} 178.8(2)°, 174.5(3)°). The geometry of the $[I_3]^-$ anions is close to linear (angle I–I–I 179.41(4)°, distances I–I 2.880(1), 2.921(1) Å).

A specific feature of the reaction of pentaphenylantimony with tetrachlorophthalic acid is that binuclear compound **29** is the reaction product even at the 1 : 1 ratio of the reactants (Scheme 4) [20].



Scheme 4.

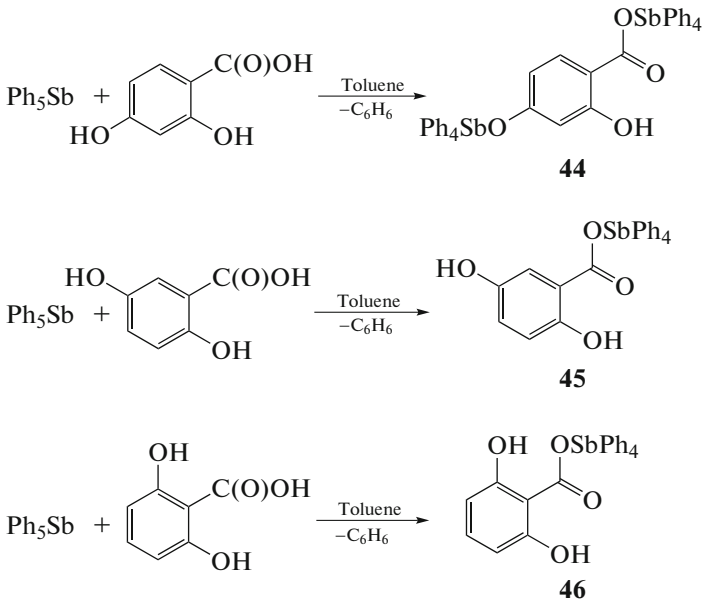
The product of the reaction of pentaphenylantimony with carboranedicarboxylic acid at the 2 : 1 molar ratio of the initial reactants (toluene, 24°C, 18 h) is binuclear antimony derivative **40** (94%), whereas the interaction of the equimolar amounts proceeds with the elimination of carbon dioxide and formation of tetraphenylantimony monocarboxylate **41** (Scheme 4) [21].

Note that the interaction of equimolar amounts of acetylenedicarboxylic acid and pentaphenylantimony was also accompanied by carbon dioxide elimination, and tetraphenylantimony propiolate **42** was formed, which was also synthesized from pentaphenylantimony and propiolic acid [22].

At the same time, *meta*-carboranedicarboxylic acid reacts with pentaphenylantimony in a benzene solution regardless of the ratio of the initial reactants to form binuclear dicarboxylate **43** only (Scheme 4) [23].

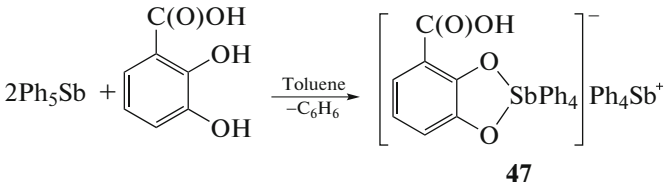
It is shown that the reaction of pentaphenylantimony with 2,4-dihydroxybenzoic acid involves the

carboxyl and *para*-hydroxyl groups regardless of the reactant ratio and affords tetraphenylantimony(V) 2-hydroxy-4-tetraphenylstiboxybenzoate **44** (Scheme 5) in the molecule of which the trigonal bipyramidal coordination mode of two antimony atoms is distorted to different extents [24]. It is found that the reactions of pentaphenylantimony with 2,5- and 2,6-dihydroxybenzoic acids involve only carboxyl groups and their products are tetraphenylantimony 2,5-dihydroxybenzoate **45** and tetraphenylantimony 2,6-dihydroxybenzoate **46**, respectively (Scheme 5) [25].



Scheme 5.

When reacting with pentaphenylantimony, 2,3-dihydroxybenzoic acid exhibits the properties of dihydroxybenzene and the carboxyl group remains inert even on heating of the reaction mixture containing pentaphenylantimony excess. The single reaction product is ionic complex **47**, namely, tetraphenylstibonium 2-carboxycatecholatotetraphenylstibotate(V), whose anion contains the five-membered metallocycle (Scheme 6).

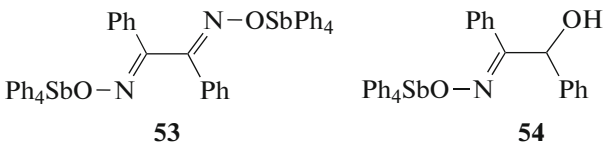


Scheme 6.

Tetraphenylantimony oximates $Ph_4SbON{=}CHR$ (R = C_6H_4(OH-2) (**48**) [26], C_6H_4(Br-2) (**49**) [27], $C_6H_4(NO_2$-2) (**50**) [27], and C_4H_3S (**51**) [27]) in which the coordination number of the central atom increases to six due to the additional coordination of the nitrogen atom of the oxime ligand with the Sb atom were synthesized from equimolar amounts of pentaphenylantimony and oxime in a solution of aromatic hydrocarbon (24 h, 20°C) [26, 27].

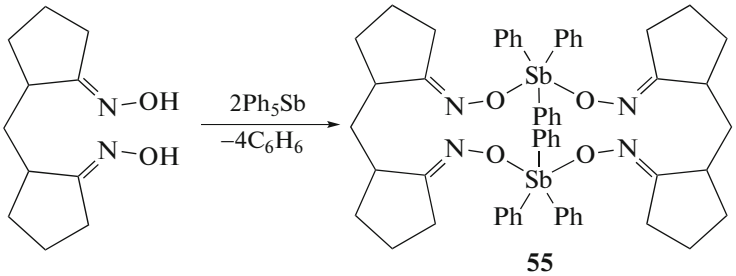
Under similar conditions, penta-*para*-tolylantimony reacts with 4-dimethylaminobenzaldoxime to form tetra-*para*-tolylantimony oximate $(4\text{-}MeC_6H_4)_4SbON{=}CHC_6H_4NMe_2$-4 (**52**) [28].

Regardless of the ratio of the initial reactants, the reaction of pentaphenylantimony with 1,2-diphenylethane dioxime or 1,2-diphenyl(1-oxy)ethane oxime-2 in toluene afforded bis(tetraphenylantimony) 1,2-diphenylethanedioximate **53** as a solvate with toluene and tetraphenylantimony 1,2-diphenyl(1-oxy)ethaneoximate-2 **54** (Scheme 7) [29].



Scheme 7.

It is shown that the reaction of methylenedicyclopentanone-2,2' with pentaphenylantimony under drastic conditions (90°C, 5 h) at the 1 : 2 molar ratio of the initial reactants results in the formation of the organoantimony compound bis-μ-[(methylenedicyclopentanone-2,2'-dioximato)triphenylantimony] **55** in the molecules of which the symmetric dioxime radicals alternate with the structural units of triphenylantimony (Scheme 8) [30].



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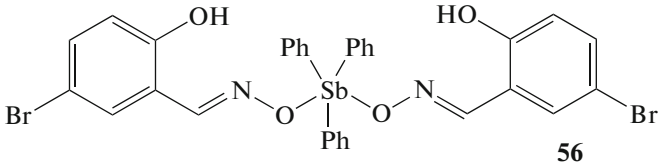

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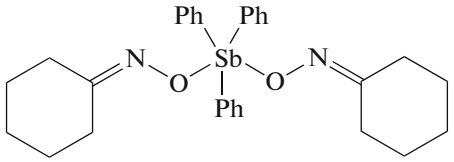

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Scheme 8.

In centrosymmetric compound **55** the antimony atoms have the trigonal bipyramidal coordination with the oxygen atoms in the axial positions.

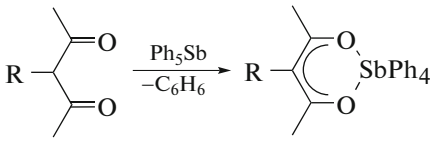
The reactions of pentaphenylantimony with 2-hydroxy-5-bromobenzaldoxime and cyclohexanone oxime (toluene, 90–100°C, 1–5 h) afford the corresponding triphenylantimony dioximates **56** and **57** (Scheme 8) along with tetraphenylantimony oximates (up to 10%) [31].

The reaction of equimolar amounts of penta-*para*-tolylantimony with hydrobromic acid leads to the formation of tetra-*para*-tolylantimony bromide **58** [32]. In some cases, tetraarylantimony halides are synthesized from antimony pentachloride and aryllithium in an ethereal solution, for example, tetrakis(pentafluorophenyl)antimony chloride $(C_6F_5)_4SbCl$ (**59**) was synthesized in 25% yield [3].

Tetraarylantimony salts can react with excess amount of the acid in the reaction mixture. For instance, tetraphenylantimony acetate and nitrate with equimolar amounts of acetic and nitric acids form the adducts $Ph_4SbOC(O)CH_3 \cdot CH_3C(O)OH$ (**60**) and $Ph_4SbONO_2 \cdot HNO_3$ (**61**), respectively [33].

The reactions of pentaphenylantimony with complex acids were studied for single examples. The reactions of pentaphenylantimony with aurichlorohydric and hexachloroplatinic acids in benzene gave tetraphenylantimony tetrachloroaurate **62** [34, 35] and bis(tetraphenylantimony) hexachloroplatinate **63** [34], respectively. Yellow crystals of complex $[Ph_4Sb(DMSO)][PtCl_5(DMSO\text{-}S)]$ (**64**) [36] were isolated from the reaction mixture when the last reaction was carried out in a dimethyl sulfoxide (DMSO) solution.

The first tetraphenylantimony γ-alkylacetylacetonates **65**–**68** in which the antimony atoms have the octahedral coordination mode with the bidentate acetylacetonate ligand were synthesized by the reactions of pentaphenylantimony with γ-ethylacetylacetone, γ-allylacetylacetone, γ-phenylacetylacetone, and γ-thiobutylacetylacetone (toluene 90°C, 10 h) (Scheme 9) [37, 38].

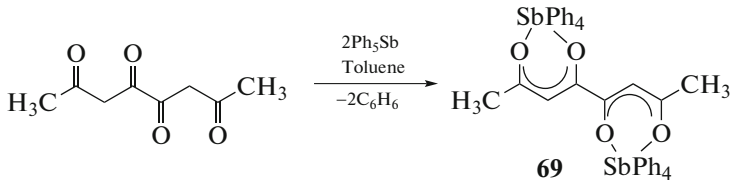


R = Et (**65**), All (**66**), Ph (**67**), BuS (**68**)

Scheme 9.

The Sb–O bond lengths in the heterocycles are close to the sum of covalent radii of the antimony and oxygen atoms.

Binuclear chelate $Ph_4Sb[OC(Me)CHC(O)–(O)C-CH(Me)CO]SbPh_4$ (**69**) was synthesized by the reaction of pentaphenylantimony with octatetraone-2,4,5,7 in a molar ratio of 2 : 1 in toluene (Scheme 10) [39].



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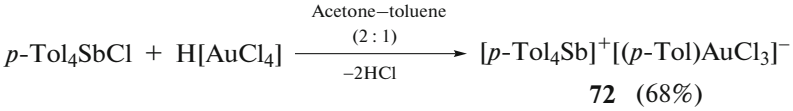
Scheme 10.

Synthesis of Ar_4SbX compounds from tetraarylantimony halides. An efficient method for the synthesis of the antimony derivatives with the general formula Ar_4SbX is based on the substitution of the halogen atom in tetraarylantimony halide by the electronegative group X. For example, the treatment of tetrakis(pentafluorophenyl)antimony chloride with trifluoromethanesulfonic acid in acetonitrile results in the formation of tetrakis(pentafluorophenyl)antimony triflate **70** (97%) [3]. The product of the reaction of aurichlorohydric acid with tetraphenylstibonium chloride in acetone is $[Ph_4Sb]^+[AuCl_4]^-$ (**62**) [34]. The reaction of tetra-*para*-tolylstibonium chloride with aurichlorohydric acid hydrate in acetone afforded tetra-*para*-tolylantimony tetrachloroaurate $[(p\text{-Tol})_4Sb]^+[AuCl_4]^-$ (**71**), whereas the reaction direction changed in an acetone–toluene solution. The evaporation of the solvent resulted in the formation of dark brown crystals consisting, according to the XRD data, of tetrahedral tetra-*p*-tolylstibonium cations and planar square anions $[(p\text{-Tol})AuCl_3]^-$ (**72**) (Scheme 11) [35].



72 (68%)

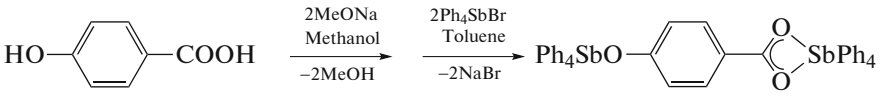
Scheme 11.

The $[(p\text{-Tol})AuCl_3]^-$ anions have the usual planar square structure (bond lengths Au–Cl 2.286(2)–2.389(2) Å and Au–C 2.028(7) Å; angles ClAuCl 89.92(9)°, 92.42(9)°, and 176.68(8)°; CAuCl 88.27(18)°, 89.57(18)°, and 175.59(19)°). It should be mentioned that the auration occurred only in the presence of tetra-*para*-tolylstibonium chloride.

Sodium or potassium salts are often used for the substitution of halogen in tetraarylantimony halides. For example, the reaction of tetraphenylantimony chloride with sodium perrhenate or potassium chloride affords tetraphenylantimony perrhenate **73** and tetraphenylantimony chlorate **74**, respectively [40].

Tetraarylantimony triflates, which are efficient catalysts of the cycloaddition of oxiranes to isocyanates, were synthesized similarly [41].

(μ_2-Oxybenzoato-*O*,*O*',*O*")bis(tetraphenylantimony) solvate with toluene (**75**) is the product of the reaction of 4-hydroxybenzoic acid disodium salt with tetraphenylantimony bromide (molar ratio 1 : 2) in toluene (Scheme 12) [42]. Stirring of a mixture of tetraphenylantimony bromide and sodium methoxide in methanol for 72 h in air results in the formation of bis(tetraphenylantimony) carbonate **76**, which crystallizes from the solution in the triclinic modification.



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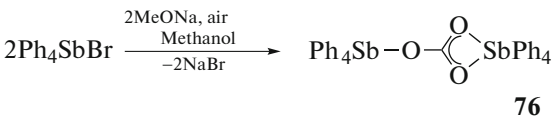

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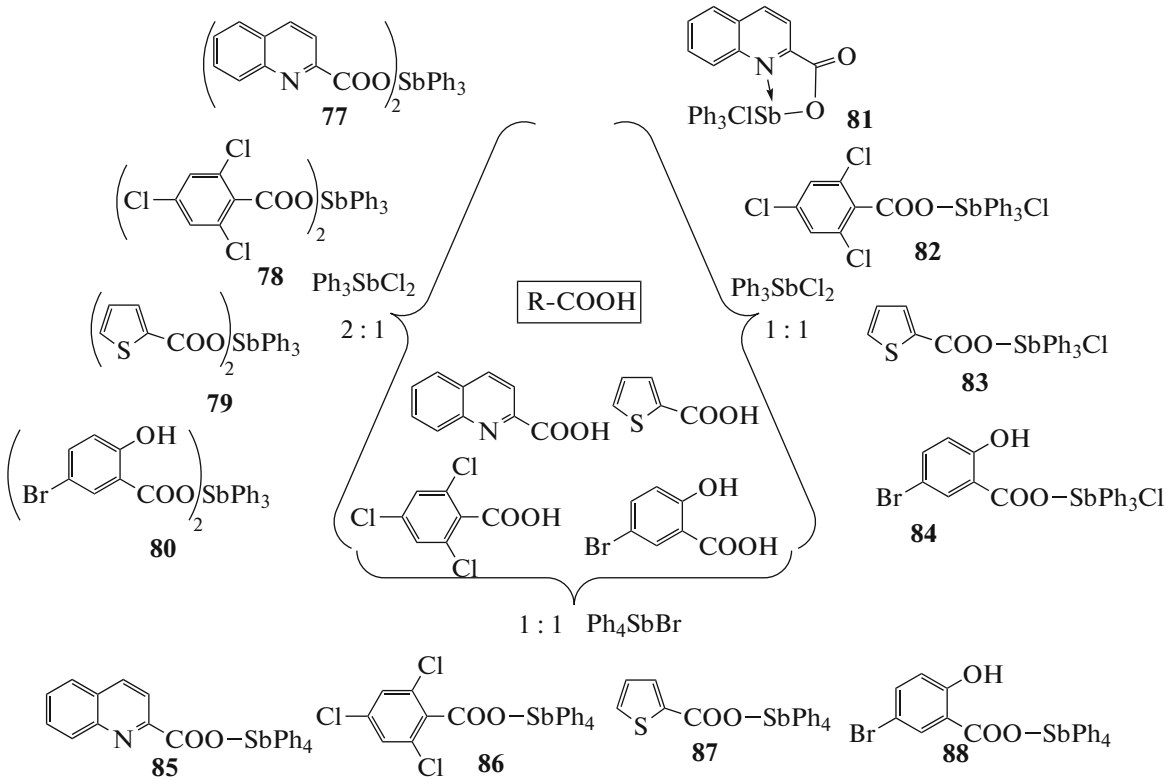
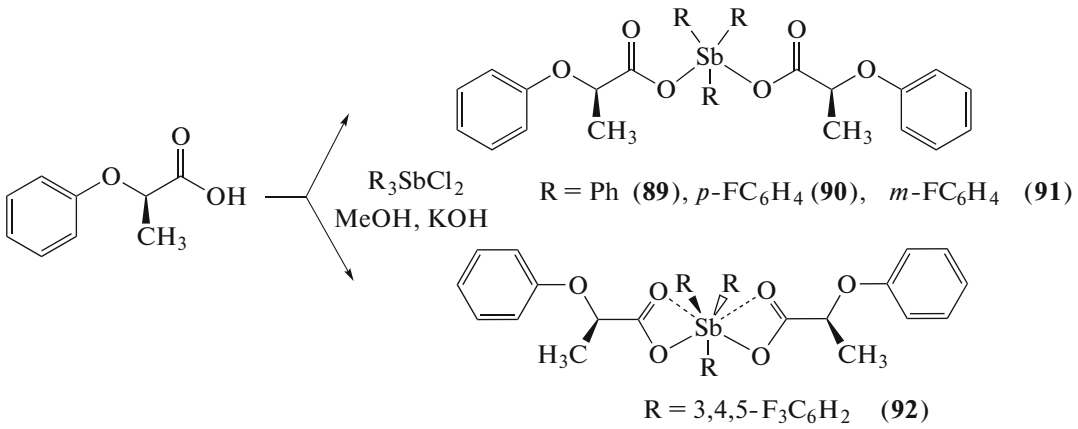
Scheme 12.

Series of other triphenylantimony bis(carboxylates) **77**–**80**, chlorotriphenylantimony carboxylates **81**–**84**, and tetraphenylantimony carboxylates **85**–**88** (Scheme 13) [43] were synthesized similarly.



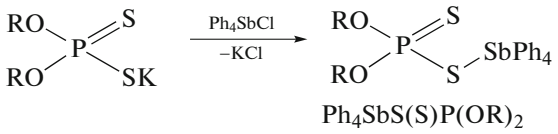
Scheme 13.

Bis(phenoxypropionato)triarylantimony derivatives **89**–**92** were synthesized in 74–80% yields from the corresponding triarylantimony dichloride and carboxylic acid potassium salt in methanol (reflux, 8 h) (Scheme 14) [44].



Scheme 14.

The first derivatives of tetraarylantimony with *O*,*O*-dialkyldithiophosphate substituents capable of manifesting structural nonequivalence were synthesized from tetraphenylantimony chloride and the corresponding potassium *O*,*O*-dialkyl dithiophosphates (Scheme 15) [45–48].



R = Et (**93**), Pr (**94**), *i*-Pr (**95**), Bu (**96**), *i*-Bu (**97**)

Scheme 15.

It is shown that the antimony atoms in the molecules of $Ph_4SbS(S)P(OR)_2$ (**93**–**97**) have the coordination mode of a distorted trigonal bipyramid with the axially arranged *O*,*O*-dialkyldithiophosphate ligands, and the main structural characteristics of the molecules are close to each other.

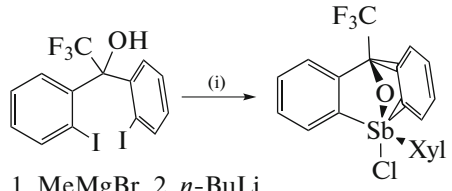
In compound **94** the antimony atom has the coordination mode of a distorted octahedron with the sulfur and carbon atoms in the equatorial plane [48]. In the molecules of the complex, the dipropyldithiophosphate ligand exhibits a nonuniform character of coordination, since one of the Sb–S bonds (3.006 Å) is appreciably shorter than another (3.557 Å). Therefore, we may conclude that the geometry of the coordination polyhedron of the antimony atom in these complexes is sensitive even to slight changes in the structure of the sulfur-containing ligand.

The reactions of tetraphenylantimony bromide with tetraketone sodium salts afford binuclear chelates of the general formula $Ph_4Sb[OC(R)CHC(O)(O)CCH(R)CO]SbPh_4$ (R = Et **98**; R = *t*-Bu **99**), analogs of complex **69**, in the yield up to 76% regardless of the molar ratio of the reagents [49].

Tetraphenylantimony carboxylates of the general formula $ArC(O)OSbPh_4$ (Ar = 3-F-4-CH_3–C_6H_3 (**100**), 4-F-2-CH_3–C_6H_3 (**101**), and 5-F-2-CH_3–C_6H_3 (**102**)) were synthesized by reflux of equivalent amounts of tetraphenylantimony bromide, carboxylic acid, and sodium ethylate in methanol for 12 h [50].

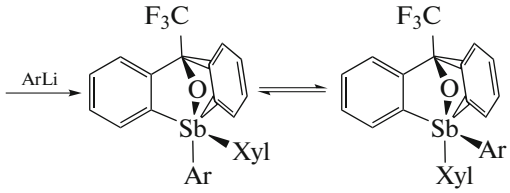
The reaction of tetraphenylantimony bromide with silver triflate in dichloromethane affords tetraphenylantimony triflate, the treatment of which with such donors as trimethylphosphine oxide or 4-methylpyridine oxide is accompanied by the formation of the addition products $[Ph_4Sb(donor)]^+[OSO_2CF_3]^-$ (**103** and **104**) [51].

The substitution of the chlorine atom by the aryl group in chloroxystiborane **105** containing the *C*,*O*,*C*'-tridentate ligand gave a mixture of two stereoisomers of antimony complexes **106** and **107** (Scheme 16) [52].



(i) Et_2O, 1. MeMgBr, 2. *n*-BuLi, 3. $XylSbCl_2$, 4. SO_2Cl_2

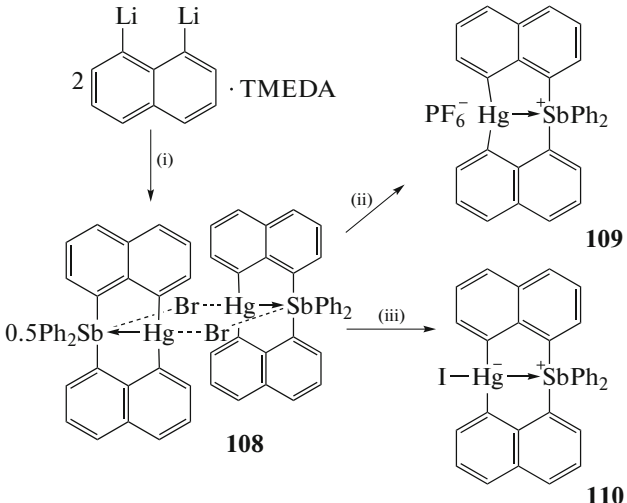
105



Ar = *p*-ClC_6H_4 (**106**), *p*-$CF_3C_6H_4$ (**107**)

Scheme 16.

The reaction of 1,8-dilithiumnaphthalene with triphenylantimony dibromide leads to the elimination of one phenyl ligand from the antimony atom and formation of tetranuclear complex **108**, which being treated with thallium hexafluorophosphate is transformed into bis(μ_2-naphthalene-1,8-diylantimony(V)-mercury(II)) hexafluorophosphate (**109**). The product of the reaction of complex **108** with tetrabutylammonium iodide is bis(μ_2-naphthalene-1,8-diyliodoantimony(V)-mercury(II)) (**110**) (Scheme 17) [53].



(i) 1. $2Ph_3SbBr_2$, THF; 2. $2HgBr_2$, THF, 12 h

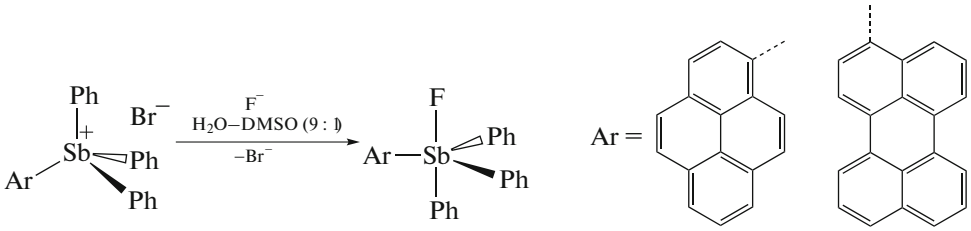
(ii) $TlPF_6$, CH_3CN

(iii) 1. $TlPF_6$; 2. $[Bu_4N]^+I^-$, THF

Scheme 17.

Tetraarylantimony bromides of the general formula $[ArSbPh_3]^+Br^-$ (Ar is 9-phenanthryl (**111**), 1-pyrenyl

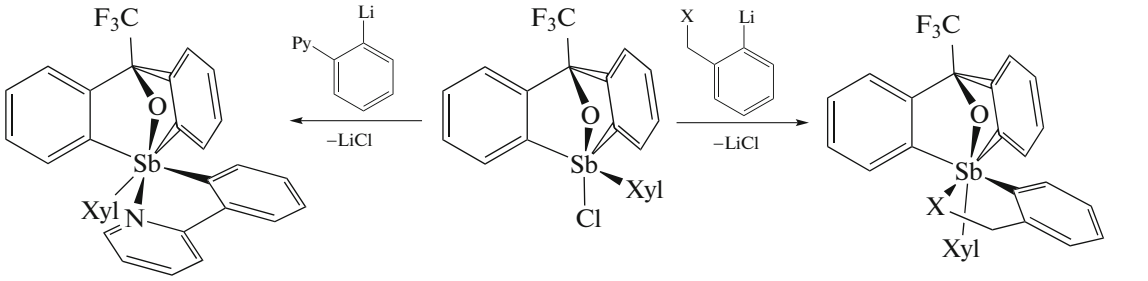
(**112**), and 3-perylenyl (**113**)) were described [54]. Compounds **111**–**113** were synthesized from triphenylantimony dibromide and lithium derivative of the corresponding condensed arene. It is found that compound **111** is not stable in water, but bromides **112** and **113** can be used as sensors for the detection of fluoride anions in aqueous solutions of DMSO (10 vol %) (pH 4.8) (Scheme 18) [54].



112, 113 **114, 115** **112, 114** **113, 115**

Scheme 18.

Under the action of aryllithium bearing the potential coordination center in the aryl ring, alkoxytriarylantimony chloride **105** forms compounds of hexacoordinated antimony **116**–**118** (Scheme 19) in which the oxygen atom and bulky 3,5-dimethylphenyl ligand are arranged oppositely to each other [55].

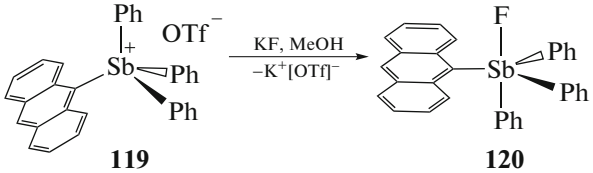


116 **105** X = OMe (**117**), NMe_2 (**118**)

Xyl = 3,5-Dimethylphenyl

Scheme 19.

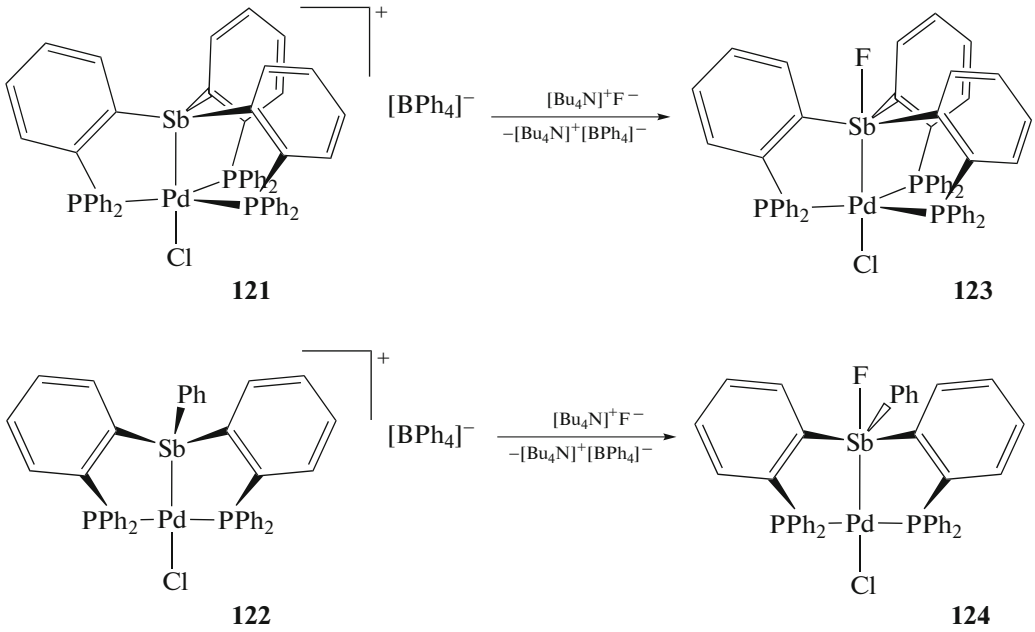
The substitution reactions can involve not only tetraarylantimony halides. For example, anthracene-9-yltriphenylantimony **120** is formed upon the interaction of water-soluble anthracene-9-yltriphenylantimony **119** with solutions containing fluoride anions (Scheme 20) [56].



119 **120**

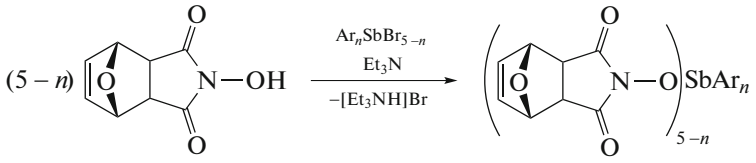
Scheme 20.

When triaryl(L_2PdCl)stibonium tetraphenylborates **121** and **122** with the ionic structures containing the L_2PdCl fragment bound to the central antimony atom via the Sb–Pd bond are treated with tetrabutylammonium fluoride in dichloromethane, they are transformed into covalent triaryl(L_2PdCl)antimony fluorides **123** and **124** (Scheme 21) [57].

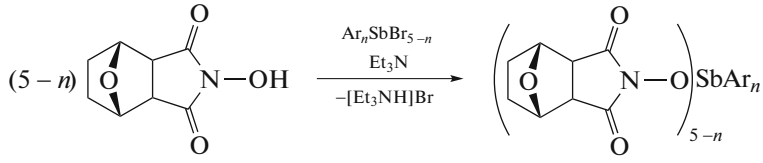


Scheme 21.

The method for the synthesis of the tetraarylantimony derivatives Ar_4SbX based on the reaction of tetraarylantimony halide with the compounds containing the active hydrogen atom in the presence of amine. The antimony derivatives Ar_4SbL and Ar_3SbL_2 (**125**–**139**), where LH is *N*-hydroxyhexahydro-4,7-epoxyisoindole-1,3-dione and *N*-hydroxy-3',4,7,7'-tetrahydro-4,7-epoxyisoindole-1,3-dione, were thus synthesized (Scheme 22) [58].



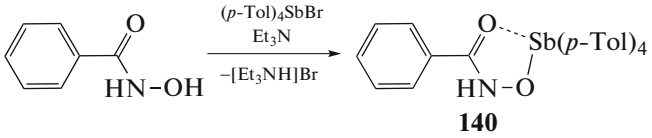
$n = 3$ Ar = Ph (**125**), *p*-Tol (**126**), *m*-Tol (**127**),
o-Tol (**128**), *p*-Cl-C_6H_4 (**129**)
$n = 4$ Ar = Ph (**130**), *p*-Cl-C_6H_4 (**131**)



$n = 3$ Ar = Ph (**132**), *p*-Tol (**133**), *m*-Tol (**134**),
o-Tol (**135**), *p*-Cl-C_6H_4 (**136**), *p*-F-C_6H_4 (**137**)
$n = 4$ Ar = Ph (**138**), *p*-Cl-C_6H_4 (**139**)

Scheme 22.

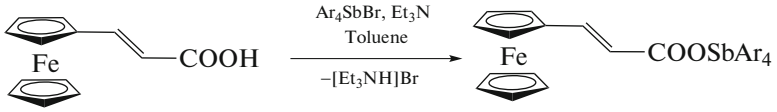
The organoantimony derivatives of arylhydroxamic acids (Scheme 23) (Ar is *p*-Tol (**140**) and Ph (**141**)) were synthesized via a similar scheme [59].



140

Scheme 23.

A series of tetraarylantimony ferrocenyl acrylates $C_5H_5FeC_5H_4CHCHC(O)OSbAr_4$ (Ar is Ph (**142**), *p*-Tol (**143**), *m*-Tol (**144**), *o*-Tol (**145**), and *p*-F-C_6H_4 (**146**) was synthesized by the addition of a solution of 3-ferrocenylacrylic acid in trimethylamine to a suspension of tetraarylantimony bromide in toluene (Scheme 24) [60].



Ar = C_6H_5 (**142**), *p*-Tol (**143**), *m*-Tol (**144**), *o*-Tol (**145**), *p*-F-C_6H_4 (**146**)

Scheme 24.

In the molecule of phenyl derivative **142**, the *d*(Sb···O=C)/*d*(Sb–O) ratio is close to 1 (2.400 Å/2.269 Å = 1.06); i.e., the carboxylate ligand is bidentate. Owing to this, the coordination mode of the antimony atom in compound **142** becomes distorted octahedral. Two carbon atoms of the phenyl groups and two oxygen atoms of the carboxy group lie in the equatorial plane, and the carbon atoms of two other phenyl substituents occupy the axial positions.

Tetraphenylantimony chloride or bromide are found to react with carbamide at 180°C with the formation of tetraphenylantimony cyanamide Ph_4Sb-NCN (**147**) in 52% yield. According to the XRD data, the central antimony atom exists in the distorted trigonal bipyramidal environment with the cyanamide and phenyl groups in the axial positions (CSbN 177.76(7)°, Sb–C 2.107(2)–2.167.2, Sb–N 2.3383(18) Å) [61]. A similar reaction of triphenylantimony dibromide with urea at 155°C gave the antimony compound (OCN)$Ph_3SbOSbPh_3$(NCO) (**148**), which crystallized from dioxane (angle SbOSb 146.2°).

Antimony-containing compounds of the ionic type $[Ar_4Sb]^+[X]^-$ can be synthesized from tetraarylantimony halide and complex salt of the transition metal. For instance, the $[p\text{-Tol}_4Sb]^+[Au(CN)_2]^-$ complex (**149**) was synthesized from tetra(*para*-tolyl)antimony chloride and potassium dicyanoaurate in water in 83% yield [62]. The Au–C bond lengths in compound **149** are 1.94(7)–2.00(6) Å, which is less than the sum of covalent radii of the gold and carbon atoms (2.11 Å) [63].

It was found that the dissolution of sodium hexachloroosmate(IV) dihydrate and tetraphenyl- or tetra-*para*-tolylstibonium chlorides (molar ratio 2 : 1) in DMSO followed by the slow evaporation of the solvent afforded green crystals of complexes $[Ph_4Sb]_2^+[OsCl_6]^{2-}$ (**150**) and $[p\text{-Tol}_4Sb]_2^+[OsCl_6]^{2-}$ (**151**) stable in air (Scheme 25) [64].

$$2Ar_4SbCl + Na_2OsCl_6 \cdot 2H_2O \xrightarrow[-2NaCl,\ -2H_2O]{DMSO} [Ar_4Sb]_2^+[OsCl_6]_2^-$$

Ar = Ph (**150**), *p*-Tol (**151**)

$$2Ar_4SbBr + Na_2OsBr_6 \cdot 2H_2O \xrightarrow[-2NaCl,\ -2H_2O]{DMSO} [Ph_4Sb\ DMSO\text{-}O]_2^+[OsBr_6]_2^-$$

152

or

$$[p\text{-Tol}_4Sb\ DMSO\text{-}O]^+[p\text{-Tol}_4Sb]^+[OsBr_6]_2^-$$

153

Scheme 25.

According to the XRD data, the crystals of complexes **150** and **151** consist of tetrahedral tetraarylstibonium cations and octahedral hexachloroosmate anions. Similar reactions of tetraphenyl- and tetra-*p*-tolylantimony bromides and sodium hexabromoosmate gave complexes **152** and **153** of the ionic type (Scheme 25). However, in these cases, the solvent molecules are incorporated into the coordination sphere of the tetraarylstibonium cation due to which the coordination number of the antimony atom increases to five taking into account the *O*-bound DMSO molecule [65]. The $[OsHal_6]^{2-}$ anions (Hal = Cl, Br) in the reactions with tetraarylstibonium halides in a DMSO solution are kinetically inert and do not enter the further inner-sphere ligand exchange reactions.

Tetraphenylantimony chloride reacts with ruthenium trichloride hydrate in a DMSO solution to form (dimethylsulfoxido)tetraphenylantimony *trans*-bis(dimethylsulfoxido)tetrachlororuthenate $[Ph_4Sb(DMSO\text{-}O)]^+[RuCl_4(DMSO\text{-}S)_2]^-$ (**154**) [66]. The antimony atoms in the cation have a distorted trigonal bipyramidal coordination mode with the oxygen atom of DMSO in the axial position (Sb–O 2.633(15), Sb–C 2.094(15)–2.146(15) Å, CSbO 178.54(16)°). In the octahedral anions of the $[trans\text{-}RuCl_4(DMSO\text{-}S)_2]^-$ complex, the DMSO ligands are coordinated to the metal atom by the sulfur atom (Ru–S 2.349(3), Ru–Cl 2.353(5), 2.355(3) and 2.332(3), 2.344(6), 2.336(4)–2.353(3) Å, respectively) and the SRuS and *trans*-ClRuCl angles are 180°.

The iridium complexes of a similar structure $[Ph_4Sb(DMSO\text{-}O)]^+[IrCl_4(DMSO\text{-}S)_2]^-$ (**155**) and $[Ph_4Sb]^+[IrX_4(DMSO\text{-}S)_2\text{-}trans]^-$ (X = Br, **156**; X = Cl, **157**) were synthesized from tetraphenylantimony halide and sodium hexachloro- and hexabromoiridate in DMSO [67]. Complex $[p\text{-}Tol_4Sb(DMSO\text{-}O)]^+[p\text{-}Tol_4Sb]^+[IrBr_6]^{2-}$ (**158**) was also observed among the products of the reaction of tetra-*para*-tolylantimony bromide with sodium hexabromoiridate in DMSO. Dark blue crystals of complex **158**, whose anions contain no coordinated DMSO molecules, are formed upon the fast removal of the solvent (3 h, 50°C) [68]. However, the formation of yellow-brown crystals of complex $[p\text{-}Tol_4Sb(DMSO\text{-}O)]^+[IrBr_4(DMSO\text{-}S)_2\text{-}trans]^-$ (**159**) is observed upon the slow evaporation of the solvent (480 h) (Scheme 26).

$$2p\text{-}Tol_4SbBr + Na_2IrBr_6 \xrightarrow[-2NaBr]{DMSO,\ 3\ h,\ 50^\circ C} [p\text{-}Tol_4Sb(DMSO\text{-}O)]^+[p\text{-}Tol_4Sb]^+[IrBr_6]^{2-}$$

158

$$\xrightarrow{DMSO,\ 480\ h} [p\text{-}Tol_4Sb(DMSO\text{-}O)]^+[IrBr_4(DMSO\text{-}S)_2\text{-}trans]^-$$

159

Scheme 26.

Note that the $[IrBr_6]^{2-}$ anion is less stable in a DMSO solution than $[OsBr_6]^{2-}$, since for the osmium complexes even the slow evaporation of the solvent did not result in the reduction and inner-sphere substitution in the anions.

At the same time, the reaction of tetra-*para*-tolylstibonium bromide and sodium hexabromorhodiate(III) in DMSO afforded red-brown crystals of complex $[p\text{-}Tol_4Sb(DMSO\text{-}O)]_2^+[RhBr_4(DMSO\text{-}S)_2\text{-}trans]^-[RhBr_4(DMSO\text{-}S)_2\text{-}cis]^-$ (**160**) (Scheme 27) [69].

$$2p\text{-}Tol_4SbBr + 2\ Na_3RhBr_6$$

$$\downarrow \begin{matrix} DMSO \\ -6NaBr \end{matrix}$$

$$[p\text{-}Tol_4Sb(DMSO\text{-}O)]_2^+[RhBr_4(DMSO\text{-}S)_2\text{-}trans]^-[RhBr_4(DMSO\text{-}S)_2\text{-}cis]^-$$

160

Scheme 27.

Isomeric octahedral anions $[RhBr_4(DMSO\text{-}S)_2\text{-}trans]^-$ and $[RhBr_4(DMSO\text{-}S)_2\text{-}cis]^-$ in compound **160** differ by the arrangement of the *S*-coordinated DMSO molecules.

The first palladium complexes with DMSO were obtained by the dissolution of $PdCl_2$ in DMSO [70]. The ionic complexes with antimony-containing cations and mononuclear anions

$[PdHal_3(DMSO\text{-}S)]^-$ (**161** and **162**) can be synthesized by the direct reaction of tetraarylantimony halides with palladium halides in DMSO (Scheme 28) [71, 72].

$$Ph_4SbHal + PdHal_2 \xrightarrow{DMSO} [Ph_4Sb(DMSO\text{-}O)]^+[PdHal_3(DMSO\text{-}S)_2]^-$$

Hal = Cl (**161**), Br (**162**)

$$2Ph_4SbI + 2PdI_2 \xrightarrow{DMSO} [Ph_4Sb(DMSO\text{-}O)]_2^+[Pd_2I_6]^{2-}$$

163

Scheme 28.

According to the XRD data, the coordination polyhedron of the palladium atom in the $[PdHal_3(DMSO\text{-}S)]^-$ anions is a distorted square, the DMSO molecules coordinate to the palladium atom by the sulfur atom, and the bond angles differ from the theoretical values.

The complex with the binuclear anion $[Ph_4Sb(DMSO\text{-}O)]_2^+[Pd_2I_6]^{2-}$ (**163**) is the product of the reaction of palladium diiodide with tetraphenylstibonium iodide (Scheme 28) [73]. According to the XRD data, in the binuclear $[Pd_2I_6]^{2-}$ anions the coordination mode of the palladium atoms is planar square, and the palladium atoms are linked to each other via two μ_2-bridging iodine atoms. The $Pd-I_{term}$ bonds (2.5836(8)–2.6093(4) Å) nearly coincide with the $Pd-I_{br}$ distances (2.5875(5)–2.6129(3) Å).

It is known that the thermal decomposition of tetraphenylstibonium halides without solvent proceeds at 250°C via the reductive elimination scheme to form triphenylstibine and halidebenzene [74]. However, in the presence of $K_2[PtCl_4]$, the reduction Sb(V) → Sb(III) occurs in a DMSO solution at room temperature, and the neutral mixed-ligand complex $(Ph_3Sb)(DMSO\text{-}S)Pt(Cl_2\text{-}cis)$ (**164**) is formed (Scheme 29) [75].

$$Ph_4SbCl + K_2PtCl_4 \xrightarrow[-PhCl\ -2KCl]{DMSO} (Ph_3Sb)(DMSO\text{-}S)PtCl_2\text{-}cis$$

164

Scheme 29.

As follows from the XRD data, complex **164** has a planar square structure characteristic of the Pt(II) compounds in which the coordination sphere of the central atom contains the *S*-coordinated DMSO molecule and triphenylstibium molecule along with two *cis*-chloro ligands [75]. The *trans*-ClPtS (177.96(4)°–178.01(6)°), *cis*-SPtSb (90.75(4)°), SPtCl(1) (90.24(6)°), SbPtCl (88.36(4)°), and ClPtCl (90.71(6)°) angles are observed. The Pt–Sb bond (2.5118(4) Å) is shorter than the sum of covalent radii of the platinum and stibium atoms (2.78 Å) [63]. Similar phosphorus compounds $(Ph_3P)(DMSO\text{-}S)PtCl_2\text{-}cis$ (**165**) and $(Ph_3P)(SOEt_2\text{-}S)PtCl_2\text{-}cis$ (**166**) are formed from 2-butenylbis(triphenylphosphonium) chloride and hexachloroplatinic acid in the presence of DMSO or diethyl sulfoxide in acetonitrile [76].

Potassium hexabromoplatinate and tetraphenylantimony bromide were used as the initial compounds for the synthesis of tetraphenylantimony hexabromoplatinate $[Ph_4Sb]_2^+[PtBr_6]^{2-}$ (**167**) [77]. According to the XRD data, the crystal of the complex consists of tetrahedral stibonium cations and octahedral $[PtBr_6]^{2-}$ anions. The recrystallization of the synthesized complex **167** from DMSO was accompanied by the inner-sphere substitution of one of the bromide atoms by the DMSO molecule to form complex **168** (Scheme 30).

$$[Ph_4Sb]_2^+[PtBr_6]^{2-} \xrightarrow[-Ph_4SbBr]{DMSO} [Ph_4Sb]^+[PtBr_5(DMSO\text{-}S)]^-$$

167 **168**

Scheme 30.

According to the XRD data, the octahedral anions $[PtHal_5(DMSO\text{-}S)]^-$ almost are not distorted.

Tetraphenylstibonium hexachlorozirconate $[Ph_4Sb]_2^+[ZrCl_6]^{2-}$ (**169**) was synthesized by the reaction of zirconium tetrachloride with tetraphenylstibonium chloride in 86% yield and was structurally characterized [78].

Synthesis of the pentavalent antimony compounds via the ligand distribution reaction. The beginning of the ligand redistribution in a series of aryl compounds of pentavalent antimony is referred to 1974 when bis(tetraphenylantimony) carbonate (**76**) was formed during the recrystallization of triphenylantimony

dihydroxide from chloroform in air [79]. Evidently, the formation of the Ph_4Sb fragment can be explained only by the exchange of the phenyl substituents between the antimony atoms.

The study of the antimony derivative synthesized from triphenylantimony dichloride and silver oxalate showed [80] that the compound had a salt-like structure $[Ph_4Sb][Ph_2Sb(Ox)_2]$ (**170**), where Ox is O_2CCO_2. It was assumed that the compound can be synthesized from triphenylantimony dichloride via Scheme 31 [80].

$$2Ph_3SbCl_2 \longrightarrow [Ph_4Sb]^+[Ph_2SbCl_4]^- \xrightarrow[-2AgCl]{OxAg_2} [Ph_4Sb]^+[Ph_2Sb(Ox)_2]^-$$

170

Scheme 31.

When decided to study the interaction of pentaarylantimony with the derivatives of the general formula Ar_3SbX_2, where X is the electronegative ligand, the authors [81] believed that either complexes of the ionic type would be formed, or the redistribution of organic ligands and synthesis of the nonsymmetric derivatives would occur. Indeed, pentaphenylantimony was found to react with triphenylantimony dihalides, dibenzoate, and dithiocyanate with the formation of nonsymmetric products **171**–**174**, which were tetraphenylntimony halide, benzoate, and thiocyanate, respectively, in the yield up to 99% (Scheme 32).

$$Ph_5Sb + Ph_3SbX_2 \longrightarrow 2Ph_4SbX$$

171–**174**

X = Cl (**171**), Br (**172**), OC(O)Ph (**173**), SCN (**174**)

Scheme 32.

The reactants react in aromatic hydrocarbon at room temperature for a day.

The possibility of similar reactions of pentaarylantimony with other derivatives of pentavalent antimony of the general formula Ar_3SbX_2, where X is the electronegative ligand, was established for triarylantimony dioximates [26], disulfonates [82], diaroxides [9, 83], and dicarboxylates [11–15, 81, 84]. Depending on the nature of ligand X, pentaarylantimony disappeared from the reaction mixture on heating (90°C) in 0.25–2 h. The single reaction product was isolated after solvent removal and solid residue recrystallization from a heptane–benzene mixture.

Continuing this trend, the possibility of synthesizing the nonsymmetric antimony derivatives of the general formula Ph_3SbXY from compounds Ph_3SbX_2 and Ph_3SbY_2 was studied. It was found that triphenylantimony chlorooximates $Ph_3Sb(Cl)ONCMePh$ (**175**) [85] and $Ph_3Sb(Cl)ONCHC_6H_4(OH\text{-}2)$ (**176**) [86] bearing various electronegative substituents can also be prepared by the reaction of ligand redistribution (Scheme 33). Note that triphenylantimony chlorooximates **175** and **176** are smoothly phenylated by pentaphenylantimony to tetraphenylantimony oximate, and the second reaction product was tetraphenylantimony chloride. A similar synthesis of triphenylantimony chloroaroxides can also be carried out for bis(4-nitrophenoxo)triphenylantimony [87], bis(2,6-dichlorophenoxo)triphenylantimony [88], and tri(*meta*-tolyl)antimony bis(benzenesulfonate) **177**–**179** (Scheme 33) [89].

$$Ph_3SbCl_2 + Ph_3Sb(ONCRR')_2 \longrightarrow 2Ph_3Sb(Cl)(ONCRR')$$

175, **176**

R = Me, R' = Ph (**175**); R = H, R' = $C_6H_4(OH\text{-}2)$ (**176**)

$$Ph_3SbCl_2 + Ph_3Sb(OAr)_2 \longrightarrow 2Ph_3Sb(Cl)(OAr)$$

177, **178**

Ar = $OC_6H_4(NO_2\text{-}4)$ (**177**), $OC_6H_3(Cl_2\text{-}2,6)$ (**178**)

$$m\text{-}Tol_3SbCl_2 + m\text{-}Tol_3Sb(OSO_2Ph)_2 \longrightarrow 2m\text{-}Tol_3Sb(Cl)(OSO_2Ph)$$

179

Scheme 33.

The radical redistribution between triarylantimony difluoride and triarylantimony bis(trifluoromethanesulfonate) in a dichloromethane solution affords nonsymmetric antimony derivatives **180** and **181**

(Scheme 34). A similar radical redistribution with the formation of derivatives **182** and **183** takes place in the reaction of triarylantimony dichloride with antimony pentachloride [90].

$$Ar_3Sb(OTf)_2 + Ar_3SbF_2 \xrightarrow{CH_2Cl_2} 2Ar_3SbF(OTf)$$

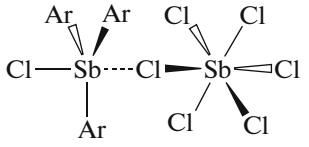
180, **181**

Ar = Ph (**180**); Mes (**181**)

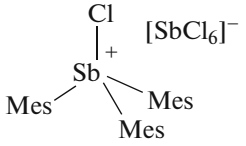
$$Ar_3SbCl_2 + SbCl_5 \xrightarrow{CH_2Cl_2} [Ar_3SbCl]^+[SbCl_6]^-$$

182, **183**

Ar = Ph (**182**); Mes (**183**)



182



183

Scheme 34.

Triphenylantimony dichloride reacts similarly with bis(pentachloro)- and bis(pentafluoroaroxy)triphenylantimony [91].

In the case of the reaction of tri(*para*-tolyl)antimony dichloride with bis(4-nitrophenoxy)-tri-(*para*-tolyl)antimony, the redistribution reaction ceases at the formation of adduct $p\text{-Tol}_3SbCl_2 \cdot p\text{-Tol}_3Sb(Cl)OC_6H_4(NO_2\text{-}4)$ (**184**) [92].

Synthesis of the antimony complexes containing tetraarylstibonium cations. It is known that tetraphenylantimony chloride reacts with tin tetrachloride in benzene to form ionic complex **185** (Scheme 35) [34]:

$$2Ph_4SbCl + SnCl_4 \xrightarrow{Acetone} [Ph_4Sb]_2^+[SnCl_6]^{2-}$$

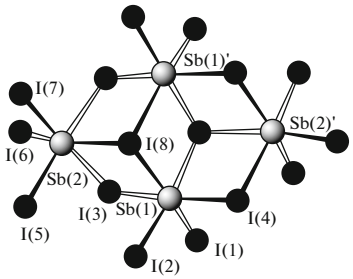
185

$$4Ph_4SbI + 4SbI_3 \xrightarrow{Acetone} [Ph_4Sb]_4^+[Sb_4I_{16}]^{4-} \cdot 2Acetone$$

186

Scheme 35.

The intermediate formation of the antimony complexes, for example, $[Ph_4Sb]^+[Ph_4SbX_2]^-$, was also assumed in the ligand redistribution reactions involving the pentavalent antimony derivatives. The antimony complexes are further transformed into the antimony derivatives of the general formula Ph_4SbX. Therefore, when studying the reaction of tetraphenylantimony iodide with antimony triiodide in acetone, the authors [93] assumed the formation of a similar complex, but complex $[Ph_4Sb]_4^+[Sb_4I_{16}]^{4-} \cdot 2(CH_3)_2CO$ was the single reaction product (**186**) (Scheme 35). The reaction was carried out at room temperature in an acetone solution, and the color changed from brown, which is characteristic of solutions of antimony triiodide, to red-cherry. According to the XRD data, the $[Sb_4I_{16}]^{4-}$ anions in complex **186** are cyclic and centrosymmetric (Scheme 36).



$[Sb_4I_{16}]^{4-}$

Scheme 36.

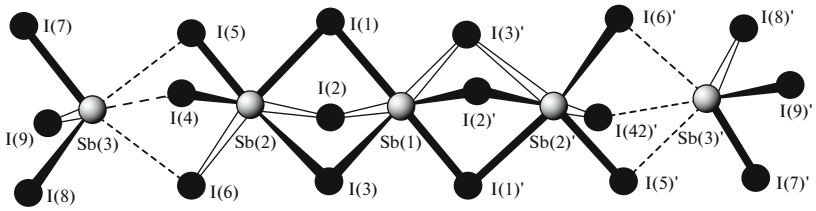
Isostructural complex $[Ph_4Sb]_4^+[Bi_4I_{16}]^{4-} \cdot 2(CH_3)_2CO$ (**187**) was synthesized via a similar scheme [94].

The reactions of tetraphenylantimony 4-methylbenzenesulfonate and 2,4-dimethylbenzenesulfonate with antimony triiodide in acetone proceed in somewhat different manner (Scheme 37) [93].

$$3Ph_4Sb(OSO_2Ar) + 6SbI_3 \xrightarrow[-Sb(OSO_2Ar)_3]{} [Ph_4Sb]_3^+[Sb_5I_{18}]^{3-}$$

188, 189

Ar = *p*-Tol (**188**), $C_6H_3(Me_2\text{-}2.4)$ (**189**)



$[Sb_5I_{18}]^{3-}$

Scheme 37.

In this case, complexes **188** and **189** consisting of tetraphenylstibonium cations and $[Sb_5I_{18}]^{3-}$ anions were isolated from the reaction mixture (Scheme 37).

The reactions of tetraphenylantimony arenesulfonates with bismuth triiodide in DMSO lead to the formation of the mixed-ligand complex of tetraphenylstibonium phenyltriiodobismuthate(III) $[Ph_4Sb]_2^+[Ph_2Bi_2I_6]^{2-} \cdot 2DMSO$ (**190**) formed of the $[Ph_4Sb]^+$ cations, $[Ph_2Bi_2I_6]^{2-}$ anions, and molecules of crystallization DMSO (Scheme 38) [95].

$$4Ph_4Sb(OSO_2Ar) + 2BiI_3 \xrightarrow[-2Ph_3Sb(OSO_2Ar)_2]{DMSO} [Ph_4Sb]_2^+[Ph_2Bi_2I_6]^{2-}$$

190

Ar = $C_6H_3Me_2$-2,5; C_6H_3(OH-4)(COOH-3); $C_6H_3Me_2$-2,4; *p*-Tol

Scheme 38.

The interaction of equimolar amounts of tetra-*para*-tolylantimony iodide with bismuth triiodide in 2-ethoxyethanol (Scheme 39) results in the formation of solvate complex **191** of the ionic type [96].

$$3p\text{-}Tol_4SbI + 3BiI_3 \xrightarrow{HOCH_2CH_2OEt} [p\text{-}Tol_4Sb]_3^+[Bi_3I_{12}]^{3-} \cdot HOCH_2CH_2OEt$$

191

Scheme 39.

The ionic complex $[p\text{-}Tol_4Sb]_2^+[Bi_2I_8(THF)]^{2-}$ (**192**) was the reaction product of equimolar amounts of tetra-*para*-tolyl)antimony iodide with bismuth triiodide, and a twofold increase in the amount of bismuth iodide and the replacement of the solvent by acetone results in the formation of the $[p\text{-}Tol_4Sb]_n^+[(Bi_2I_7)_n]^{n-}$ complex (**193**) with the polymeric anion [97].

Mercury or cadmium diiodides react similarly with tetraphenylantimony iodide to form the complexes of the ionic type. The interaction between the indicated reagents at room temperature in an acetone solution (12 h) is accompanied by the formation of the organoantimony derivatives of the general formula $[Ph_4Sb]_2^+[E_2I_6]^{2-}$ (E = Cd (**194**), Hg (**195**)) (Scheme 40) [98].

$$2Ph_4SbI + 2EI_2 \xrightarrow{\text{Acetone}} [Ph_4Sb]_2^+[E_2I_6]^{2-}$$

E = Cd (**194**), Hg (**195**)

$$2Ph_5Sb + 3HgI_2 \xrightarrow{\text{Acetone}} [Ph_4Sb]_2^+[Hg_2I_6]^{2-} \cdot Ph_2Hg$$

196

Scheme 40.

The synthesized compounds have a high melting temperature and are highly soluble in organic solvents. It is found that pentaphenylantimony phenylates mercury iodide to complex $[Ph_4Sb]_2^+[Hg_2I_6]^{2-} \cdot Ph_2Hg$ (**196**) regardless of the ratio of the initial reactants. The maximum yield of complex **196** is reached at the 2 : 3 molar ratio of the initial reactants (Scheme 40).

Yellow crystals of compound **197** were isolated by fractional recrystallization from the products of the reaction of tetraphenylantimony 2,4-dimethylbenzenesulfonate with mercury diiodide in acetone at room temperature (Scheme 41).

$$2Ph_4Sb(OSO_2C_6H_3Me_2\text{-}2,4) + 5HgI_2 \xrightarrow{\text{Acetone}} [Ph_4Sb]_2^+[Hg_4I_{10}]^{2-}$$

197

Scheme 41.

It is shown that a change in the molar ratio of the initial reactants in the reaction of tetra-*para*-tolylantimony iodide with mercury iodide results in a change in the structure of the mercury-containing anion of the addition complex [99]. For example, the reaction of equimolar amounts of tetra-*para*-tolylantimony iodide and mercury iodide afforded bis(tetra-*para*-tolylantimony) (di-μ_2-iodo)tetraiododimercurate **198** in 92% yield (Scheme 42).

$$2[p\text{-}Tol_4Sb]I + 2HgI_2 \xrightarrow{\text{Acetone}} [p\text{-}Tol_4Sb]_2^+[Hg_2I_6]^{2-}$$

198

$$2[p\text{-}Tol_4Sb]I + 4HgI_2 \xrightarrow{\text{Acetone}} [p\text{-}Tol_4Sb]_2^+[Hg_4I_{10}]^{2-}$$

199

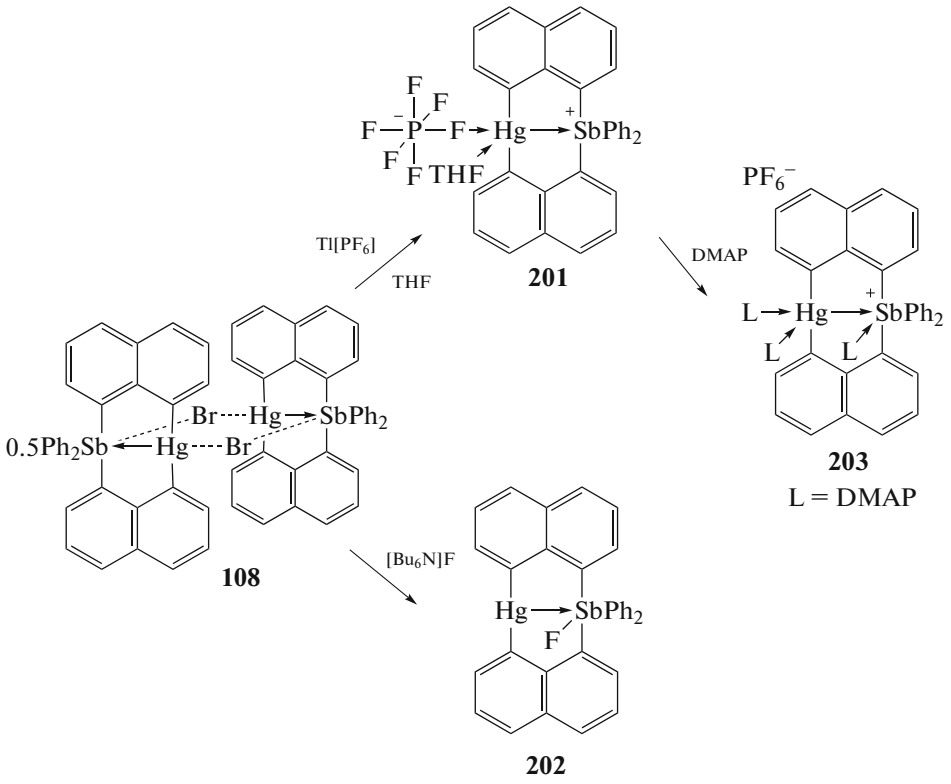
$$2[p\text{-}Tol_4Sb]I + HgI_2 \xrightarrow{\text{Acetone}} [p\text{-}Tol_4Sb]_2^+[HgI_4]^{2-}$$

200

Scheme 42.

It follows from the XRD data that the crystal of complex **198** consists of the tetra-*para*-tolylstibonium cations and centrosymmetric binuclear anions $[Hg_2I_6]^{2-}$. The structure of the mercury-containing anion in the target product becomes more complicated with an increase in the mercury iodide concentration in the reaction mixture (molar ratio 1 : 2). The reaction occurs in yield of 91% with the formation of complex **199** representing yellow transparent crystals (Scheme 42). On the contrary, an increase in the amount of tetra-*para*-tolylantimony iodide in the reaction mixture (2 : 1 mol/mol) results in the single product **200** with the mononuclear anion, bis(tetra-*para*-tolyl)antimony tetraiodomercurate, as the target product (Scheme 42). The crystal of complex **200** contains tetraiodomercurate anions $[HgI_4]^{2-}$ together with crystallographically independent tetra-*para*-tolylstibonium cations of two types.

Diphenyl[bis(μ_2-1,8-naphthalenediylmercury)]-antimony bromide **108** in which two naphthyl ligands are linked to each other via the mercury atoms is transformed into complex **201** with the coordinated tetrahydrofuran (THF) molecule or into fluoride **202** under the treatment of thallium hexafluorophosphate in THF or tetrabutylammonium fluoride, respectively [100]. The subsequent addition of 4-dimethylaminopyridine (DMAP) to a solution of compound **201** in THF affords adduct **203** with three DMAP molecules (Scheme 43).



Scheme 43.

SYNTHESIS METHODS AND SOME REACTIONS OF ANTIMONY DERIVATIVES Ar_3SbX_2

Compounds Ar_3SbX_2, where X is the electronegative ligand, are among the most studied aryl derivatives of pentavalent antimony. There are several efficient methods for their synthesis of which the substitution of halogen atoms by other groups should be distinguished. These are primarily the reactions of triarylantimony dihalides with sodium, potassium, or silver salts of acids and similar compounds.

Synthesis of the antimony derivatives from triarylantimony dihalides. The treatment of tris(4-*N*,*N*-dimethylaminophenyl)antimony dichloride with sodium fluoride in an aqueous-acetone solution results in an almost quantitative transformation into tris(4-*N*,*N*-dimethylaminophenyl)antimony difluoride **204**, being colorless crystals that become darker in the light (Scheme 44) [101].

$$(4\text{-}Me_2NC_6H_4)_3SbCl_2 + 2NaF \xrightarrow[-2NaCl]{} (4\text{-}Me_2NC_6H_4)_3SbF_2$$

204

$$(4\text{-}Me_2NC_6H_4)_3SbCl_2 + 2AgOC(O)Ph \xrightarrow[-2AgCl]{} (4\text{-}Me_2NC_6H_4)_3Sb(OC(O)Ph)_2$$

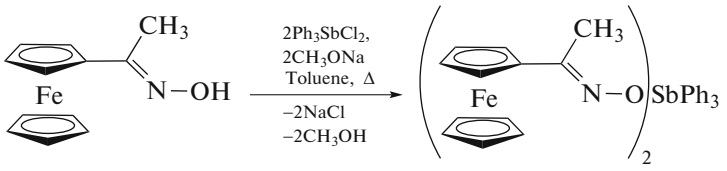
205

Scheme 44.

Tris(4-*N*,*N*-dimethylaminophenyl)antimony benzoate **205** was also synthesized by the exchange reaction of silver benzoate and tris(4-*N*,*N*-dimethylaminophenyl)antimony dichloride (Scheme 44).

Triphenylantimony diazide **206** was synthesized by the reaction (methanol, 10 min) of triphenylantimony dibromide with sodium azide (72% yield) [102].

The reaction of triphenylantimony dichloride with acetylferroceneoxime (molar ratio 1 : 2) in the presence of sodium methylate in toluene (4 h, 110°C) was shown to give triphenylantimony bis(ferrocenylethanone oximate) **207**. The coordination polyhedron of the antimony atom in compound **207** represents a trigonal bipyramid with phenyl substituents in the equatorial positions and oximate ligands in the axial positions (Scheme 45) [103].

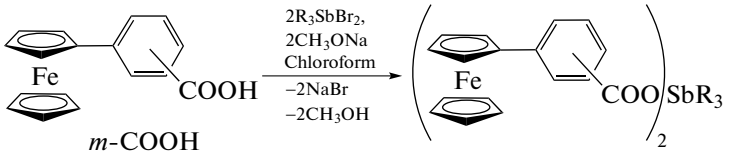


207

Scheme 45.

The reaction of triphenylantimony dibromide with ferrocenylethanone oxime (12 h, THF) results in the formation of the same compound in 72% yield [104].

Triarylantimony dicarboxylates **208**–**210** were synthesized via a similar scheme from triarylantimony dibromide and *meta*- or *para*-ferrocenylbenzoic acid sodium salt in chloroform (Scheme 46) [105], and triphenylantimony dicarboxylates **211** and **212** were synthesized from triphenylantimony dichloride and 2-trifluoromethyl- and 3-trifluoromethylbenzoic acid sodium salts, respectively, in the yields up to 84% [106].

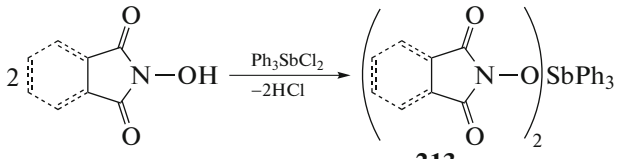


m-COOH
p-COOH

m-COOH, R = Ph (**208**)
m-COOH, R = *p*-Tol (**209**)
p-COOH, R = *p*-Tol (**210**)

Scheme 46.

No base is required in the reactions of triphenylantimony dichloride with *N*-oxyphthalimide and *N*-oxysuccinimide (molar ratio 1 : 2) (Scheme 47) [107]. Both synthesized compounds Ph_3SbX_2 (**213** and **214**) are promising anticancer agents, more active than cisplatin.

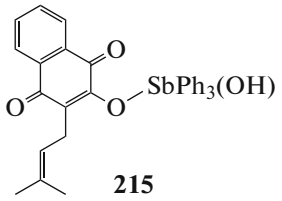


N-oxysuccinimide
N-oxyphthalimide

213
214

Scheme 47.

The reaction of triphenylantimony dichloride with lapachol (LpH) afforded the organoantimony derivative of lapachol (Lp)Ph_3SbOH (**215**) (Scheme 48), which inhibited the growth of chronic myelogenic leukemia cells [108].



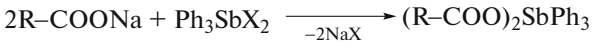
215

Scheme 48.

Bis(2-hydroxybenzaldoximato)triphenylantimony (**216**) was synthesized in 86% yield from 2-hydroxybenzaldoxime sodium salt and triphenylantimony dichloride [109].

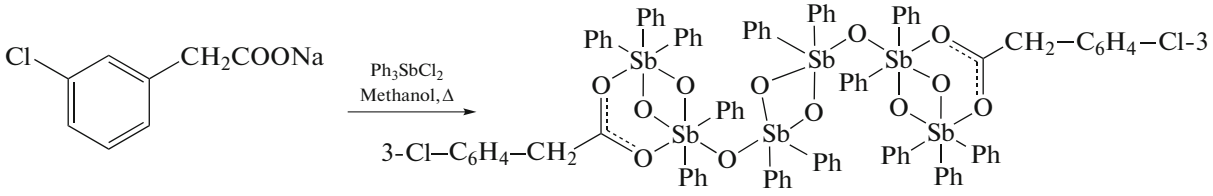
Bis(2-amino-4-chlorobenzoato)triphenylantimony (**217**) [110], bis(2-acetylbenzoato)triphenylantimony (**218**), and bis(4-acetylbenzoato)triphenylantimony (**219**) characterized by anticancer activity were synthesized from triphenylantimony and sodium salts of 2-amino-4-chlorobenzoic acid, 2-acetylbenzoic, and 4-acetylbenzoic acid, respectively, in methanol (0.5–3 h, stirring) (Scheme 49) [111]. Similar antimony compounds **220** and **221** were synthesized similarly from 2-chlorophenylacetic and 4-chlorophenylacetic

acids in alcohol. However, only the hexanuclear derivative of pentavalent antimony (**222**) was isolated from the reaction mixture in the case of 3-chlorophenylacetic acid (Scheme 50) [112].



X = Cl
R = 2-NH_2–4-ClC_6H_3 (**217**), 2-$(C(O)CH_3)C_6H_4$ (**218**), 4-$(C(O)CH_3)C_6H_4$ (**219**), 2-$ClC_6H_4CH_2$ (**220**), 4-$ClC_6H_4CH_2$ (**221**), 2-$(OC(O)CH_3)C_6H_4$ (**223**), 3-$(OC(O)CH_3)C_6H_4$ (**224**), 5-NH_2–2-ClC_6H_3 (**225**), 4-$CF_3C_6H_4$ (**226**)
X = Br
R = Ph (**227**), 2-$NH_2C_6H_4$ (**228**), *p*-Tol (**229**), 2-$NHPhC_6H_4$ (**230**), 3,5-$Cl_2C_6H_3$ (**231**), Et (**232**), 3-Py (**233**), 2-$OCH_3C_6H_4CH_2$ (**234**), 4-$OCH_3C_6H_4CH_2$ (**235**), 4-$ClC_6H_4CH_2$ (**236**)

Scheme 49.

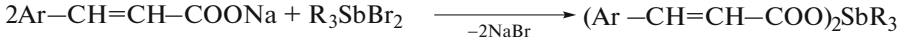


222

Scheme 50.

The organoantimony derivatives of acetylsalicylic (**223**) and 3-acetoxybenzoic (**224**) acids are characterized by antileishmaniosis and antibacterial activities *in vivo* and cytotoxicity against macrophages [113] and were synthesized via the same scheme (in methanol or toluene) as bis(5-amino-2-chlorobenzoato)triphenylantimony (**225**) [114] and bis(4-trifluoromethylbenzoato)triphenylantimony (**226**) [115] (Scheme 49), as well as other triarylantimony dicarboxylates **227–236** [116].

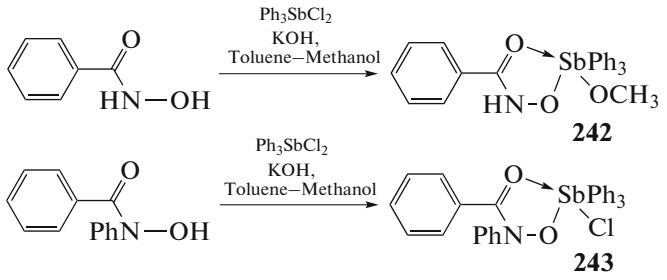
Triarylantimony dicarboxylates (4-ClC_6H_4-$CH{=}CHCOO)_2SbPh_3$ (**237**) and (4-$OMeC_6H_4$-$CH{=}CHCOO)_2Sb(p\text{-Tol})_3$ (**238**) with anticancer activity and their analogs **239–241** were synthesized in the yield up to 82% from triarylantimony dibromide and sodium salts of the corresponding carboxylic acids in toluene (Scheme 51) [117].



Ar = 4-ClC_6H_4, R = Ph (**237**)
Ar = 4-ClC_6H_4, R = *p*-Tol (**238**)
Ar = 2-$NO_2C_6H_4$, R = Ph (**239**)
Ar = 2-$NO_2C_6H_4$, R = *p*-Tol (**240**)
Ar = 4-$OCH_3C_6H_4$, R = *p*-Tol (**241**)

Scheme 51.

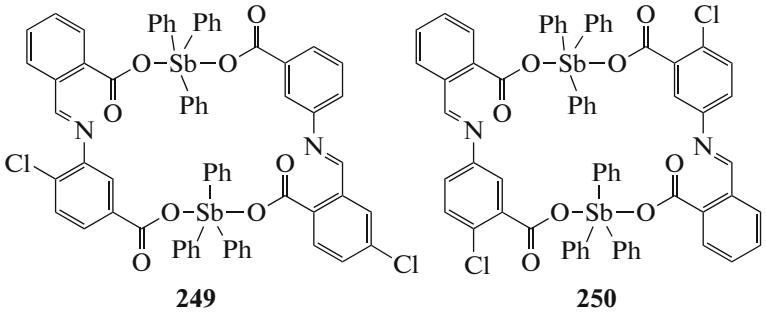
The interaction of equimolar amounts of benzoylhydroxamic and *N*-phenylbenzoylhydroxamic acid potassium salts with triphenylantimony dichloride in a mixture of solvents (methanol–toluene (1 : 1), stirring for 0.5 h) affords the biologically active derivatives of pentavalent antimony: benzoylhydroxamatotriphenylantimony methoxide (**242**) and *N*-phenylbenzoylhydroxamatotriphenylantimony chloride (**243**) (Scheme 52) [118].



Scheme 52.

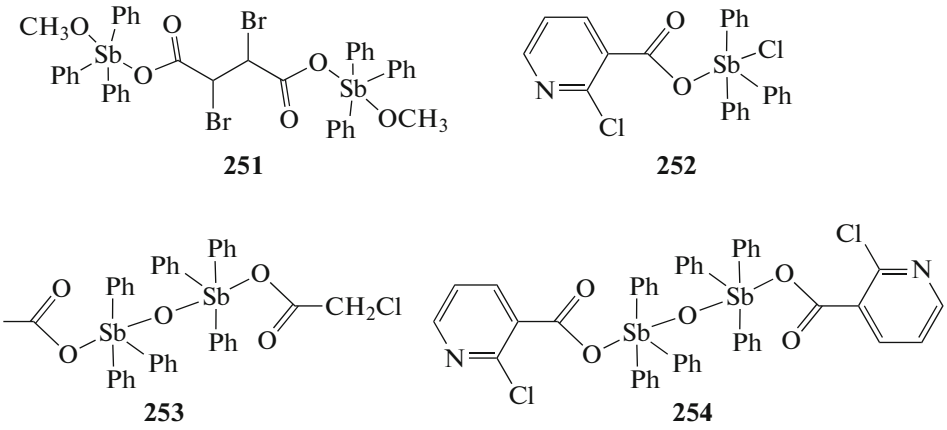
The reaction of 3-methoxy-2,4,5-trifluorobenzoic acid and sodium ethoxide in methanol with triphenylantimony dichloride on stirring for 12 h at room temperature gave the target product $(3\text{-}OCH_3\text{-}2,4,5\text{-}F_3C_6H_2\text{-}COO)_2SbPh_3$ (**244**) in 86% yield after recrystallization from a dichloromethane–methanol (1 : 1) mixture [119]. Other triphenylantimony dicarboxylates $(4\text{-}NH_2C_6H_4\text{-}COO)_2SbPh_3$ (**245**) [120], $(3\text{-F-}4\text{-}CH_3C_6H_3COO)_2SbPh_3$ (**246**), $(4\text{-F-}2\text{-}CH_3C_6H_3COO)_2SbPh_3$ (**247**), and $(5\text{-F-}2\text{-}CH_3C_6H_3COO)_2SbPh_3$ (**248**) [121] were synthesized using a similar procedure. Supramolecular structures are formed in the crystals of compounds **246** and **247** due to intermolecular C–H···O, C–H···F, and π–π-stacking interactions.

The supramolecular structures caused by several types of nonvalent interactions (C–H...π, C–Cl...π, C–H...Cl) are also observed in the crystals of two compounds $[Ph_3SbL^1]_2$ (**249**) and $[Ph_3SbL^2]_2$ (**250**) (H_2L^1 is 5-{[(2-carboxymethyl)methylene]amino}-4-chlorobenzoic acid, and H_2L^2 is 5-{[(2-carboxymethyl)methylene]amino}-2-chlorobenzoic acid), which were synthesized from triphenylantimony dichloride, Schiff bases, and sodium ethylate and represent 24-membered symmetric macrocycles each containing two antimony atoms linked by the bridging Schiff bases (Scheme 53) [122]:



Scheme 53.

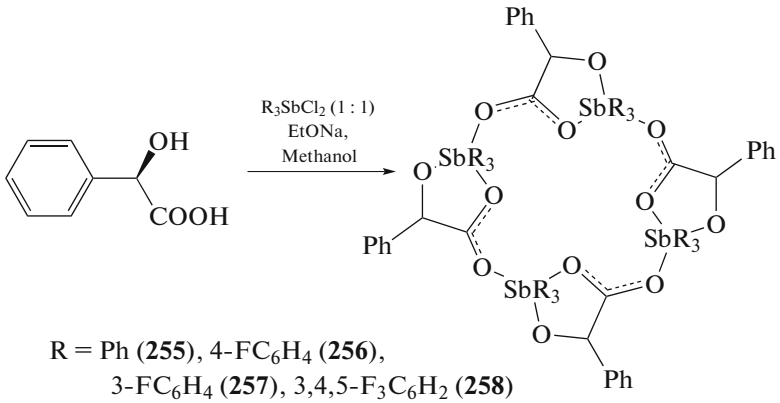
The reaction of 2,3-dibromobutanedioic acid and sodium methoxide with triphenylantimony dichloride in methanol affords antimony compound **251** in which two Ph_3Sb fragments linked via the bridging residue of 2,3-dibromobutanedioic acid contains terminal methoxyl substituents as well (Scheme 54) [123].



Scheme 54.

The nonsymmetric antimony derivative, chlorido(2-chloronicotinato)triphenylantimony (**252**), can be synthesized by the reflux (8 h) of a mixture of equimolar amounts of 2-chloronicotinic acid, sodium methoxide, and triphenylantimony dichloride in toluene [124]. The antimony atom in the crystal of compound **252** has an ideal trigonal bipyramidal coordination mode with the chlorine atom and carboxylate ligand in the axial positions. A series of triphenylantimony bromooximates $Ph_3Sb(Br)(ON{=}CRR')$ was synthesized via a similar scheme using triphenylantimony dibromide, oxime, and sodium methylate, the mixture of which was stirred in a dichloromethane solution for 10–12 h [125]. Oxobis[(chloraceto)triphenylantimony] (**253**) [126] and oxobis[(2-chloropyridinecarboxylato)triphenylantimony] (**254**) (Scheme 54) [127] were synthesized in the yield up to 85% via similar reactions from oxobis[(chloro)triphenylantimony], sodium methoxide, and chloroacetic or 2-chloropyridyl-3-carboxylic acid, respectively, in toluene (24 h, T_{room}). The antimony atoms in compounds **253** and **254** have a trigonal bipyramidal configuration with the carboxyl ligand and bridging oxygen atom in the axial positions.

The tetranuclear derivatives of pentavalent antimony (**255**–**258**) with the anticancer properties were synthesized via the same scheme from triarylantimony dichloride, α-oxyphenylacetic acid, and sodium ethoxide in methanol (Scheme 55) [128].



R = Ph (**255**), 4-FC_6H_4 (**256**),
3-FC_6H_4 (**257**), 3,4,5-$F_3C_6H_2$ (**258**)

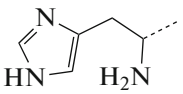
Scheme 55.

A series of biologically active tri-*p*-tolylantimony dicarboxylates (**259**–**266**) were synthesized similarly using potassium or sodium salts of carboxylic acids and triarylantimony dibromide (Scheme 56) [129].

$$2R'\text{–}COOM + p\text{-}Tol_3SbBr_2 \xrightarrow[-2MBr]{\text{Toluene, }\Delta} p\text{-}Tol_3Sb[OC(O)R']_2$$

M = Na, K

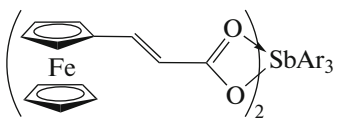
R' = *p*-Tol (**259**), 2-$NHPhC_6H_4$ (**260**), 3,5-$Cl_2C_6H_3$ (**261**), Et (**262**), 3-Py (**263**), 2-$OCH_3C_6H_4CH_2$ (**264**), 4-$OCH_3C_6H_4CH_2$ (**265**),



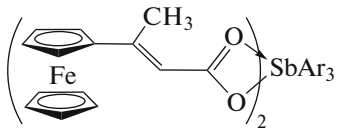
(**266**)

Scheme 56.

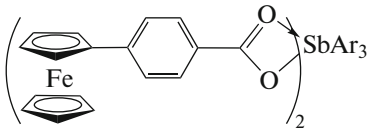
It is shown that the reactions of triarylantimony dihalide with the compounds bearing the active hydrogen atom in the presence of amine result in the substitution of the halogen atoms and formation of antimony derivatives Ar_3SbX_2 in a high yield. The successive addition of 3-ferrocenylacrylic acid and trimethylamine to a suspension of triarylantimony dibromide Ar_3SbBr_2 (Ar is C_6H_5, *p*-Tol, *m*-Tol, *o*-Tol, and 4-F-C_6H_4) in toluene followed by the stirring of the reaction mixture for 24 h, filtration, and solvent removal from the filtrate led to the formation of triarylantimony dicarboxylates **267**–**271** in a high yield (Scheme 57) [60].



Ar = Ph (**267**), *p*-Tol (**268**), *m*-Tol (**269**), *o*-Tol (**270**), 4-FC_6H_4 (**271**)



Ar = Ph (**272**), *p*-Tol (**273**), 4-ClC_6H_4 (**274**), 4-FC_6H_4 (**275**)



Ar = Ph(**276**), *p*-Tol (**210**), 4-ClC_6H_4 (**277**), 4-FC_6H_4 (**278**)

Scheme 57.

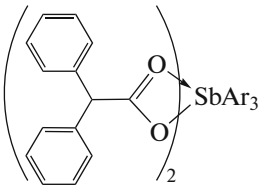
Other triarylantimony dicarboxylates **272**–**275** with ferrocenyl methacrylate substituents and compounds **210** and **276**–**278** with 4-ferrocenyl benzoate substituents were synthesized via a similar procedure [130].

Heterocyclic triphenyl- and tri-*para*-tolylantimony diacrylates **279** and **280**, which were synthesized via the indicated scheme, manifest themselves as efficient tools in leishmaniosis and staphylococcus control [131]. The reaction of triphenylantimony dibromide with *N*-phenylglycine was carried out via a similar scheme but in a THF solution, and triphenylantimony bis(*N*-phenylglycinate) **281** was isolated [132]. The molecules of the listed triarylantimony dicarboxylates are characterized by the expected trigonal bipyramidal configuration with the nonsymmetric coordination of two oxygen atoms of the carboxyl groups to the antimony atom. The aforementioned triarylantimony dicarboxylates exhibit anticancer activity in vitro.

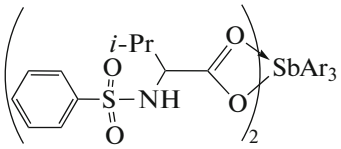
The stirring of a toluene solution of equimolar amounts of triphenylantimony dichloride with 8-

oxyquinoline or 2-pyridineethanol in the presence of trimethylamine results in the formation of octahedral antimony derivatives **282** and **283** in the yield up to 37% in which the bidentate N,O-donor ligands occupy the axial and equatorial positions at the central metal atom (coordination number 6) [133].

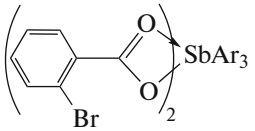
Several triarylantimony dicarboxylates [$Ar_3Sb(OOCR)_2$] (Ar is Ph, *p*-Tol; R is 4-$NO_2C_6H_4$, 2-Br-C_6H_4, $CHPh_2$, $CH_2CH(i\text{-Pr})NHSO_2Ph$) (**284**–**291**) were synthesized by the substitution reaction using triphenyl- or tri-*para*-tolylantimony dibromides, the corresponding carboxylic acid, and trimethylamine in toluene in 78–81% yield (Scheme 58). The biological activity of the synthesized compounds was studied [134]. The tris(*para*-tolyl)antimony derivatives were shown to have a more pronounced antileishmaniosis activity.



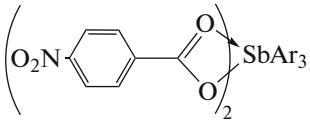
Ar = Ph (**284**), *p*-Tol (**285**)



Ar = Ph (**288**), *p*-Tol (**289**)



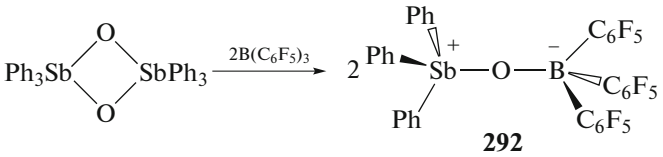
Ar = Ph (**286**), *p*-Tol (**287**)



Ar = Ph (**290**), *p*-Tol (**291**)

Scheme 58.

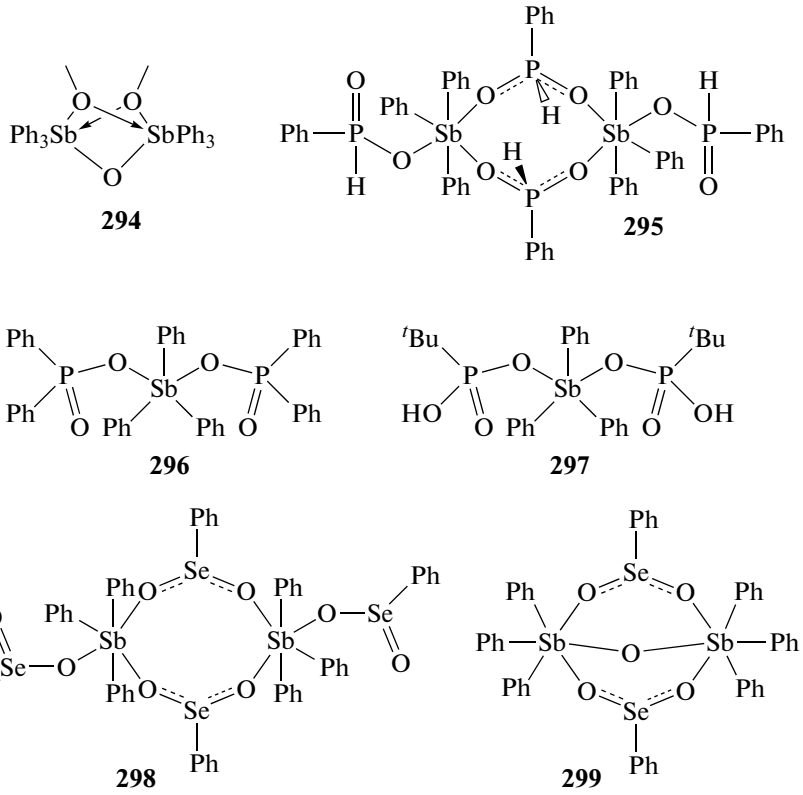
The reactions of triarylantimony oxides $(Ph_3SbO)_2$ and $[(2,6\text{-}(Me_2NCH_2)_2C_6H_3)_3SbO]_2$ with the Lewis acid $B(C_6F_5)_3$ are accompanied by the formation of the addition products $Ph_3SbOB(C_6F_5)_3$ (**292**) (Scheme 59) and $2,6\text{-}(Me_2NCH_2)_2C_6H_3SbOB(C_6F_5)_3$ (**293**) containing very shor Sb–O bonds [135].



292

Scheme 59.

The reaction of triphenylantimony oxide with methanol affords binuclear solvate **294** (Scheme 60) [136]. The reactions of the polymeric form of triphenylantimony oxide with phenylphosphinic, diphenylphosphinic, *tert*-butylphosphonic, and phenylselenic acids result in the formation of mono- and binuclear organic antimony derivatives **295**–**299** (Scheme 60) [137].



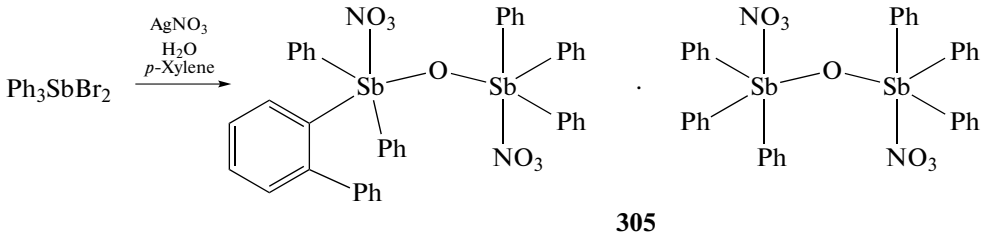
Scheme 60.

The hydrolysis of triphenylantimony dibromide or tri(*o*-tolyl)antimony dibromide in benzene gave solvates $(Ph_3SbBr)_2O \cdot 2PhH$ (triclinic modification) (**300**) and $[(2\text{-}MeC_6H_4)_3SbBr]_2O \cdot 1/2PhH$ (**301**) in which the Sb atoms have a distorted trigonal bipyramidal coordination mode with the aryl ligands in the equatorial positions and the bridging oxygen atom and terminal Br ligand in the axial positions [138].

Oxide $[(4\text{-}F\text{-}C_6H_4)_3SbCNS]_2O$ (**302**) was synthesized from tris(4-fluorophenyl)antimony dibromide and potassium isocyanate in an aqueous-acetone solution [139]. The antimony atoms in the molecules of the oxide have a distorted trigonal bipyramidal coordination mode with the electron-withdrawing ligands in the axial positions.

Tricymantrenylantimony dichloride treated with potassium hydroxide in alcohol is transformed into tricymantrenylantimony dihydroxide **303** in which the antimony atoms have a distorted trigonal bipyramidal coordination mode with the hydroxyl groups in the axial positions [140].

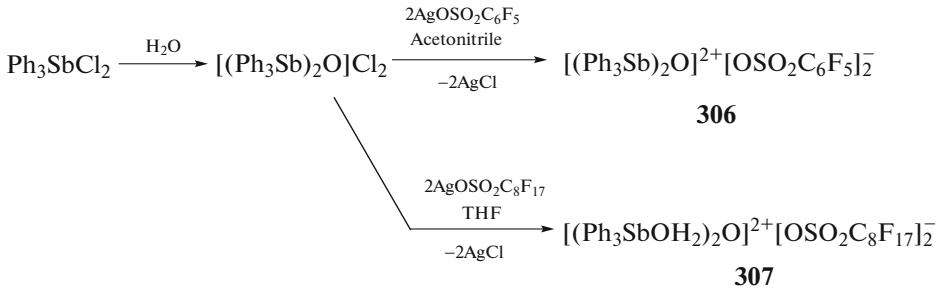
The antimony compounds of the bridging type μ-oxobis[(nitrato)triphenylantimony] (**304**) and $(Ph_2(2\text{-}PhC_6H_4)(NO_3)SbOSbPh_3(NO_3) \cdot (Ph_3SbNO_3)_2O$ adduct (**305**) were synthesized from triphenylantimony dibromide and silver nitrate in solutions of benzene and *para*-xylene, respectively [141]. The first complex **304** was immediately isolated from the reaction mixture, whereas complex **305** was recrystallized from benzene. The formation of complexes **305** in *para*-xylene containing molecules of two types, μ-oxobis[(nitrato)triphenylantimony] and μ-oxo[(nit-rato)(2-phenylphenyl-enyl)diphenylantimony]-[(nitra-to)triphenylantimony], is of doubtless interest, since the *ortho*-phenylation of the phenyl substituent at the Sb(V) atom takes place in this reaction (Scheme 61).



Scheme 61.

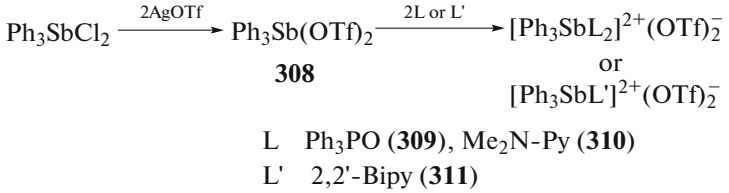
The formation of the last complex in 48% yield can be explained only by the phenylation of the triphenylantimony oxonitrate molecules with triphenylantimony dibromide under the reaction conditions. Perhaps, the reaction proceeds via the formation of an activated complex containing two molecules of the organoantimony compound and solvate molecules of the solvent, which is further transformed into the phenylated oxonitrate.

The consecutive reactions of triphenylantimony dichloride with water and silver organosulfonates in acetonitrile or THF afford thermally stable ionic antimony complexes **306** and **307** (Scheme 62) [142].



Scheme 62.

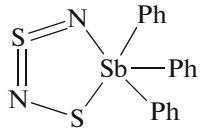
The reaction of triphenylantimony dichloride with silver triflate gives covalent triphenylantimony bis(trifluoromethanesulfonate) **308** [143], which is transformed into ionic products **309**–**311** with the $[Ph_3SbL_2]^{2+}$ cations upon the addition of such neutral donor ligands as bipyridyl or triphenylphosphine oxide (Scheme 63).



L Ph_3PO (**309**), Me_2N-Py (**310**)
L' 2,2'-Bipy (**311**)

Scheme 63.

Heterocyclic antimony compound **312** containing the five-membered ring with alternating nitrogen, sulfur, and antimony atoms was synthesized from thiotrithiazyl chloride and triphenylantimony dichloride in liquid ammonia (Scheme 64) [144].



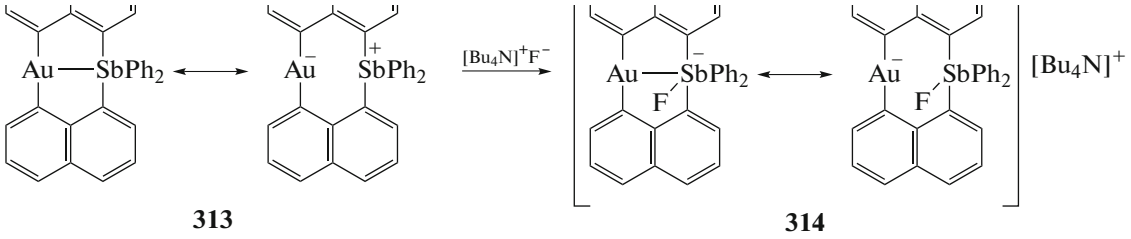
312

Scheme 64.

The bonds of the sulfur atoms with the nitrogen atom in the –S–N=S=N– fragment are nonequivalent (two bonds are shorter, and one bond is longer).

The consecutive treatment of triphenylantimony dibromide with 1,8-dilithiumnaphthalene, the gold complex AuCl(Tht) (Tht is tetrahydrothiophene), and triphenylphosphine in THF gave organogold anti-

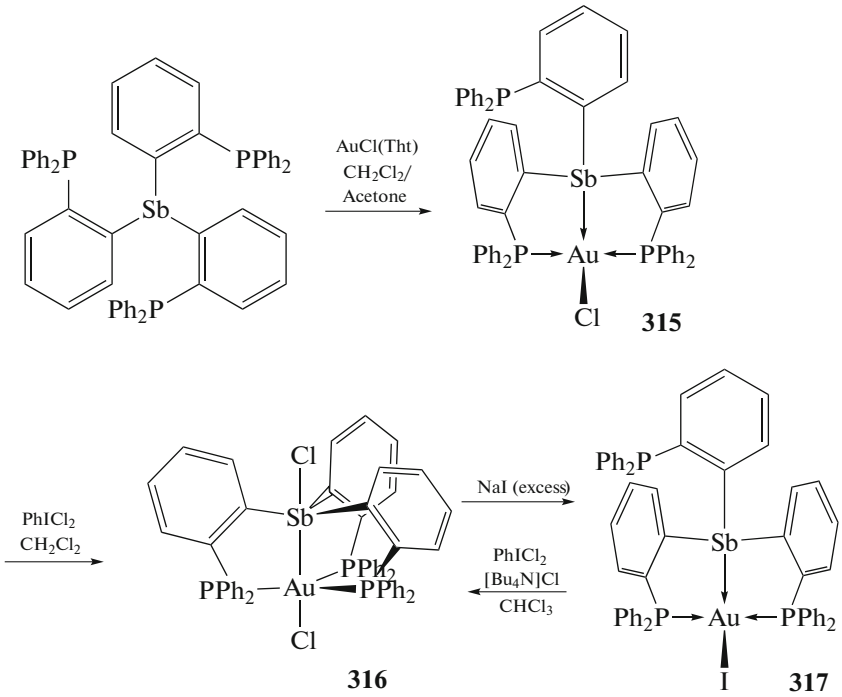
mony compound **313** [145] in which the Au···Sb coordination bond (2.77 Å) is close to the sum of covalent radii of gold and antimony atoms (2.65 Å [63]). The treatment of complex **313** with tetrabutylammonium fluoride in chloroform affords ionic complex **314** with the anion existing in two resonance forms (Scheme 65).



313 **314**

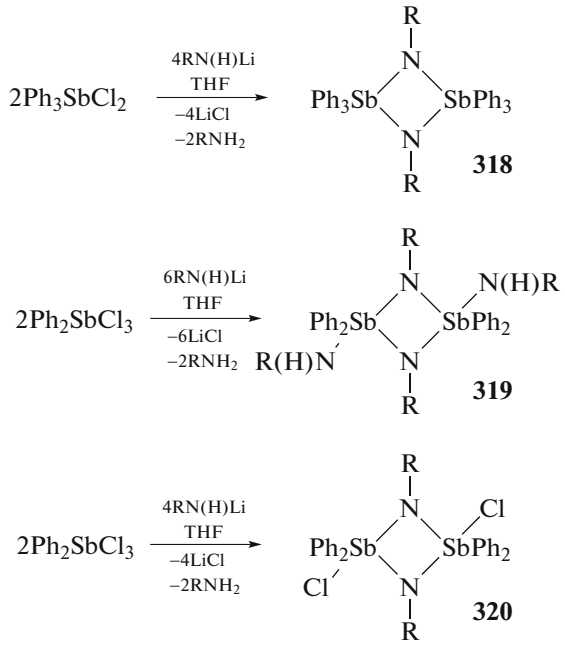
Scheme 65.

Another binuclear Sb,Au-containing compound **315** was synthesized from tris(2-diphenylphosphinophenyl)stibine and complex AuCl(Tht). The treatment of compound **315** with phenyliodonium dichloride results in the transformation of the corresponding dichloride **316** (Scheme 66). The reaction of the latter with sodium iodide is accompanied by the reduction of antimony and formation of Au-containing monoiodide **317** [146].



Scheme 66.

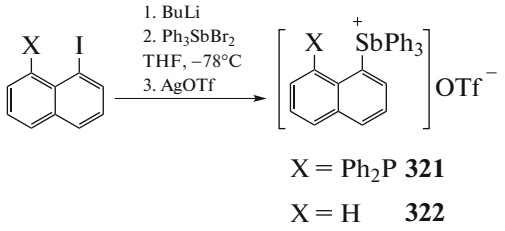
The reactions of organolithium derivatives of primary amines with triphenylantimony dichloride and diphenylantimony trichloride (Scheme 67) are of interest [147]. The reaction of lithium amide with triphenylantimony dichloride (2 : 1, THF) afforded cyclodistibazanes **318** in which two Ph_3Sb fragments are linked to each other via two bridging nitrogen atoms of the NR group. The products of similar reactions of lithium amide with diphenylantimony trichloride (3 : 1, THF) were analogous dimers **319** with two terminal Ph_2SbNHR fragments, but dimer **320** with the terminal Ph_2SbCl groups is formed when the molar ratio of the initial reactants changed to 2 : 1.



Scheme 67.

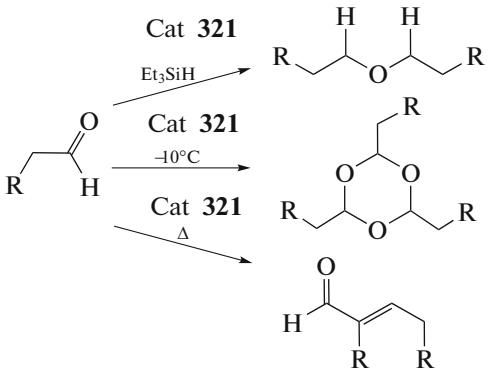
The treatment of triphenylantimony dichloride with aryllithium containing the *i*-Pr_2P group in the aryl substituent generated triphenylarylantimony chloride $Ph_3SbArCl$ **10** (Scheme 1) [4]. Diphenylarylantimony dichloride **11** is the product of the reaction of equimolar amounts of aryllithium and diphenylantimony trichloride (Scheme 1).

1-Diphenylphosphinonaphthyl-8-triphenylstibonium triflate **321** was synthesized from 1-lithium-8-diphenylphosphinonaphthalene and triphenylantimony dibromide followed by the elimination of the bromine atom by silver triflate (Scheme 68). Analog **322** without phosphine group was prepared similarly.



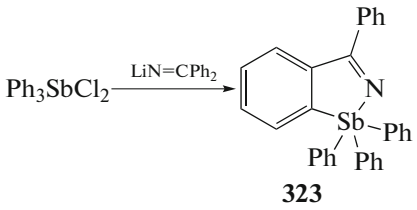
Scheme 68.

Compound **321** resistant to oxygen and water is a catalyst of the reactions of aldehydes with triethylsilane leading to the synthesis of symmetric esters (Scheme 69). At the same time, triflate **321** catalyzes aldol condensation. A decrease in the reaction temperature to −10°C results in the formation of 1,3,5-trioxanes in 50–90% yield [148].



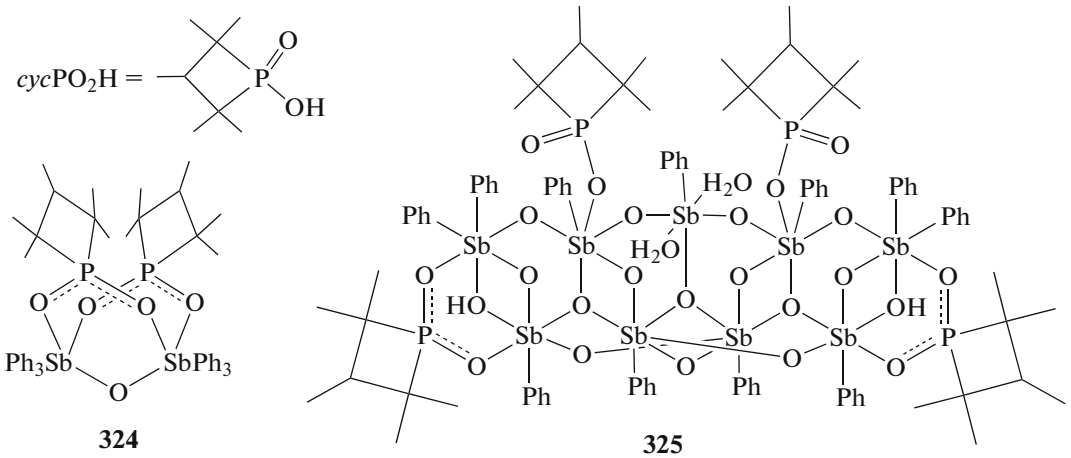
Scheme 69.

The case of *ortho*-metallation of one of the phenyl rings of the initial organolithium compound derived from phenyllithium and benzonitrile was observed for the reaction of triphenylantimony dichloride with lithium imide $LiN{=}CPh_2$ in THF (Scheme 70) [149].



Scheme 70.

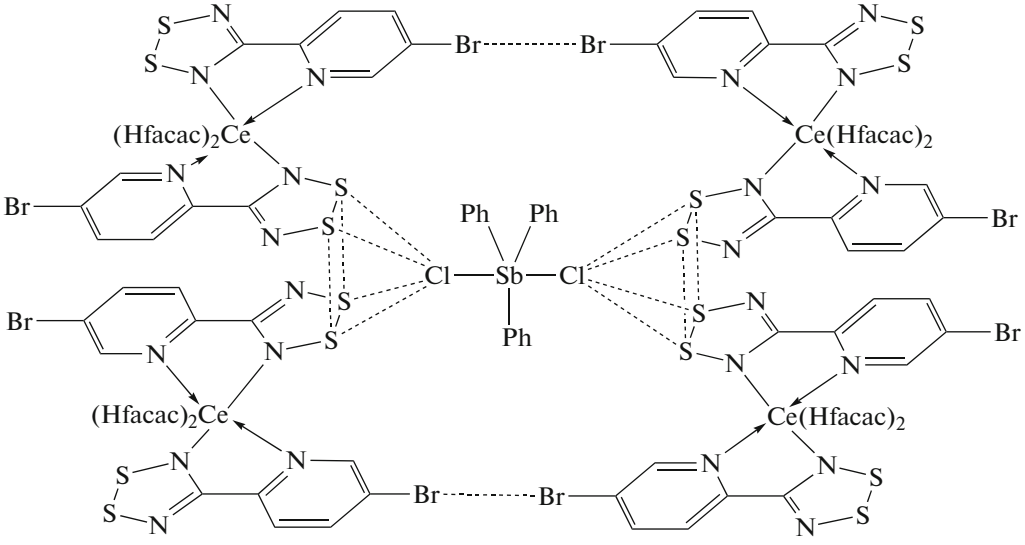
The binuclear antimony derivative $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$ (**324**) was synthesized from the product of hydrolysis of triphenylantimony dichloride and 1,1,2,3,3-pentamethyltrimethylenephosphinic acid in benzene (*cyc*PO_2 is 1,1,2,3,3-pentamethyltrimethylenephosphinate). The recrystallization of compound **324** from aqueous acetonitrile results in its transformation into the nonanuclear antimony complex $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2] \cdot 2CH_3CN \cdot H_2O$ (**325**) (Scheme 71) [150].



324 **325**

Scheme 71.

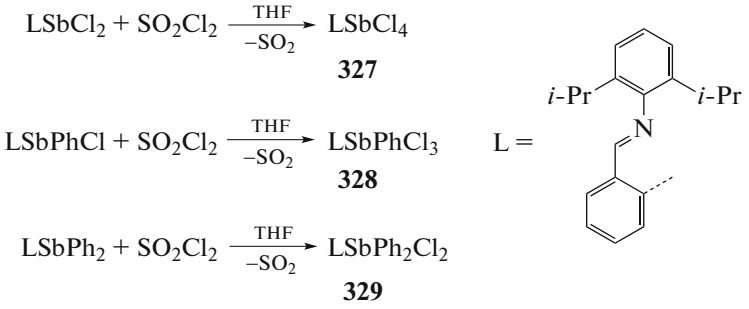
The stabilization effect of triphenylantimony dichloride appears in the crystal of its adduct **326** with bis[4-(5-bromopyridin-2-yl)-1,2,3,5-dithiadiazolyl-*N*,*N*')-tris(hexafluoroacetylacetonato-*O*,*O*')cerium] including the nonvalent interactions: S···S, Cl···S, and Br···Br contacts (Scheme 72) [151].



326

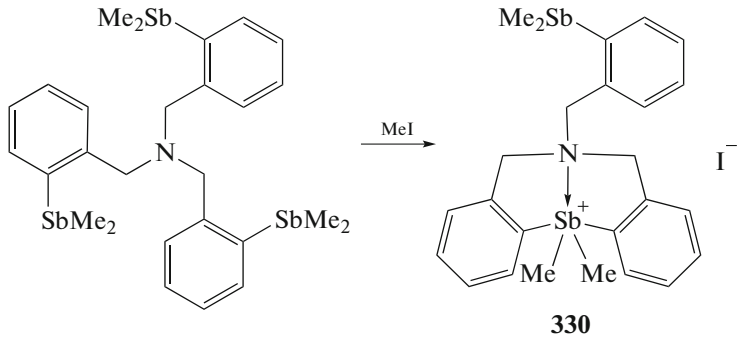
Scheme 72.

Oxidation of the Ar_3Sb derivatives by organic and inorganic oxidants. An important method for the synthesis of the antimony(V) compounds is oxidative addition. For example, the treatment of stibines by sulfuryl chloride results in stibine transformation into pentavalent antimony derivatives **327**–**329** (Scheme 73) [152].



Scheme 73.

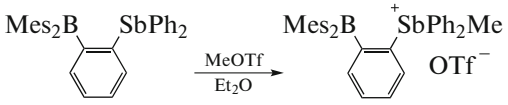
The known oxidative addition reaction where alkyltriarylstibonium halide is formed from triarylatibine and alkyl halide [74] occurs, in some cases, with the formation of different addition products, for example, the methylation of tris(2-dimethylstibinephenylmethyl)amine by methyl iodide (Scheme 74) results in the formation of the heterocyclic compound of pentacoordinated antimony (**330**) bearing the anomalously short Sb···N bond (2.565(4) Å) [153].



330

Scheme 74.

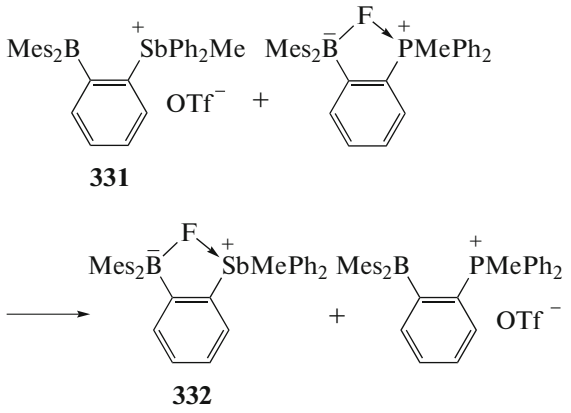
The quaternization of triarylstibine containing the Mes_2B group in position 2 of one of the phenyl substituents affords ionic diphenylarylmethylstibonium trifluoromethanesulfonate **331** (Scheme 75) [154].



331

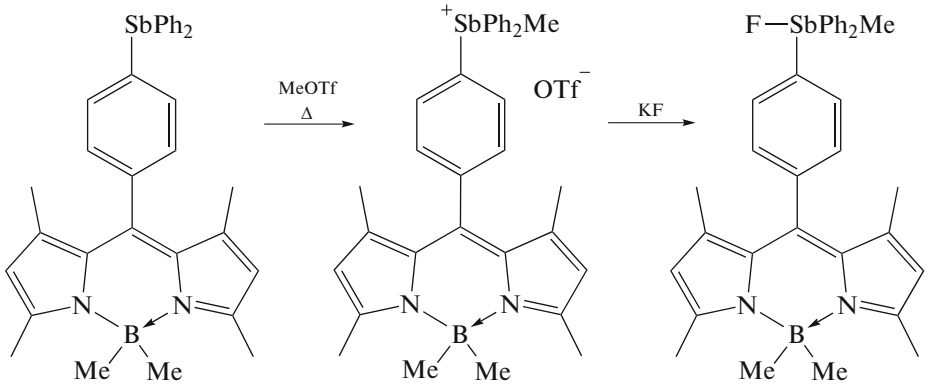
Scheme 75.

Studying the reaction of compound **331** with fluoro-(2-dimesitylborylphenyl)methyldiphenylphosphorane, the authors found the formation of more stable derivative **332** (Scheme 76) with the anomalously short Sb–F bond (2.450(2) Å), which is significantly shorter than the P–F bond (2.666(2) Å) in analogous initial phosphorene in spite of the smaller size of the phosphorus atom.



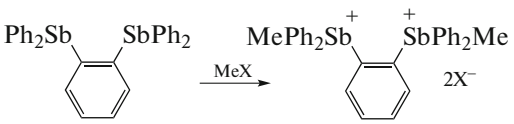
Scheme 76.

The usual scheme of quaternization is observed when compound **333** is treated with methyl triflate (Scheme 77) [155]. The formed addition product **334** treated with KF is transformed into methyldiphenylarylantimony fluoride **335**.



Scheme 77.

Distibonium salts **336** and **337** can be synthesized by the treatment of *o*-phenylenebis(diphenylstibine) with methyltrifluoromethanesulfonate (MeOTf) and trimethyloxonium tetrafluoroborate ($[Me_3O]^+[BF_4]^-$), respectively (Scheme 78) [156].



MeX =

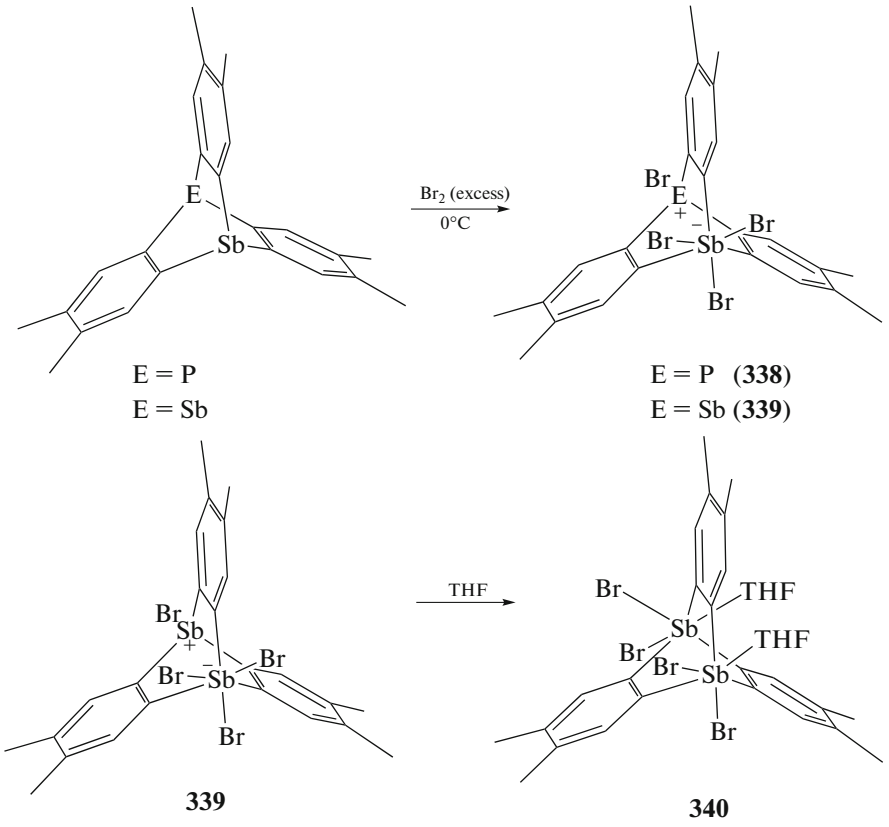
MeOTf (4 equiv.) $X^- = OTf^-$ (**336**)

$[Me_3O]^+[BF_4]^-$ (2.05 equiv.) $X^- = [BF_4]^-$ (**337**)

Scheme 78.

It has been shown at the early 1900s that triarylstibines are readily and quantitatively oxidized by halogens, divalent copper halides, and other halogen derivatives in organic solvents [74]. At present triarylantimony dihalides are synthesized by the same method.

It is found that 2,3,6,7,14,15-hexamethyl-9-phospha-10-stibatriptycene and 2,3,6,7,14,15-hexamethyl-9,10-distibatriptycene are oxidized by bromine to the corresponding tetrabromides **338** and **339** (Scheme 79), and the recrystallization of the latter from THF results in its transformation into solvate **340** in which two THF molecules coordinate to the antimony atom [157].



Scheme 79.

Tris(4-*N*,*N*-dimethylaminophenyl)antimony is shown to be oxidized by copper dichloride in an alcohol–acetone solution at room temperature to tris(4-*N*,*N*-dimethylaminophenyl)antimony dichloride **341** (Scheme 80), which was isolated from the reaction mixture in 60% yield as colorless photosensitive crystals [101].

$$(4\text{-}Me_2NC_6H_4)_3Sb \xrightarrow[-2CuCl\ -4H_2O]{2CuCl_2} (4\text{-}Me_2NC_6H_4)_3SbCl_2$$

341

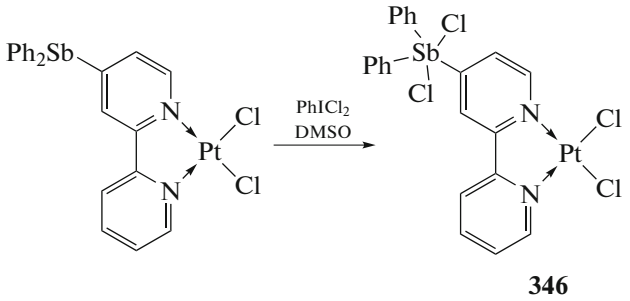
Scheme 80.

The reaction of tris(4-fluorophenyl)antimony with copper dibromide in acetone gave tris(4-fluorophenyl)antimony dibromide $(4\text{-}FC_6H_4)_3SbBr_2$ (**342**), whose recrystallization from ethanol resulted in the formation of the adduct $(4\text{-}FC_6H_4)_3SbBr_2 \cdot [(4\text{-}FC_6H_4)_3SbBr]_2O$ (**343**) [139].

The similar bromination of tricymanthrenylantimony in chloroform afforded tricymanthrenylantimony dibromide **344** [140].

Tris(4-bromophenyl)antimony (**345**) was synthesized by the consecutive chlorination of triarylantimony in petroleum ether, removal of the solvent, and recrystallization of the residue from dichloromethane in 43% yield [158].

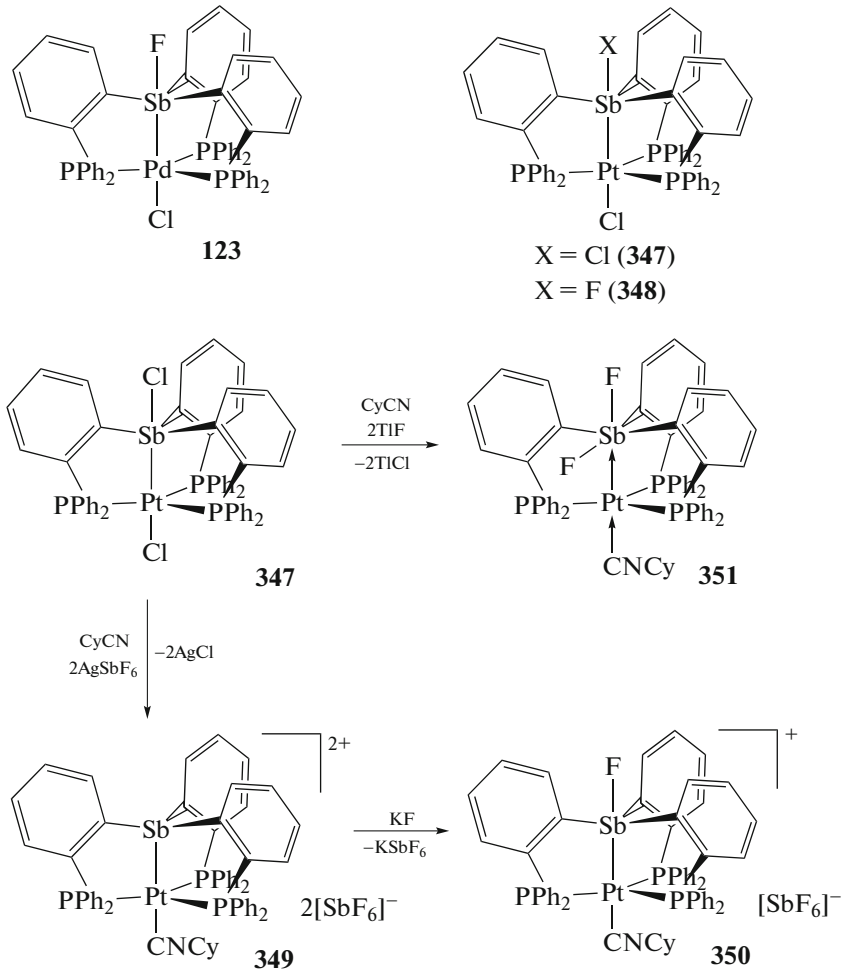
The treatment of the platinum complex containing the Ph_2Sb group in the 2,2'-Bipy ligand with iodobenzene dichloride in a DMSO solution results in the transformation into the corresponding platinum-containing triarylantimony dichloride **346** (Scheme 81), which catalyzes the reaction of mesitylene addition with ethyl acetylenecarboxylate [159].



Scheme 81.

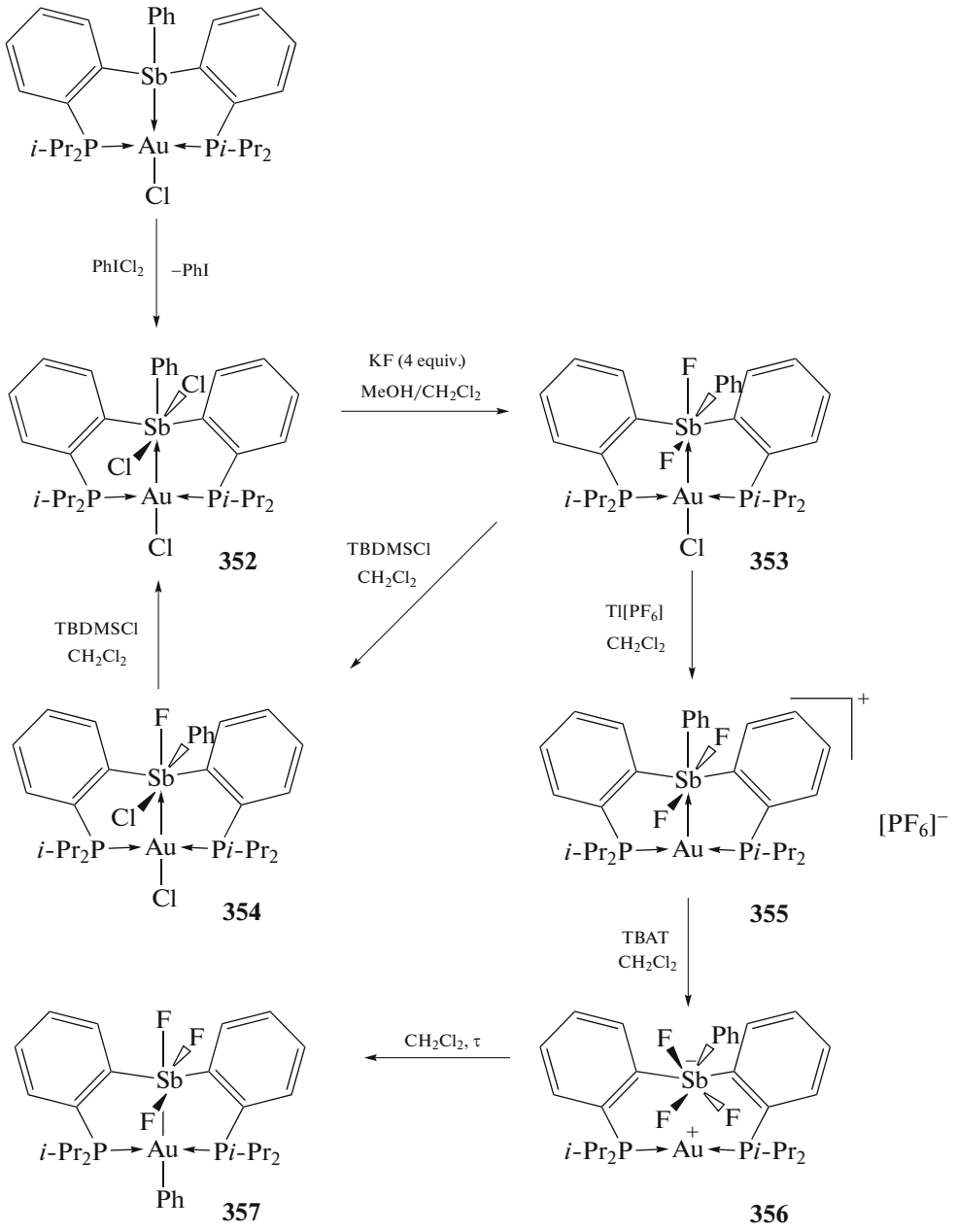
Note that other reactions of alkynes catalyzed by the platinum compounds, for example, tolane oxidation by air oxygen to form diphenylethanedione-1,2 in 91% yield [160].

The reactions of complex (o-(Ph_2P)–$C_6H_4)_3$-SbCl)Pt(Cl) (**347**) generated from stibine ((o-$(Ph_2P)C_6H_4)_3Sb$ and $(Et_2S)_2PtCl_2$) with fluorides afford the fluorostiboranyl complex ((o-(Ph_2P)-$C_6H_4)_3SbF)Pt(Cl)$ (**348**) (Scheme 82), which is an analog of the palladium complex (**123**). Compound **347** was used to synthesize $[((o\text{-}(Ph_2P)C_6H_4)_3$-Sb)Pt(CyNC)$]^{2+}[SbF_6]_2^-$ (**349**), $[((o\text{-}(Ph_2P)C_6H_4)_3$-SbF)Pt(CyNC)$]^+[SbF_6]^-$ (**350**), and ((o-(Ph_2P)-$C_6H_4)_3SbF_2)Pt(CyNC)$ (**351**) (Cy is cyclohexyl) via the exchange reactions. In these compounds, the fluoride ligands are bound to the antimony atom. The structural studies of this series show that the Sb–Pt bond elongates upon the consecutive coordination of fluorides at the antimony atom, which is consistent with the weakening of the Sb–Pt interaction [161].



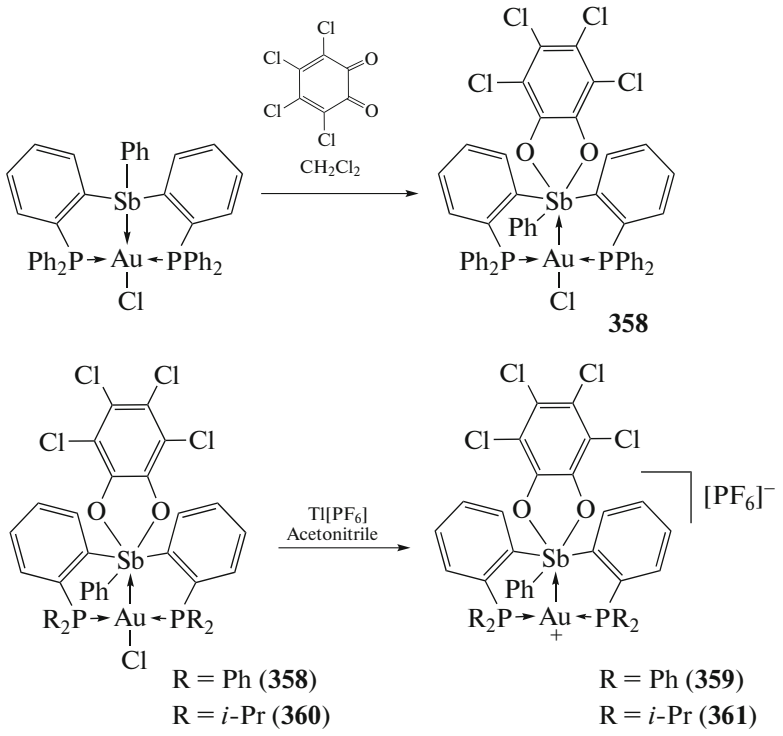
Scheme 82.

The controlled migration of the phenyl group in binuclear Au–Sb complexes **352**–**357** (Scheme 83) by the action of various reagents was reported [162]. The initial compound ((*o*-(*i*-Pr_2P)C_6H_4)$_2$SbPhCl_2)Au(Cl) (**352**) for the whole series of transformations was synthesized via the oxidative addition treating the binuclear Au–Sb complex ((*o*-(*i*-Pr_2P)–C_6H_4)$_2$SbPh)Au(Cl) with phenyliodonium chloride.



Scheme 83.

The synthesis and reactivity of analogous binuclear Au–Sb complex ((*o*-(Ph_2P)–C_6H_4)$_2$SbPh)Au(Cl) with diphenylphosphine substituents in the *ortho*-positions of two aryl groups were studied [163, 164]. The trivalent antimony derivative was found to react with *ortho*-chloranil at room temperature in a dichloromethane solution with the formation of hexacoordinated antimony complex **358** in 60% yield. In turn, the treatment of complex **358** with potassium hexafluorophosphate in acetonitrile led to its transformation into ionic complex **359** containing the tricoordinated gold atom (Scheme 84).

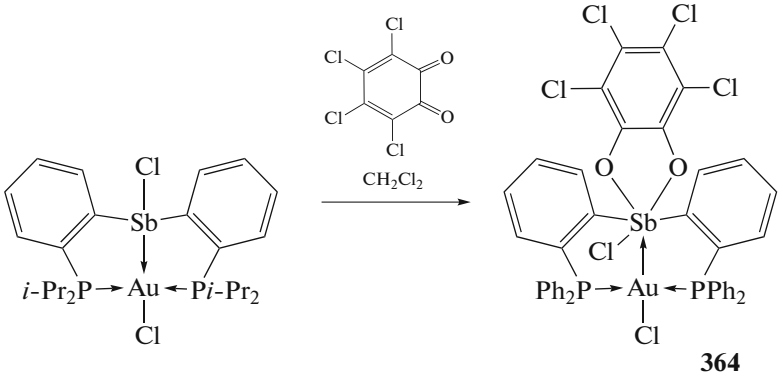


Scheme 84.

A similar reaction of diisopropylphosphine derivative **360** with thallium hexafluorophosphate affords similar ionic complex **361** (Scheme 84).

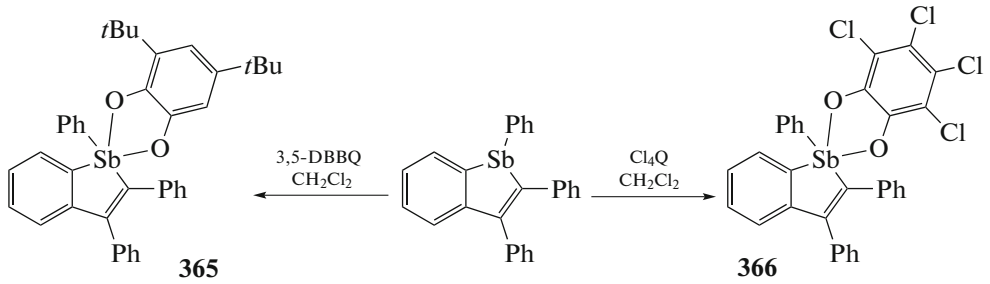
Complex ((*o*-(Ph_2P)C_6H_4)$_2$$SbCl_3$)Au(Cl) (**362**), which was synthesized similarly to complex **352** but under the action on the precursor of tetrabutylammonium fluoride instead of phenyliodonium chloride, is transformed into the corresponding trifluoride ((*o*-(Ph_2P)C_6H_4)$_2$$SbF_3$)Au(Cl) (**363**) resembling complex ((*o*-(*i*-Pr_2P)-C_6H_4)$_2$$SbF_3$)Au(Ph) (**357**) in structure [165].

The oxidation of complex ((*o*-(*i*-Pr_2P)-C_6H_4)$_2$SbCl)–Au(Cl), which is the chlorodiarylstibine derivative with gold chloride containing the *i*-Pr_2P groups in the *ortho*-position of the aryl substituent, by *ortho*-chloranil also results in the formation of pentavalent antimony derivative **364**, being an analog of complex **358** (Scheme 85) [166].



Scheme 85.

Pentavalent antimony derivatives **365** and **366** were synthesized similarly (Scheme 86) (stirring for 15–30 min, dichloromethane) using the oxidation of the corresponding stibine by 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBBQ) and *o*-chloranil (Cl_4Q) [167].



Scheme 86.

The oxidation of triphenylantimony by *N*-chlorotriphenylphosphoraneimine in a dichloromethane solution affords the addition product, triphenylphosphineiminotriphenylstibonium chloride $[Ph_3PNSbPh_3]Cl$ (**367**), in which the phosphorus and antimony atoms have the tetrahedral and trigonal bipyramidal coordination modes, respectively [168].

The study of the reactions of tri-*para*-tolylantimony with trifluoroacetic, trichloroacetic, iodoacetic, and toluenesulfonic acids and 2,4,6-trinitrophenol (HX) in a toluene solution in the presence or absence of air oxygen showed that the indicated reagents reacted via two competitive routes (Scheme 87) to form the pentavalent antimony derivatives of the general formula $p\text{-Tol}_3SbX_2$, where X is the residue of carboxylic and toluenesulfonic acids or of 2,4,6-trinitrophenol [169].

$$p\text{-Tol}_3Sb + 2HX \xrightarrow[-H_2]{} p\text{-Tol}_3SbX_2$$

$$p\text{-Tol}_3Sb + 2HX + 1/2O_2 \xrightarrow[-H_2O]{} p\text{-Tol}_3SbX_2$$

Scheme 87.

Triphenylantimony bis(trifluoromethanesulfonate), which was synthesized by the exchange reaction from silver triflate and triphenylantimony dichloride in dichloromethane, is treated with such electron-donating ligands as phosphines to transform into the ionic complex with triphenylstibine elimination (Scheme 88) [51].

$$Ph_3Sb(OTf)_2 + 2PR_3 \longrightarrow [R_3P{-}PR_3][OTf]_2 + SbPh_3$$

R = Me, *n*-Pr

Scheme 88.

The adduct of triphenylantimony with silver nitrate was used for the preparation of triphenylantimony dicarboxylates (Scheme 89) [170].

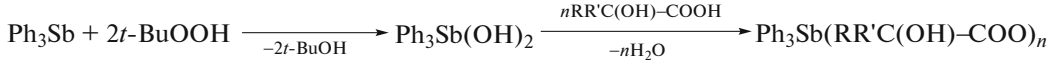
$$Ag(Ph_3Sb)_3NO_3 \xrightarrow[MeOH/CH_3CN]{SalH_2,\ Et_3N} Ag(Ph_3Sb)_3(SalH) \xrightarrow{(CH_3C(O))_2O} (CH_3COO)_2SbPh_3$$

Scheme 89.

Oxidative method for synthesis of aryl derivatives of antimony(V) from triarylantimony derivatives, acid HX, and peroxide. One of the efficient methods for the synthesis of the pentavalent antimony compounds is based on oxidative addition via which the aryl derivatives of pentavalent antimony Ar_3SbX_2 are synthesized from the antimony triaryl compounds, acid HX, and peroxide. This reaction was first carried out for the synthesis of triphenylantimony diacetate from triphenylantimony, acetic acid, and hydrogen peroxide [171]. Just this scheme was used to synthesize triphenylantimony dicrotonate $Ph_3Sb(O_2CCH{=}CHCH_3)_2$ (**368**) [172], triphenylantimony bis(1-adamantanecarboxylate) (**369**) [173], tris(2-methoxy-5-bromophenyl)antimony bis(bromoacetate) (**370**) [174], triphenylantimony bis(2-nitrobenzoate) (**371**) [175], tri-*m*-tolylantimony bis(1-adamantanecarboxylate) (**372**) [176], tri-*p*-tolylantimony bis(phenylcarboranyl carboxylate) (**373**) [177], triphenylantimony bis(2-methylcarboranyl carboxylate) (**374**) [178], triphenylantimony bis(2-methoxybenzoate) (**375**) [179], tris(5-bromo-2-methoxyphenyl)antimony bis(cyclopropane carboxylate) (**376**) [180], $[Ph_3Sb(O_2CCH{=}CHC_6H_4NO_2\text{-}m)_2 \cdot C_6H_6]$ (**377**) [181], triphenylantimony bis(salicylaldoximate) (**378**) [26], triphenylantimony bis(2-hydroxy-5-bromobenzaldoximate) (**56**) [31], tri-*para*-tolylantimony bis(cyclohexane oximate) (**379**) [31], tris(4-*N*,*N*-dimethylaminophenyl)antimony dibenzoate (**205**) [101], tris(4-*N*,*N*-dimethylaminophenyl)antimony bis(2-methyl benzoate) (**380**) [182], tris(4-*N*,*N*-dimethylaminophenyl)antimony bis(4-methyl benzoate) (**381**) [183], tris(4-*N*,*N*-dimethylaminophenyl)antimony bis(2,4,6-tribromophenoxide) (**382**) [182], tris(5-bromo-2-methoxyphenyl)antimony bis(2-nitrobenzoate) (**383**) [184], tris(5-bromo-2-methoxyphenyl)antimony bis(chloroacetate) (**384**), tris(5-bromo-2-methoxyphenyl)antimony bis(bromoacetate) (**385**) and tris(5-bromo-2-

methoxyphenyl)antimony bis(iodoacetate) (**386**) [185], tris(5-bromo-2-methoxyphenyl)antimony bis(4-nitrophenyl acetate) (**387**), tris(5-bromo-2-methoxyphenyl)antimony bis(2-methoxybenzoate) (**388**) and tris(5-bromo-2-methoxyphenyl)antimony bis(phenyl propiolate) (**389**) [186], and triphenylantimony bis(4-oxybenzenesulfonate) (**390**) [187]. Bis-[(*E*)-3-(4-methoxyphenyl)pro-2-enoato]triphenylantimony solvate with benzene (**391**) was synthesized by the oxidation of triphenylantimony with hydrogen peroxide in the presence of phenylcinnamic acid in THF followed by recrystallization from a benzene–hexane mixture [188]. A mixture of solvents is applied more rarely in oxidative addition, for example, the oxidation of triphenylantimony with hydrogen peroxide in the presence of methacrylic acid is carried out in an isopropanol–diethyl ether (4 : 1 vol/vol) mixture, and the yield of triphenylantimony dimethacrylate reaches 79% in this case [189].

A series of triphenylantimony α-hydroxycarboxylate complexes **392**–**395** was synthesized via oxidative addition from triphenylantimony, carboxylic acid, and *tert*-butyl hydroperoxide (Scheme 90) [190].



R = R' = H, *n* = 1 (**392**)

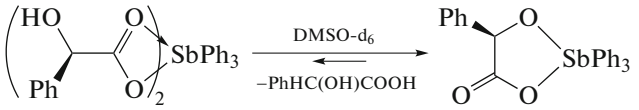
R = Ph, R' = H, *n* = 1 (**393**)

R = Ph, R' = H, *n* = 2 (**394**)

R = R' = Ph, *n* = 2 (**395**)

Scheme 90.

When dissolved in such a polar solvent as DMSO, triphenylantimony dicarboxylate **394** is transformed into more stable complex **396** (Scheme 91).



394 **396**

Scheme 91.

Note that *ortho*-phthalic acid reacts with triphenylantimony in the presence of hydrogen peroxide via the classical scheme of oxidative addition in spite of the presence of two carboxyl groups in this acid [191]. A specific feature of the molecular structure of triphenylantimony diflate is the absence of the intramolecular hydrogen bond characteristic of *ortho*-phthalic acid.

Triphenylantimony bis-μ-[(methylenedicyclopentanone-2,2'-dioximate) (**55**), which was earlier synthesized from pentaphenylantimony and dioxime on heating [30], in oxidative addition is formed in the nearly quantitative yield [192] as triphenylantimony bis(phenylmethanesulfonate) **397** [193]. The formation of compound **397** via the indicated scheme occurred in 91% yield, whereas the yield of triphenylantimony bis(2-naphthalenesulfonate) (**398**) and triphenylantimony bis(1-naphthalenesulfonate) (**399**) reached 46 and 25%, respectively. Possibly, this is related to an increase in the volume of the organic fragment in the arenesulfonate ligand. The reaction of triphenylantimony and phenylmethanesulfonic acid chloranhydride in the presence of hydrogen peroxide affords organoantimony zwitterion **400**, which was recrystallized from toluene as colorless crystals in 91% yield (Scheme 92) [193].

400

Scheme 92.

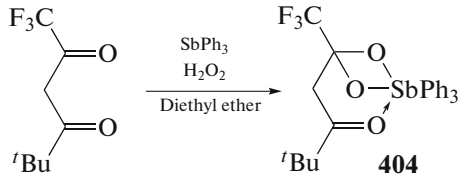
According to the XRD data, the antimony atoms in compound **400** are characterized by a distorted tetrahedral coordination, and two molecules of compound **400** are bound to each other by hydrogen bonds via the hydrogen atom of the methine group and the oxygen atom of the alkanesulfonate substituent, which is coordinated to the oxygen atom of the second molecule (the Sb–O(1') distance is 3.019(2) Å). In addition, in each molecule of compound **400** the distance between the O(3) oxygen atom and Sb atom is 2.988(2) Å. The length of one of the S–O bonds in the sulfo group (S–O(2) 1.433(2) Å) significantly differs from two others (S–O(1,3) 1.446(2), 1.454(2) Å respectively), which can be explained by an additional interaction of the O(1,3) atoms with the Sb and H atoms of the methine group.

Bis(4-iodophenoxy)triphenylantimony **401** is smoothly formed via the oxidative addition scheme from triphenylstibine, phenol, and hydrogen peroxide in ether [83].

The interaction of equimolar amounts of triarylantimony, acid HX, and hydrogen peroxide in ether generates the antimony compounds of the bridged type $(Ar_3SbX)_2O$ (**402**), which is observed, for example, in the reactions of tri(*ortho*-tolyl)antimony with 2-hydroxy-5-bromobenzaldoxime and furfural oxime [194]. In the absence of oxime in the reaction mixture, the initial tetraarylantimony is oxidized to the dimeric form of triarylantimony oxide.

In the case of a similar reaction of triphenylstibine with salicylic acid, the bridged antimony compound **403** characterized by anticancer activity is formed in 40% yield [195].

The (6,6,6-trifluoro-3-hexanone-5,5-diolato)triphenylantimony complex (**404**) was synthesized by the reaction of triphenylantimony with 6,6,6-trifluoro-2,2-dimethylhexanedione-3,5 in the presence of hydrogen peroxide in ether (Scheme 93) [196].



404

Scheme 93.

According to the XRD data, the Sb atom in the complex is characterized by a distorted octahedral coordination mode. The Sb–C distances vary in a range of 2.123(4)–2.131(4) Å, and the Sb–O(1,2,3) bond lengths are 2.052(2), 2.047(3), and 2.669(2) Å, respectively.

The reactions of 2-hydroxybenzaldoxime with tris(*para*-tolyl)antimony, tris(3-fluorophenyl)antimony, and tris(4-fluorophenyl)antimony taken in equimolar amounts in the presence of hydrogen peroxide in ether afford binuclear heterocyclic antimony compounds **405**–**407** [197].

The reaction of triarylantimony with organic peroxides in the presence of acid HX can be considered as an efficient method for the synthesis of the aryl derivatives of pentavalent antimony. It is shown that alcohols, phenols, oximes, and carboxylic, sulfonic, inorganic, and other OH and CH acids can act as acids. As a rule, *tert*-butyl hydroperoxide plays the role of the oxidant in the reactions. This method has a series of undisputable advantages over other methods: the reaction occurs in one step at room temperature with a high yield of target products. For instance, tri-*o*-tolylantimony bis(cyclohexanone oximate) (*o*-Tol)$_3$Sb(ON=C_6H_{10}-*cyclo*)$_2$ (**408**) was synthesized from tri-*ortho*-tolylantimony and cyclohexanone oxime in the presence of *tert*-butyl hydroperoxide (molar ratio 1 : 2 : 1). The adduct (*o*-Tol)$_3$Sb(ON=C_6H_{10}-*cyclo*)$_2$ · [(*o*-Tol)$_3$SbO]$_2$ (**409**) was isolated from the reaction mixture at the 1 : 1 : 1 molar ratio of the reactants [198].

Triphenylantimony bis(2-bromobenzaldoximate) (**410**), triphenylantimony bis(3-nitrobenzaldoximate) (**411**), triphenylantimony bis(3-bromobenzaldoximate) (**412**), and triphenylantimony bis(5-nitrofurfuraldoximate) (**413**) were synthesized similarly [199]. Other triarylantimony dioximates containing substituents in the aryl rings (tris(*para*-tolyl)antimony bis(2-oxybenzaldoximate) (**414**), tris(*para*-tolyl)antimony bis(2-nitrobenzaldoximate) (**415**), tris(*para*-tolyl)-antimony bis(2-bromobenzaldoximate) (**416**), tris(3-fluorophenyl)antimony bis(2-oxybenzaldoximate) (**417**), tris(4-fluorophenyl)antimony bis(2-bromobenzaldoximate) (**418**), and tris(4-fluorophenyl)antimony bis(2-nitrobenzaldoximate) (**419**) [200]; tris(*ortho*-tolyl)antimony bis(5-nitrofurfuraldoximate) (**420**) and tris(*ortho*-tolyl)antimony bis(thiophene-2-carbaldoximate) (**421**) [201]; tris(*ortho*-tolyl)antimony bis[4-*N*,*N*-dimethylamino)benzaldoximate] (**422**), tris(*ortho*-tolyl)antimony bis(acetophenone oximate) (**423**), tris(*meta*-tolyl)antimony bis(furfuraldoximate) (**424**) [202]; tris(*meta*-tolyl)antimony bis(2-nitrobenzaldoximate) (**425**) and tris(*ortho*-tolyl)antimony bis(2-nitrobenzaldoximate) (**426**) [203], and tris(*meta*-tolyl)antimony bis(5-nitrofurfuraldoximate) (**427**) [204] were synthesized similarly.

The reactions of tris(*para*-tolyl)antimony with phenols in the presence of *tert*-butyl hydroperoxide (molar ratio 1 : 2 : 1) in diethyl ether afforded tris(*para*-tolyl)antimony diaroxides (*p*-Tol$_3$Sb(OAr)$_2$, Ar is $C_6H_3Br_2$-2,4 (**428**), $C_6H_2Br_3$-2,4,6 (**429**) [205], C_6H_4Br-4 (**430**) [206], and $C_6H_4(NO_2$-4) (**431**) [206].

Tris(4-fluorophenyl)antimony diaroxides (4-F-$C_6H_4)_3$Sb(OAr)$_2$ (Ar is $C_6H_3Br_2$-2,4 (**432**), C_6H_4Cl-4 (**433**), C_6H_4Br-4 (**434**) [207], $C_6H_4(NO_2$-4) (**435**), C_6F_5 (**436**), and C_6Cl_5 (**437**)) were synthesized [206] from triarylantimony, phenols, and *tert*-butyl hydroperoxide in ether in 70–91% yield. Triphenylantimony bis(2,6-dibromo-4-methylphenoxide) (**438**) [9], triphenylantimony bis(4-bromophenoxide) (**439**) [208], and tris(3-fluorophenyl)antimony diaroxides (3-F$C_6H_4)_3$Sb(OAr)$_2$ (Ar = $C_6H_3Br_2$-2,4 (**440**) and OC_6Cl_5 (**441**)) were synthesized via the same scheme [209]. According to the XRD data, the antimony atoms in the synthesized compounds have the coordination mode of a distorted trigonal bipyramid with oxygen-containing substituents in the axial positions. However, under similar conditions, tris(*para*-tolyl)antimony reacts with 2,4-dinirophenol regardless of the ratio of the initial reagents to form the bridged-type compound (*p*-Tol$_3$SbOC$_6$H$_3$(NO$_2$)$_2$-2,5]$_2$O (**442**) only [210], which is likely due to steric hindrances.

The scheme of oxidative addition remains unchanged upon the addition of *tert*-butyl hydroperoxide to a solution of triphenylantimony and 4-nitro-

phenol in heptane [87]. The reactions of triarylantimony with carboxylic acids in ether in the presence of *tert*-butyl hydroperoxide afford triphenylantimony dicarboxylates: triphenylantimony bis(phenylpropiolate) (**443**) [13], triphenylantimony bis(4-oxybenzoate) (**444**) [14], triphenylantimony bis(propiolate) (**445**) [22], tris(4-fluorophenyl)antimony bis(iodoacetate) (**446**) and tris(4-fluorophenyl)antimony bis(pentafluorobenzoate) (**447**) [211], tris(4-fluorophenyl)antimony bis(1-adamantanecarboxylate) (**448**) and tris(4-fluorophenyl)antimony bis(cyclopropanecarboxylate) (**449**) [212], tris(4-fluorophenyl)antimony bis(chloroacetate) (**450**), tris(4-fluorophenyl)antimony bis(4-nitrophenylacetate) (**451**) and tris(4-fluorophenyl)antimony dibenzoate (**452**) [213], tris(3-fluorophenyl)antimony dicarboxylates (**453**) [214, 215], and triphenylantimony diacrylates (**454**) [216, 217].

The reactions of tri(*meta*-tolyl)antimony with benzenesulfonic acid [218] and benzoic acid [219], as well as the reaction of tri(*para*-tolyl)antimony with 3,4-dimethylbenzenesulfonic acid [220] proceed via a similar scheme.

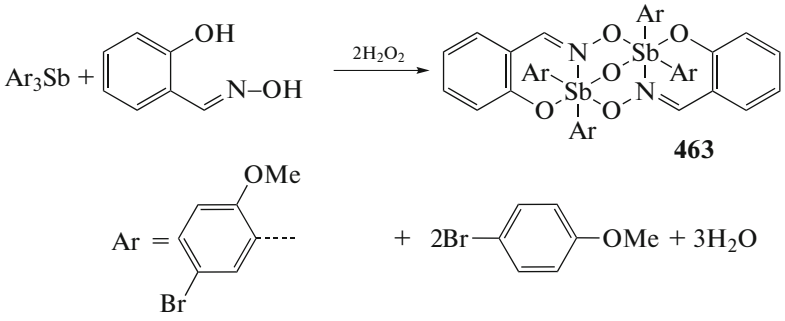
Donor–acceptor antimony complexes can be formed using donor ligands in similar reactions, for example, the reaction of triarylantimony with ethylene glycol or pyrocatechol in benzene in the presence of DMSO [221].

Note that the oxidative addition reactions occur with the formation of bridged-type compounds in the case of the interaction of equimolar amounts of the initial reagents. For instance, the reaction of triphenylantimony with propiolic acid in the presence of hydrogen peroxide (molar ratio 1 : 1 : 1) in diethyl ether affords μ_2-oxo-bis[(propiolato)triphenylantimony] $[Ph_3SbOC(O)C{\equiv}CH]_2O$ (**455**) [22].

The μ_2-oxo-bis[(aroxy)triarylantimony] derivatives of the general formula $[Ar_3Sb(OAr')]_2O$ (Ar is Ph, Ar' is $C_6H_2Cl_3$-2,4,6 (**456**), $C_6H_2Br_2$-2,6-(*t*-Bu)-4 (**457**); Ar is *p*-Tol, Ar' is $C_6H_2(NO_2)_3$-2,4,6 (**458**) [222], and Ar is *p*-Tol, Ar' = $C_6H_2Br_3$-2,4,6 (**459**), C_6Cl_5 (**460**), $C_6H_3(NO_2)_2$-2,4 (**461**) [223]) were also synthesized via a similar scheme.

The oxidation of tris(5-bromo-2-methoxyphenyl)antimony with an equimolar amount of *tert*-butyl hydroperoxide in a THF solution affords bis[μ_2-oxo-tris(5-bromo-2-methoxyphenyl)antimony] (**462**) in which the metal atoms have the trigonal bipyramidal coordination mode with the oxygen atoms in the axial positions [224].

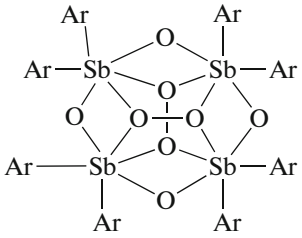
In some cases, unexpected products were isolated from the reaction mixture of oxidative addition instead of the target substance. For example, the reaction of tris(5-bromo-2-methoxyphenyl)antimony with 2-oxybenzaldoxime in the presence of hydrogen peroxide afforded (in 94% yield) bis(μ_3-2-oxybenzaldoximato-*O*,*O*',*N*)-(μ_2-oxo)bis(5-bromo-2-methoxyphenyl)antimony (**463**) (Scheme 94) in which various coordination modes of two donor atoms (oxygen and nitrogen) of the oxime ligand take place [225].



Scheme 94.

In the molecule of the complex, the antimony atom links with the ligand via the oxygen atom (Sb–O 2.0768(11) Å), the intramolecular Sb···N distances are 2.882(14) Å, and the hydroxyl groups in the aromatic ring of the oximate ligand are involved in the formation of the intramolecular hydrogen bonds.

The oxidative addition reactions involving triarylantimony, hydrogen peroxide, and acetoxime or acetophenoxime in dioxane were accompanied by the formation of tetranuclear organoantimony peroxide solvates with dioxane (**464** and **465**) (Scheme 95), which crystallize with different numbers of solvent molecules in the crystal cell (1.5 and 6) [226].

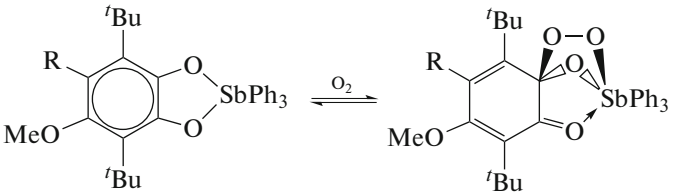


Ar = Ph (**464**), *p*-Tol (**465**)

Scheme 95.

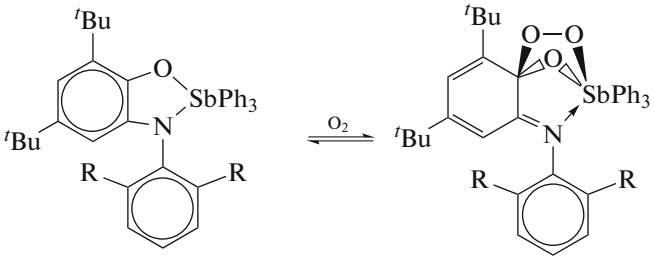
Note that the structure of similar compound **464** as a solvate with chloroform has previously been described [227].

Oxidative method for synthesis of organic antimony(V) derivatives from triorganylantimony and ortho-quinones. R.R. Holmes and coauthors [228] pioneered in reporting the oxidative addition reaction of triarylantimony and *ortho*-benzoquinone leading to the formation of triphenylantimony(V) 3,4,5,6-tetrachlorocatecholate (**466**). Some later it has been shown that diverse substituted *o*-benzoquinones and *o*-iminobenzoquinones react with triorganylantimony via a similar scheme [229–243]. Some catecholates of the general formula (Cat)$SbAr_3$ (**467**) containing electron-donating groups and triphenylantimony(V) *o*-amidophenolates (AP)$SbAr_3$ (**468**) react reversibly with molecular oxygen to form cyclic endoperoxide complexes of the types $L^{Cat}(OO)SbAr_3$ (**469**) and $L^{AP}(OO)SbPh_3$ (**470**) bearing the five-membered trioxastibolane cycle (Scheme 96) [224–252].



(Cat)$SbPh_3$
467
R = H, OMe

$L^{Cat}(OO)SbPh_3$
469

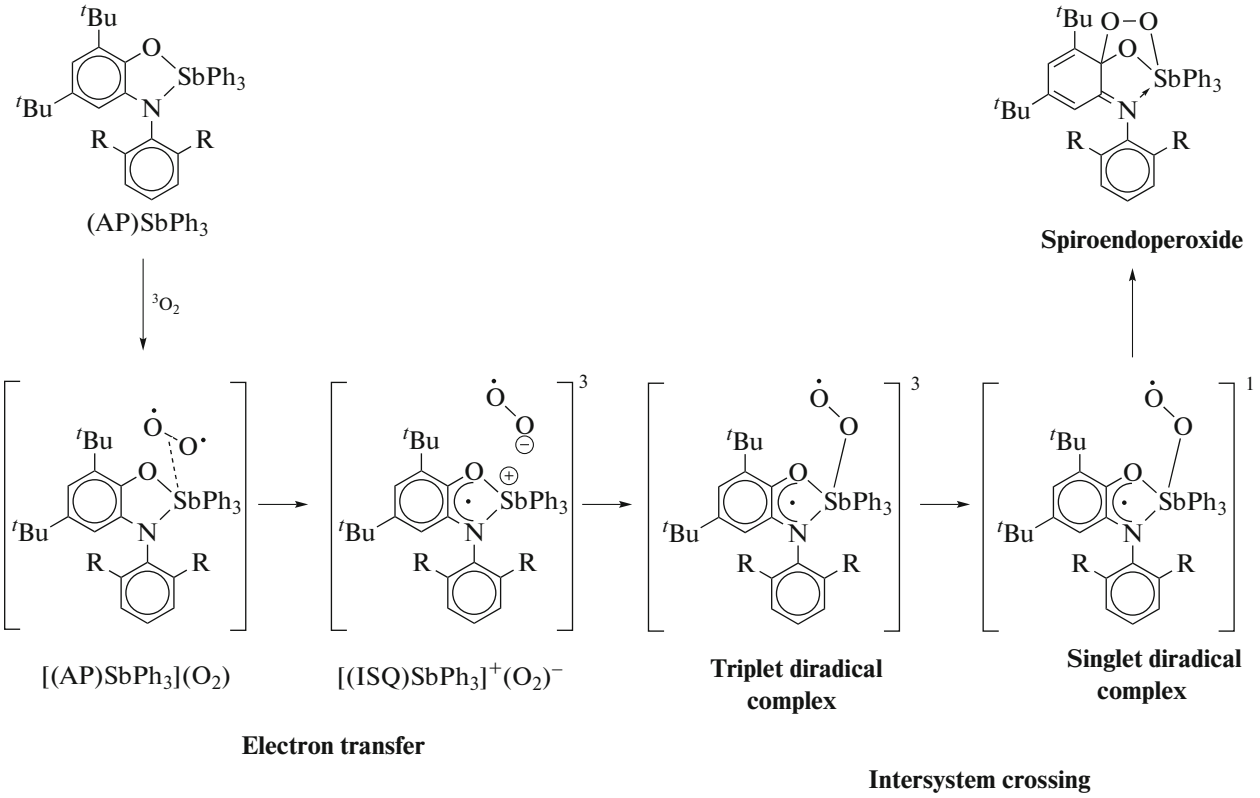


(AP)$SbPh_3$
468
R = Me, Et, *i*-Pr

$L^{AP}(OO)SbPh_3$
470

Scheme 96.

The mechanism of the reaction of the complexes with molecular oxygen was proposed [244, 246, 247]. It is established that the one-electron oxidation of the dianionic ligand to the radical-anionic ligand is one of the key steps of the process (Scheme 97).



Scheme 97.

The one-electron oxidation of the ligand (*o*-amidophenolate, catecholate, or phenanthrene-9,10-diolate) with molecular oxygen is assumed in this step with the formation of the molecular antimony-containing cation $[(ISQ)SbPh_3]^+$ and superoxide anion. Then the ion pair recombinates to form a triplet diradical complex bearing the *o*-iminobenzosemiquinone (or *o*-semiquinone) and superoxide ligands. The subsequent process is the intersystem crossing of the triplet diradical complex to the singlet one. It is known that the intersystem crossing of the triplet state to the singlet state is facilitated in the presence of heavy atoms. In this case, this atom is the antimony atom having a higher spin-orbital coupling constant. The subsequent recombination of the singlet diradical pair leads to the formation of endoperoxide.

The factors affecting the ability of the complexes of this class to the reversible addition of molecular oxygen were established and studied in detail [253–257]. It is shown that the introduction of acceptor substituents into the redox-active catecholate ligand increases the oxidation potential of the complex and leads to its inertness toward oxygen. On the contrary, electron-donor substituents decrease the oxidation potential and increases the reactivity of the corresponding complex in the reaction with molecular oxygen.

The variation of the substituents at the central antimony atoms makes it possible to precisely specify the redox potentials of the derivatives of the complexes and to control their reactivity in the reaction of molecular oxygen in spite of their remoteness from the redox-active ligand [258–263].

The influence of steric factors on the reactivity of the antimony complexes in this reaction was found. The possibility of controlling the structures of the formed endoperoxides using steric factors was shown [247, 249].

The catecholate and *o*-amidophenolate complexes were studied concerning antiradical activity and as inhibitors of peroxide lipid oxidation [264–271].

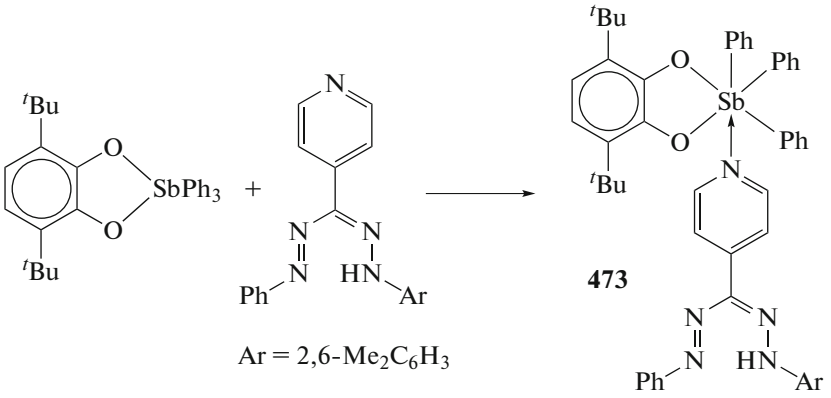
The reactions of the tridentate *N*-2-hydroxyphenyl-substituted ligands with triorganylstibines proceed via the oxidative addition mechanism but is accompanied by the proton migration from the hydroxyl group to the nitrogen atom and affords the antimony(V) aminobis(*o*-phenolate) complexes of the $(L^{ONHO})SbR_3$ type (**471**) [272–274]. These compounds also exhibit an appreciable antiradical activity and can be applied as radical scavengers. Trialkylantimony-based complexes of the type of **471** easily eliminate alkane and transform into amidobis(phenolate) dialkylantimony derivatives of the $(L^{ONO})SbR_2$ type (**472**). This process is accelerated in the presence of oxygen and affords the corresponding ethers.

The polymeric materials containing *o*-benzoquinone fragments in lateral chains were functionalized using the oxidative addition reactions to form anti-

mony-containing polymers characterized by activity toward molecular oxygen [275–277].

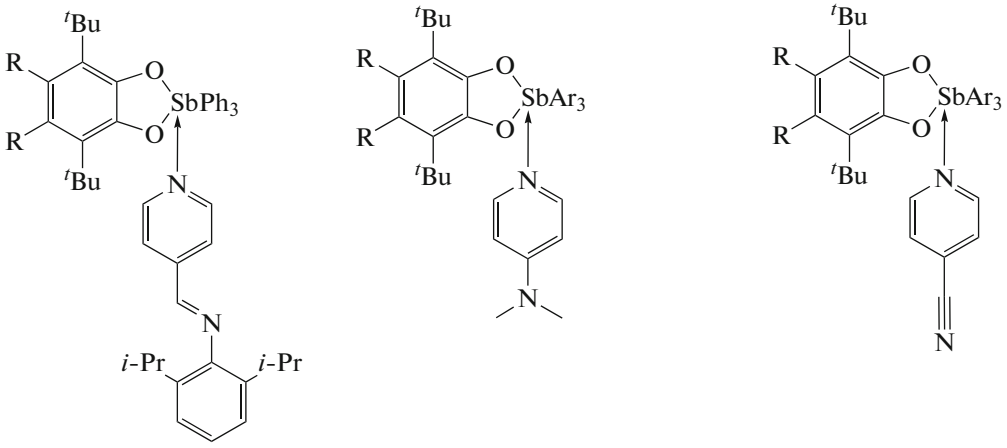
In some cases, where the corresponding *o*-benzoquinone is unstable, the catecholate complex is synthesized by the exchange reaction of pyrocatechol and triorganylantimony(V) dihalide in the presence of the base [231, 232, 269, 278, 279].

Triphenylantimony catecholates can form complexes with N-donor ligands in which the coordination number of the central metal atom increases to six [280]. For instance, hexacoordinated antimony complex **473** was synthesized from triphenylantimony 3,6-di-*tert*-butylcatecholate and 5-(2,6-dimethylphenyl)-3(4-pyridyl)-1-phenylformazane (Scheme 98).



Scheme 98.

Similar hexacoordinated triphenylantimony complexes **474**–**476** based on various substituted *o*-benzoquinones and iminomethylpyridine of the (Cat)$SbPh_3$ · ImPy type were described [281]. The molecular structures and specific features of the electrochemical behavior of triarylantimony(V) complexes **477**–**483** with *p*-*N*,*N*-dimethylaminopyridine and *p*-cyanopyridine (Scheme 99) were considered [282]. It is found that the coordination of an additional ligand can shift the electrochemical oxidation potentials and also can change the oxidation mechanism of the redox-active catecholate ligands.



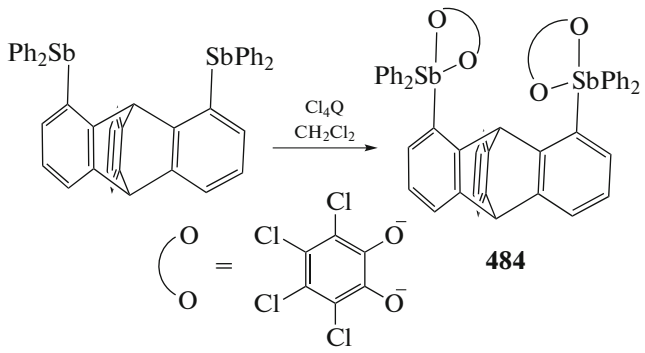
R = H (**474**)
R = N(CH$_2$CH$_2$)$_2$N (**475**)
R = Cl (**476**)

R = H, Ar = Ph (**477**)
R = N(CH$_2$CH$_2$)$_2$N, Ar = Ph (**478**)
R = Cl, Ar = Ph (**479**)
R = H, Ar = *p*-Tol (**480**)

R = H, Ar = Ph (**481**)
R = Cl, Ar = Ph (**482**)
R = H, Ar = *p*-Tol (**483**)

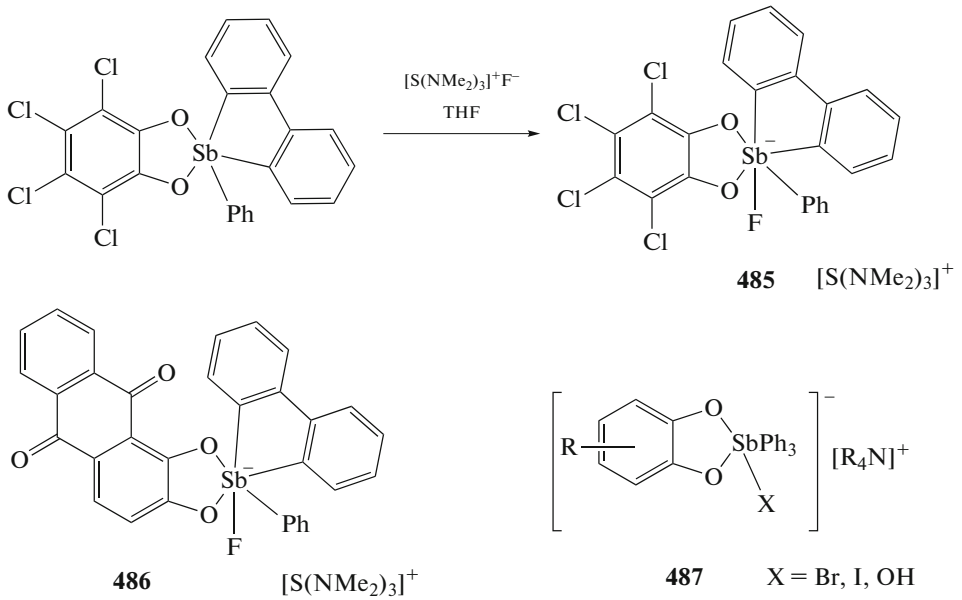
Scheme 99.

The authors [283] showed that the treatment of binuclear stibine with *ortho*-chloranil in dichloromethane at room temperature affords binuclear pentavalent antimony derivative **484** (Scheme 100).



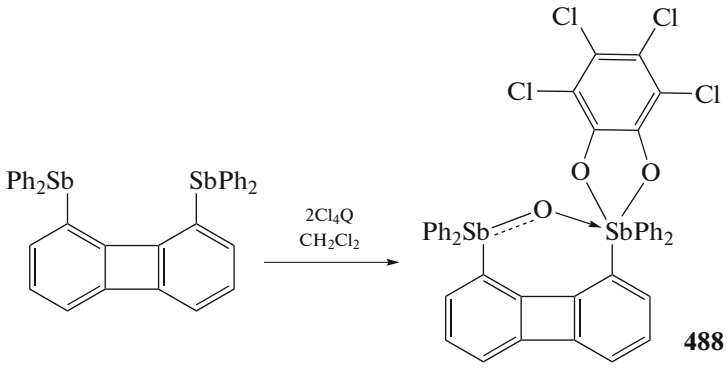
Scheme 100.

Organostiboranes bearing the 2,2'-biphenylenephenyl group and *ortho*-quinone residue were shown to transform (under the treatment of tris(dimethylamino)sulfonium fluoride) into salts **485** and **486**, whose anions contain hexacoordinated antimony atoms (Scheme 101) [284]. A group of diverse ionic complexes of the $[(Cat)SbPh_3X]^-[R_4N]^+$ type (**487**) was produced by the treatment of triphenylantimony catecholates with tetraalkylammonium salts in acetonitrile (Scheme 101) [256].



Scheme 101.

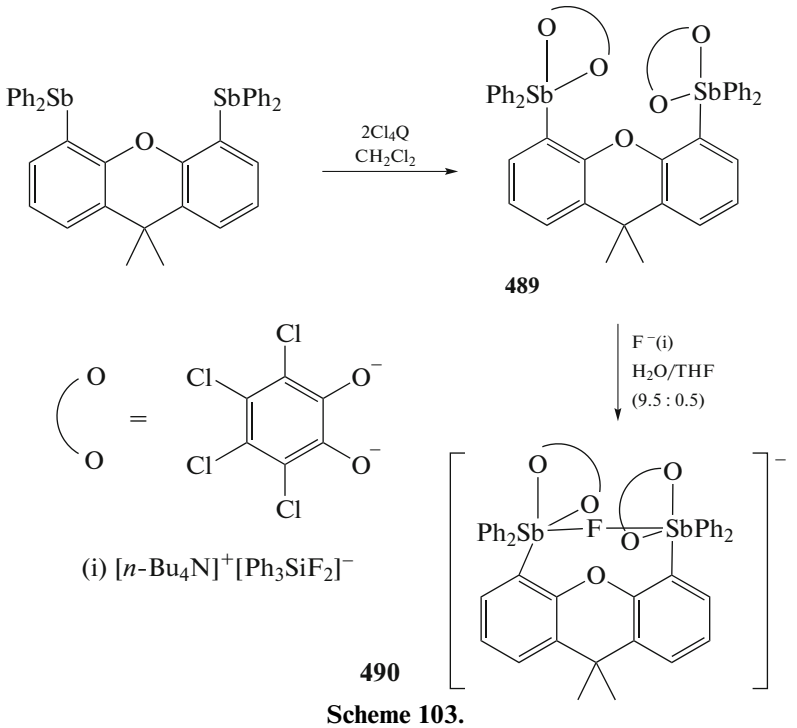
The product of the oxidative addition of 3,4,5,6-tetrachloro-1,2-benzoquinone by 1,8-bis(diphenylstibino)biphenylene is binuclear antimony compound **488** in which the metal atoms have different coordination numbers (4 and 6) (Scheme 102) [285].



Scheme 102.

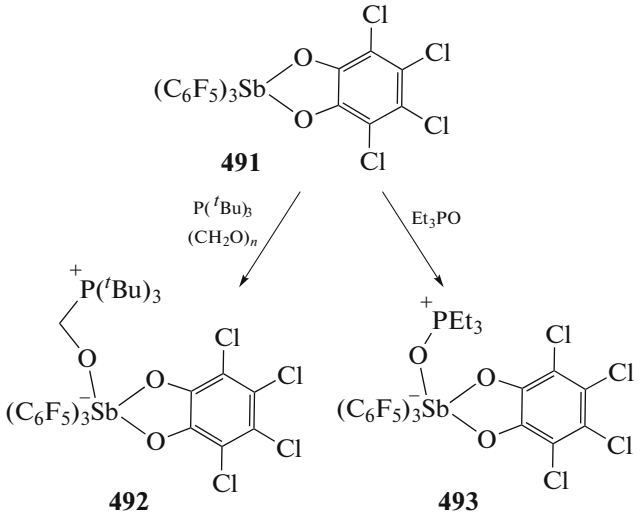
Compound **489**, which was synthesized by the oxidation of 4,5-bis(diphenylstibino)-9,9-dimethylxanthene by two moles of *o*-chloranil Cl_4Q, under the action of $[n\text{-}Bu_4N]^+[Ph_3SiF_2]^-$ (Scheme 103) is transformed into

ionic complex **490** [286], whose anion contains a chain of the Sb–F–Sb atoms (Sb(1)–F(1) 2.1684(17), Sb(2)–F(1) 2.1622(18) Å) approaching the sum of covalent radii of the indicated atoms: 2.12 Å [63]).



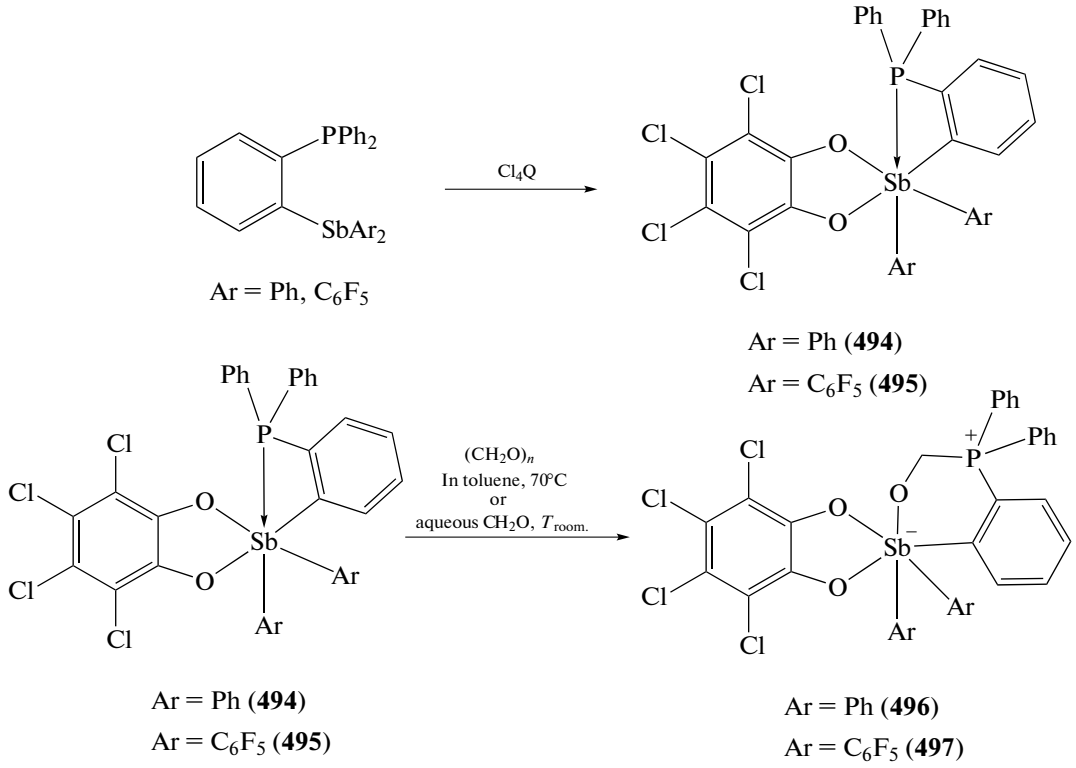
Scheme 103.

The oxidation of tris(pentafluorophenyl)antimony with *o*-chloranil gave stiborane **491**. The treatment of compound **491** with tris(*tert*-butyl)phosphine and paraform (Scheme 104) results in its transformation into zwitterion **492**, and the reaction of stiborane **491** with triethylphosphine oxide (L) affords addition product **493** in which ligand L coordinates to the antimony atom via the oxygen atom [287].



Scheme 104.

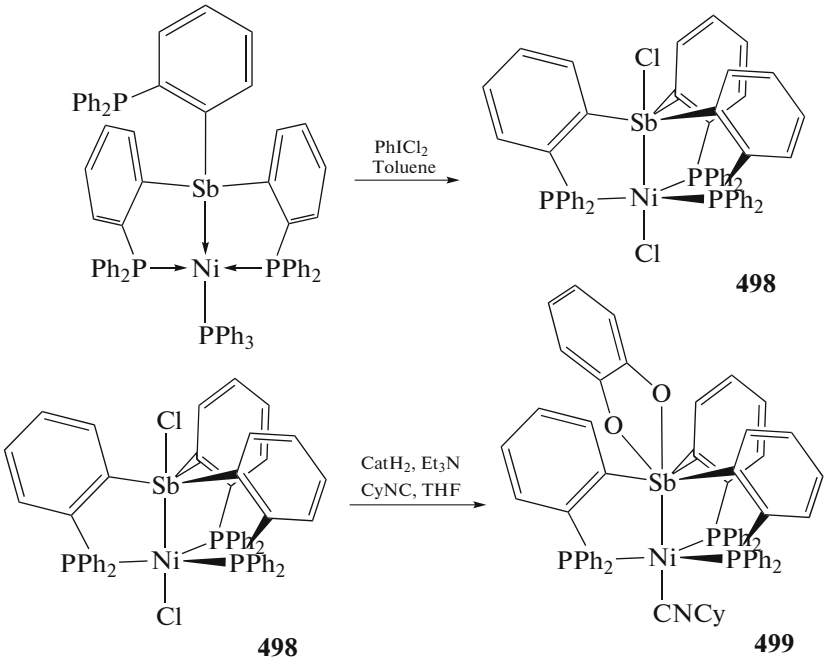
The presence of the diphenylphosphine group in one of the aryl ligands of triarylantimony does not change the scheme of oxidation of the trivalent antimony derivative. However, target products **494** and **495** have the coordination of the phosphorus atom to the antimony atom due to which the coordination number of the latter increases to six (Scheme 105) [287].



Scheme 105.

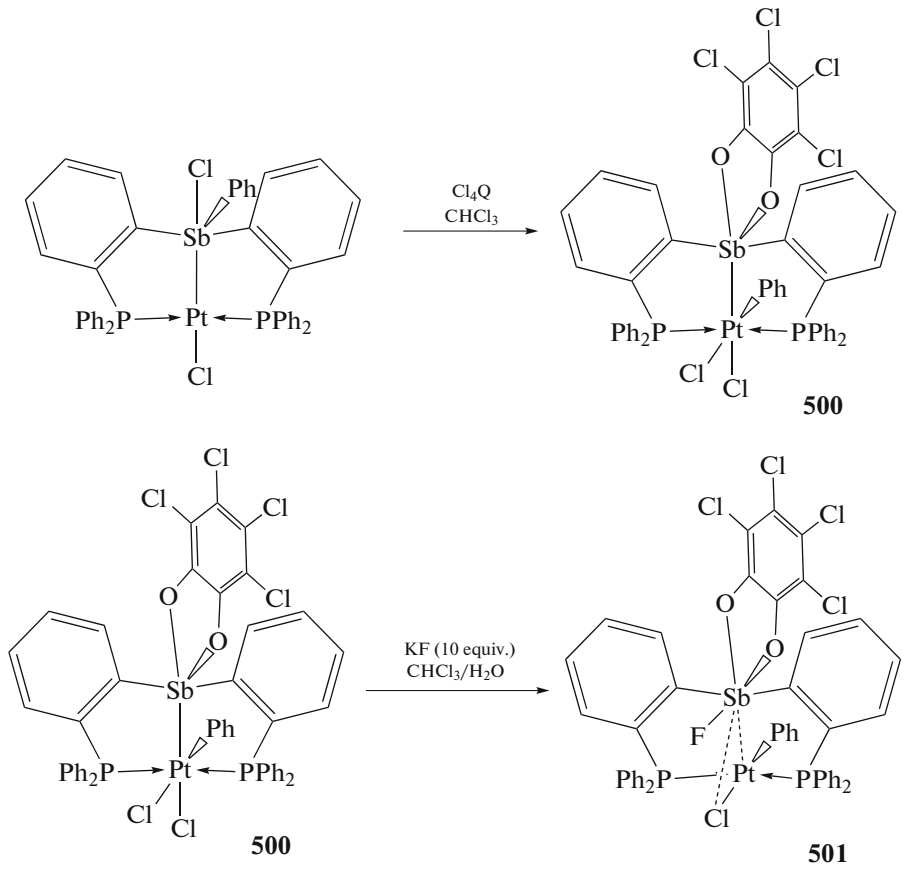
The reactions of synthesized phosphinostiboranes **494** and **495** with paraform (toluene, 70°C) or formaldehyde (H_2O, T_{room}) results in the formation of heterocyclic antimony compounds **496** and **497** (Scheme 105) [287].

The oxidation of (*o*-$(Ph_2P)C_6H_4)_3SbNi(PPh_3)$ with $PhICl_2$ is accompanied by the conversion of stibine to the stiboranyl ligand [(*o*-$(Ph_2P)C_6H_4)_3ClSb]NiCl$ (**498**). In addition, the reaction of compound **498** with the catecholate dianion in the presence of cyclohexyl isocyanide (Scheme 106) affords the nickel complex [(*o*-$(Ph_2P)C_6H_4)_3(Cl_4Cat)Sb]Ni(CNCy)$ (**499**) in which the nickel atom coordinates to the antimony atom [288].



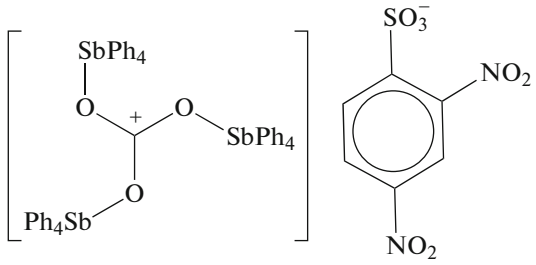
Scheme 106.

Catecholate complex **500** derived from [(*o*-$(Ph_2P)C_6H_4)_2$SbClPh]PtCl and *o*-chloranil in the presence of fluoride anions (treated with potassium fluoride excess; Scheme 107) is transformed into fluorostiborane [(*o*-$(Ph_2P)C_6H_4)_2(Cl_4Cat)$SbF]PtClPh (**501**). This transformation is accompanied by the removal of the chloride ligand from the platinum atom and attachment of the fluoride ligand to the antimony atom [289].



Scheme 107.

It should be mentioned that the products of the reactions involving carbon dioxide, acid, and pentaarylantimony with an unusual structure (tricoordinated carbon atom in the cation, for example, $[(Ph_4SbO)_3C]^+[OSO_2C_6H_3(NO_2)_2$-2,4$]^-$ (**502**)) (Scheme 108) were isolated and structurally characterized [290].



502

Scheme 108.

ANTIMONY DERIVATIVES Ar_2SbX_3 AND $ArSbX_4$ AND THEIR REACTIONS

The problems of the synthesis and reactivity of the pentavalent antimony derivatives with one or two aryl groups at the central atom are considered to a significantly lower extent than analogous compounds with three and four organic substituents.

The antimony(V) derivatives of the molecular or ionic structure with one or two aryl groups at the antimony atom can be synthesized by the reactions of ligand redistribution, oxidation, or substitution. It is shown that complexes **503**–**508** with the octahedral anions $[R_2SbCl_4]^-$ (Scheme 109) can easily be obtained from phosphonium, stibonium, or ammonium salts and diorganylantimony trihalides [291]. In this case, methyltriorganylantimony iodide reacts with the released iodine to form compound **509**, which is the ionic derivative of the methyltriorganylstibonium cation.

$$R'_4ECl + R_2SbCl_3 \longrightarrow [R'_4E]^+[R_2SbCl_4]^-$$

R = Me, R' = Ph, E = P **503**
R = Ph, R' = Et, E = N **504**
R = Ph, R' = Bu, E = N **505**

$$2R'_3MeSbI + 3R_2SbCl_3 \xrightarrow[-I_2]{-R_2SbCl} 2[R'_3MeSb]^+[R_2SbCl_4]^-$$

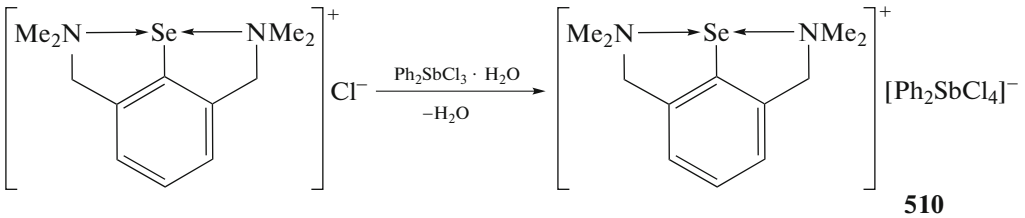
R = Me, R' = Me **506**
R = Ph, R' = Me **507**
R = Ph, R' = Et **508**

$$R'_3MeSbI + I_2 \longrightarrow [R'_3MeSb]^+[I_3]^-$$

509

Scheme 109.

Diphenylantimony trichloride reacts with arylselenium chloride (Scheme 110) to form complex **510** containing diphenyltetrachloroantimony anions [292].

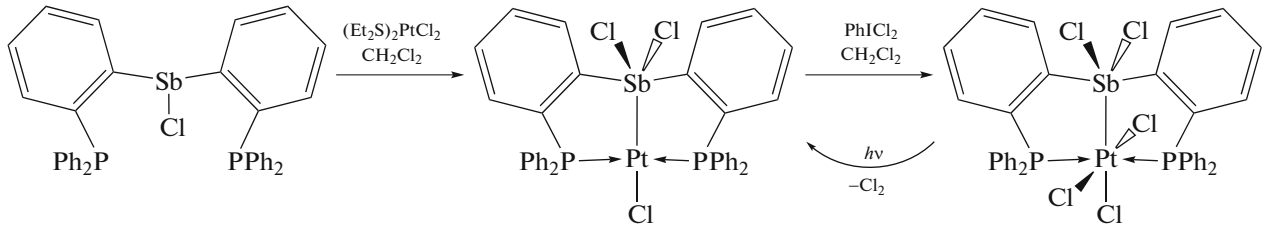


510

Scheme 110.

Oxidation. Under the action of sulfuryl chloride, stibines $LSbCl_2$ and LPhSbCl are transformed into the neutral pentavalent antimony derivatives $LSbCl_4$ (**327**) and $LPhSbCl_3$ (**328**) (Scheme 73) [152].

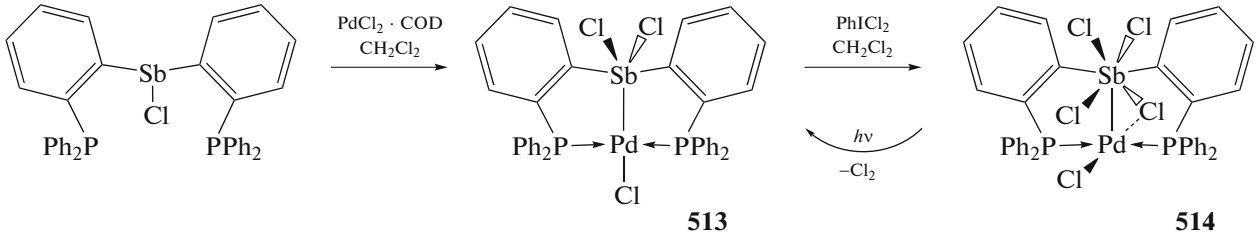
Platinum compounds can be used as oxidants. For example, the oxidation of chlorodiarylstibine by the platinum derivative (Scheme 111) followed by the treatment with phenyliodonium chloride results in the consecutive chlorination at the antimony and platinum atoms to form complexes **511** and **512**. The photolysis of the final oxidation product is accompanied by the elimination of chlorine and formation of the pentacoordinated antimony compound [293].



511 **512**

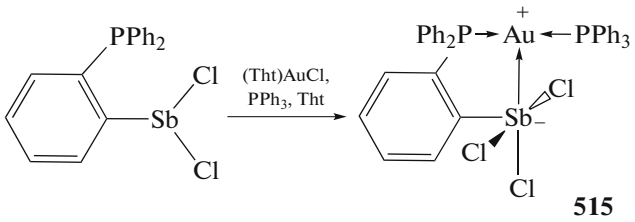
Scheme 111.

The treatment of complex **513**, which was synthesized from palladium chloride and chlorodiarylstibine (Scheme 112), with phenyliodonium chloride results in the oxidation of the palladium and antimony atoms with the formation of derivative **514**. The formed complex **514** eliminates chlorine under photolysis and is recovered to the initial state [294].



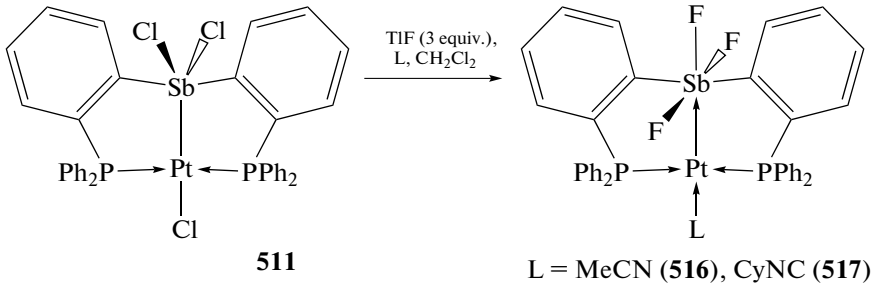
Scheme 112.

Pentacoordinated antimony derivative **515** can be prepared from [(2-diphenylphosphanyl)phenyl]dichlorostibine and AuCl(Tht) in THF (Scheme 113) [295].



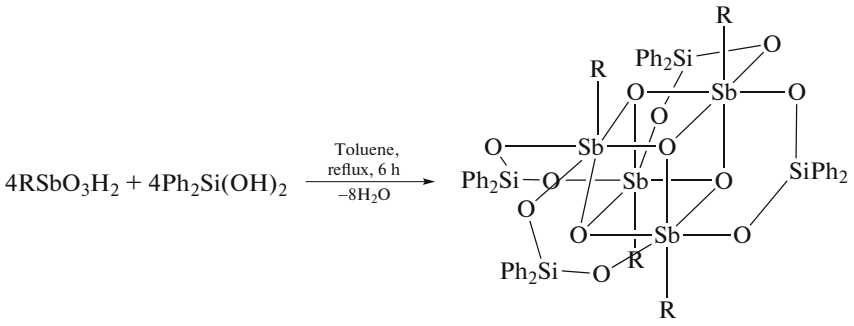
Scheme 113.

Substitution. The treatment of complex **511** with thallium fluoride (Scheme 114) gives trifluorostiboranes **516** and **517** [296].



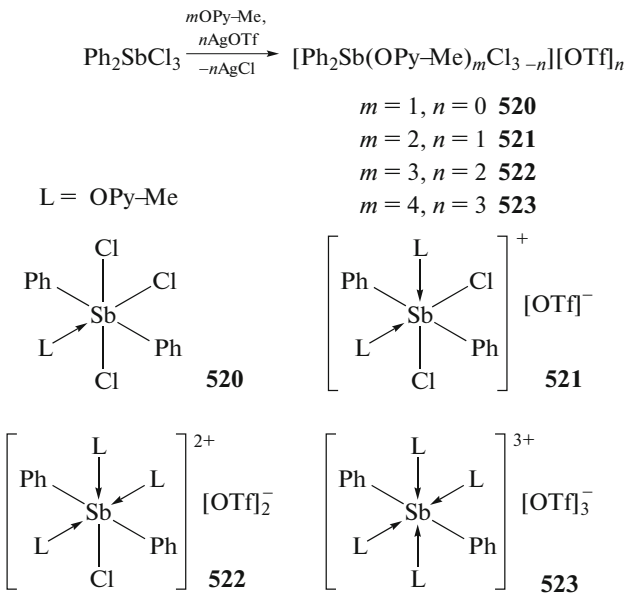
Scheme 114.

The reactions of equimolar amounts of *para*-halogenphenylstibic acids with diphenylsilanol in boiling toluene (6 h) afford the tetranuclear antimony complexes $[(p\text{-}ClC_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ (**518**) and $[(p\text{-}BrC_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ (**519**) (Scheme 115). Clusters **518** and **519** are isostructural and contain the central distorted cubic fragment Sb_4O_4 [297].



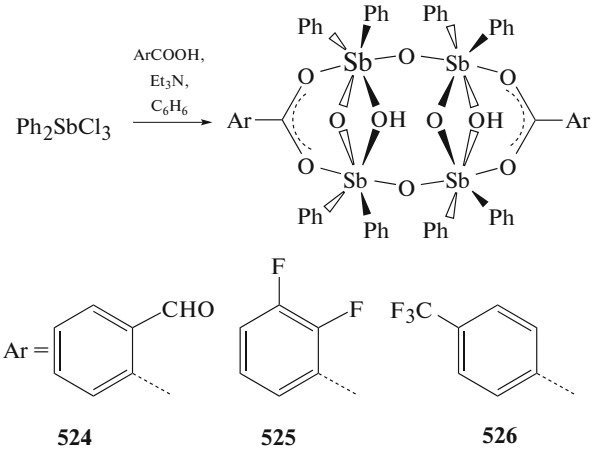
Scheme 115.

The reaction of diphenylantimony trichloride with silver triflate in the presence of *p*-methylpyridine *N*-oxide taken in various ratios (Scheme 116) produces hexacoordinated antimony compounds of four types (**520**–**523**) [298].



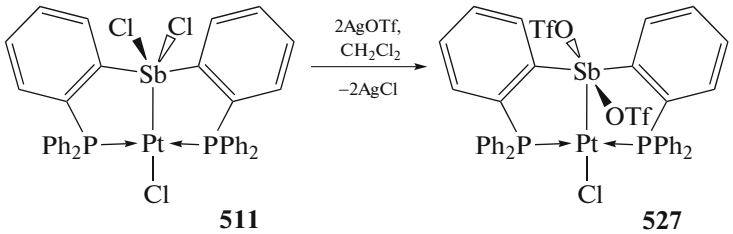
Scheme 116.

The reactions of substituted benzoic acids with diphenylantimony trichloride in benzene in the presence of triethylamine (Scheme 117) are accompanied by the formation of the tetranuclear oxo derivatives of diphenylantimony **524**–**526** with two symmetric residues of carboxylic acids arranged oppositely to each other [299].



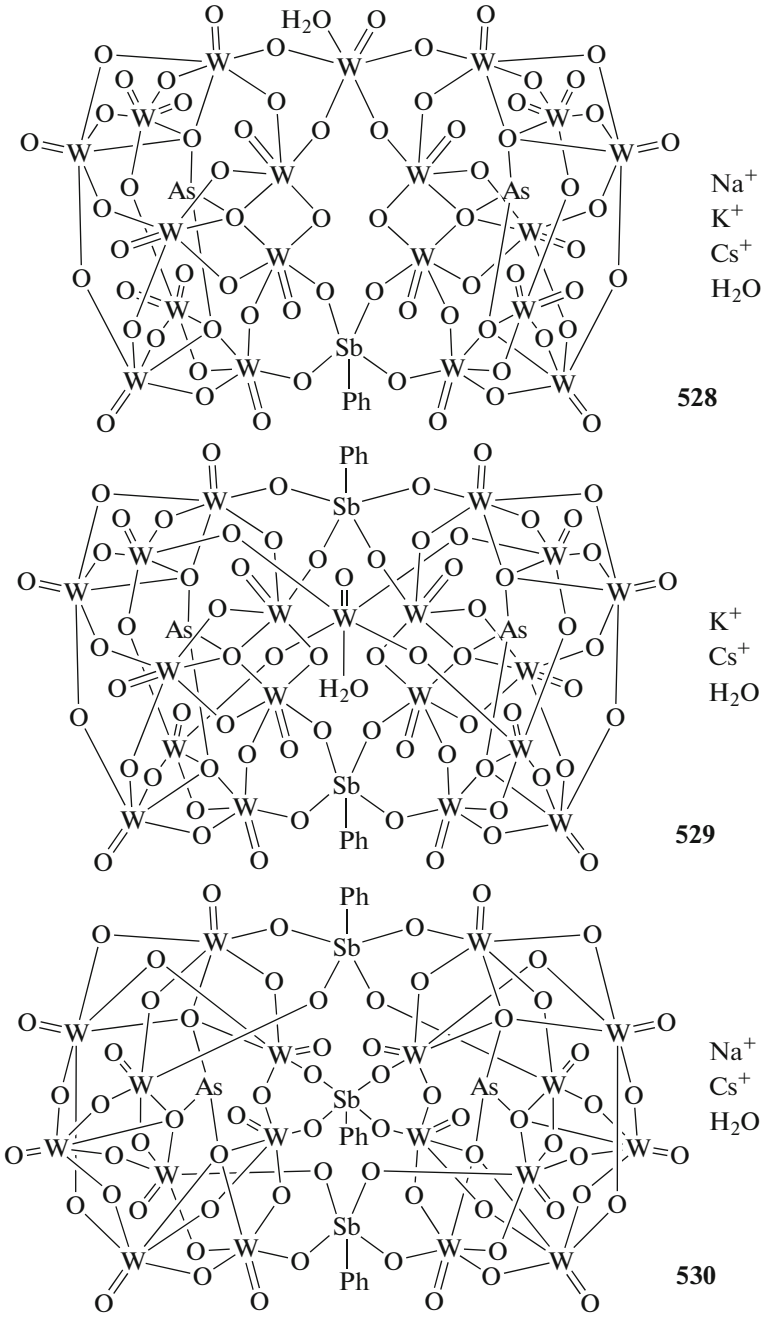
Scheme 117.

Triflate complex **527** is formed from chlorine-containing platinum complex **511** and silver triflate in dichloromethane (Scheme 118) [300].



Scheme 118.

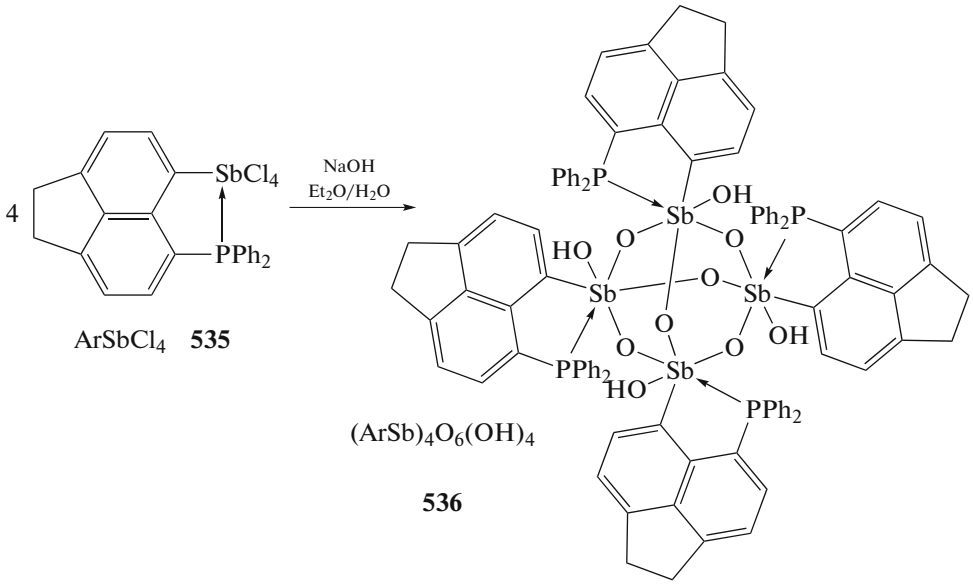
A series of tungsten arsenate salts **528**–**530** (Scheme 119) containing one, two, or three PhSb groups was synthesized from inorganic salts of tungsten arsenates and dichlorophenylstibine in an acetic acid solution [301].



Scheme 119.

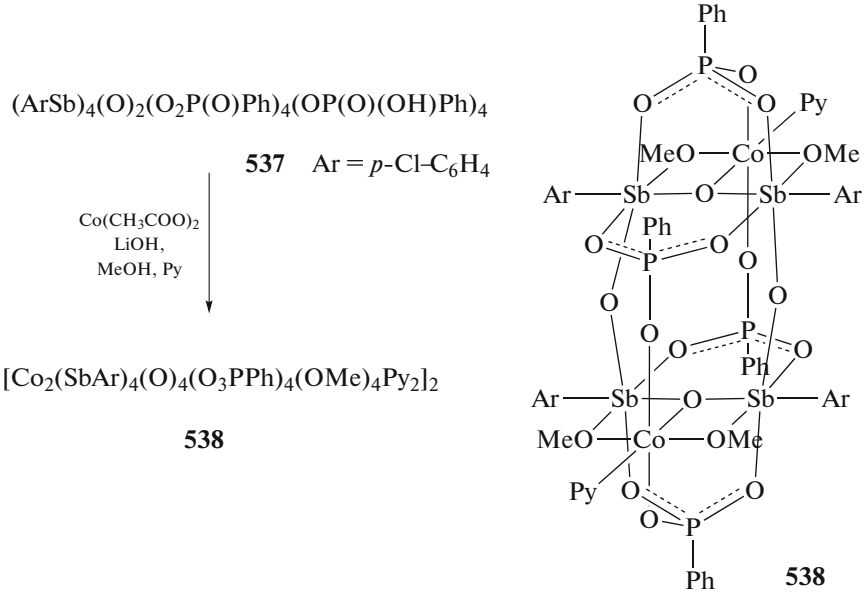
Polynuclear cluster compounds [Co(*p*-TolSb)$_{12}$O$_{28}${Co(H$_2$O)$_3$}$_4$]Cl$_2$ · 6H$_2$O (**531**), [Co(*p*-Cl–C$_6$H$_4$–Sb)$_{12}$O$_{28}${Co(H$_2$O)$_3$}$_4$]Cl$_2$ · 22H$_2$O (**532**), (PhCH$_2$NMe$_3$)$_2$[Zn(*p*-Cl–C$_6$H$_4$–Sb)$_{12}$O$_{28}$Zn$_4$Cl$_{2.54}$Br$_{1.46}$] · 8MeCN · H$_2$O (**533**), and [BaCoH$_4$(*p*-MeC$_6$H$_4$Sb)O$_{28}$] · 5H$_2$O (**534**) containing ArSb groups (Ar = 4-R–C$_6$H$_4$, R = Me, Cl) and cobalt, zinc, barium, and oxygen atoms were synthesized by the addition of the metal salts to a solution of arylstibic acid and ammonia in water [302]. The target products were obtained after stirring of the reaction mixture to the complete dissolution of the initial reagents, solvent removal, and recrystallization of the residue from aqueous acetonitrile.

Arylantimony tetrachloride $ArSbCl_4$ (**535**) was synthesized by the chlorination of arylantimony dichloride with sulfuryl chloride (Scheme 120). The hydrolysis of compound **535** resulted in the formation of the oxygen-containing antimony compound $(ArSb)_4O_6(OH)_4$ (**536**) with the adamantane-like structure [303].



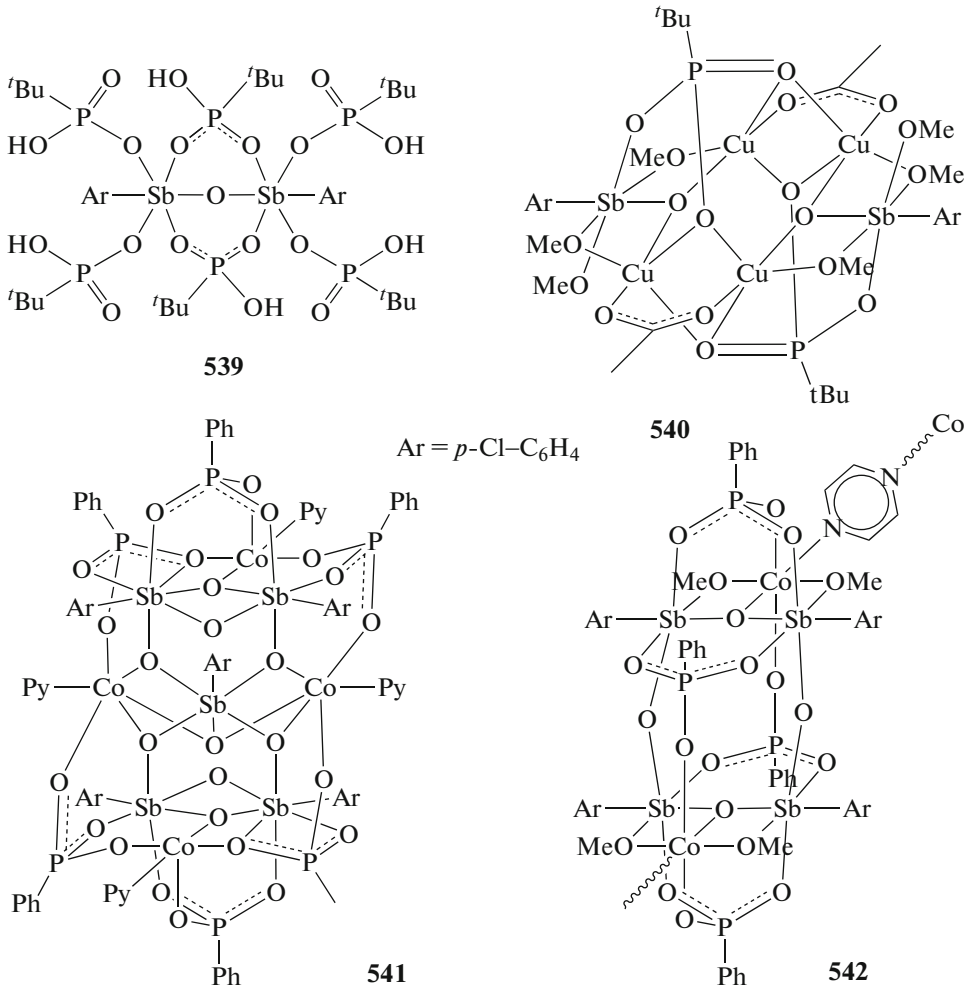
Scheme 120.

Polynuclear derivative **538** was first synthesized by the reaction of complex $(ArSb)_4(O)_2(O_2P(O)Ph)_4(OP(O)(OH)Ph)_4$ (**537**) (condensation product of 1 equiv. of chlorophenylstibic acid $ArSbO(OH)_2$ (Ar = *p*-Cl–C_6H_4) and 2 equiv. of phenylphosphinic acid $PhPO(OH)_2$) with cobalt(II)acetate (Scheme 121) [304].



Scheme 121.

The synthesis of the polynuclear compound $(ArSb)_2O(OP(O)(OH)t\text{-}Bu)_6$ (**539**) from *para*-chlorophenylstibic and *tert*-butylphosphinic acid was reported [305]. This complex contains two antimony atoms linked by the bridging oxygen atom and two bridging and four terminal residues of *tert*-butylphosphinic acid (Scheme 122).



539 **540** **541** **542**

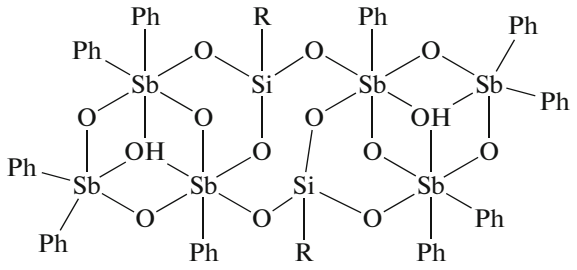
Scheme 122.

The reaction of complex **539** with copper acetate affords tri-, tetra-, penta-, or octanuclear copper complexes, depending on the reaction conditions, for example, complex **540**.

The products of the reactions of the polynuclear oxygen-containing organoantimony compounds $(ArSb)_4(O)_2(O_2P(O)Ph)_4(OP(O)(OH)Ph)_4$ (**537**) and $(ArSb)_2O(OP(O)(OH)t\text{-}Bu)_6$ (**539**) with cobalt(II) acetate in the presence of lithium methoxide and pyridine in methanol are cobalt complexes **538** and **541**, respectively (Scheme 122) [306]. The pyridine molecules in the complexes can be replaced by other amines, which are introduced into the reaction mixture instead of pyridine. For instance, the replacement of pyridine in complex **538** by pyrazine results in the formation of coordination polymer **542** (Scheme 122).

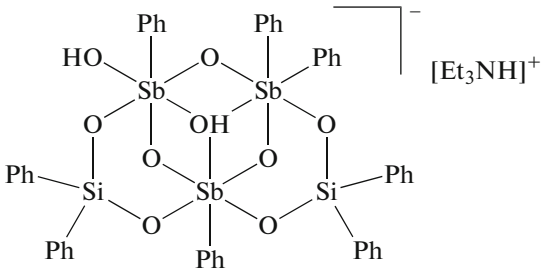
The synthesis of new polyoxometallates Sb_{12} (**543**) and Sb_{14} (**544**) from *para*-tolylstibic acid and metal salts in the presence of the base was described [307].

The reactions of Ph_2SbCl_3 with $RSi(OH)_3$, where R is *tert*-Bu, *cyclo*-C_6H_{11}, and $Ph_2Si(OH)_2$, in toluene in the presence of trimethylamine gave the antimony(V) compounds and oxohydroxoantimony clusters of the mixed valence (III/V). Interestingly, at least one cleavage of the Sb–C bond is observed in all reactions, which results in the formation of new cluster derivatives $[(Ph_2Sb)_4(PhSb)_2{-}(C_4H_9SiO_3)_2(O)_6(OH)_2]$ (**545**), $[(Ph_2Sb)_4(PhSb)_2(C_6H_{11}{-}SiO_3)_2(O)_6(OH)_2]$ (**546**), $[(Ph_2Sb)(PhSb)_2(Ph_2SiO_2)_2(O)_3{-}(OH)_2]^{-}Et_3NH^{+}$ (**547**), and $[(Ph_2Sb)_4(Sb)_2(Ph_2SiO_2)_2(O)_6{-}(OH)_2]$ (**548**), respectively (Scheme 123) [308].

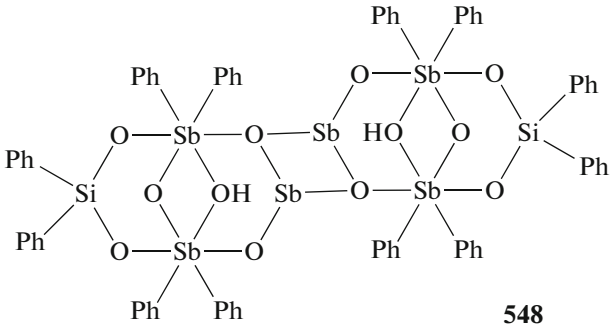


R = ^{t}Bu **545**

R = Cyclohexyl **546**



547



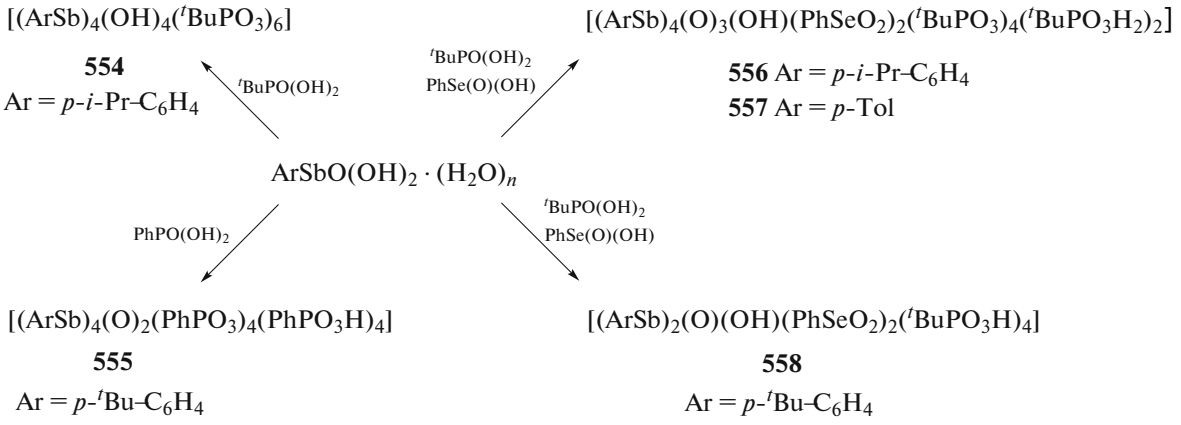
548

Scheme 123.

The trinuclear antimony derivatives of the type {[C_5H_5NH] · [(ArSb)$_3${(*t*-Bu)$_4Si_4O_9$}-{(*t*-Bu)$_2Si_2O_5$}-(μ^3-O)(μ-OH)]}, where Ar is *p*-Cl–C_6H_4 (**549**), *p*-Br–C_6H_4 (**550**), and 3,5-Cl_2–C_6H_3 (**551**), and of the type [(ArSb)$_3${(*t*-$BuSiO_2$)$_4$(*t*-$BuSiO_2OH$)$_2$}(μ^3-O)(μ-OH)$_2$] (Ar = *p*-I–PrC_6H_4, **552**) are formed from arylstibonic acid and *tert*-butylsilanetriol (toluene, 110°C, 8 h) [309].

Specific features of the synthesis and structures of arylstibonic acids and their potassium and sodium salts were discussed [310]. It was shown that the crystals of the complexes containing 12-nuclear anionic antimony compounds, for example, $[K_2H_8(p\text{-Cl}–C_6H_4Sb)_{12}O_{30}]^{2-}$ anion (**553**), were formed after the dissolution of arylstibonic acids in an aqueous solution of alkali, water removal, and recrystallization of the residue from aqueous acetonitrile.

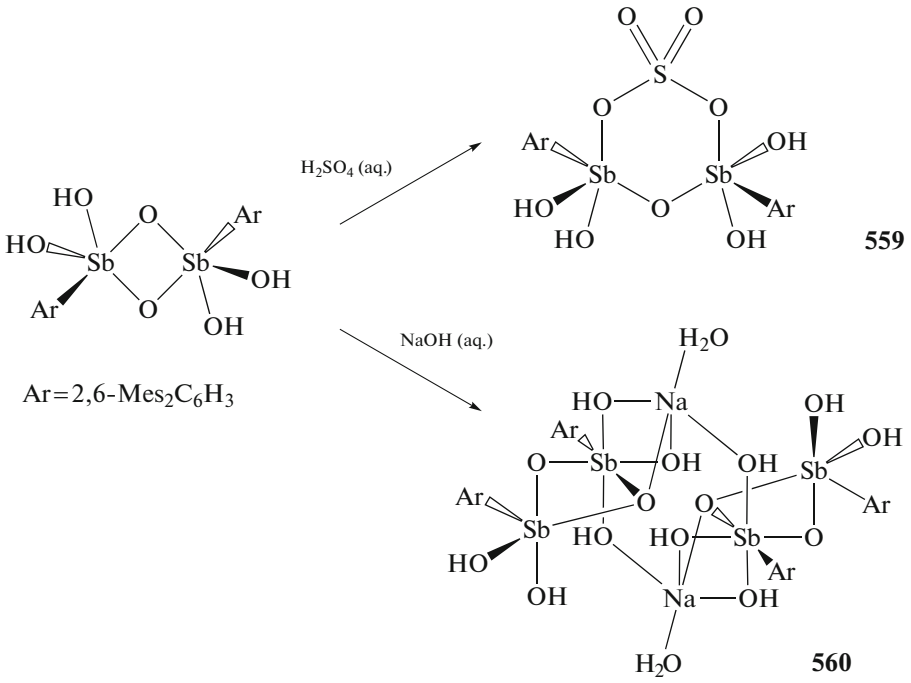
Monoarylantimony phosphonates and phosphoselenates **554**–**558** (Scheme 124) were synthesized in 54–86% yield from arylstibonic acids and organylphosphinic and phenylselenic acids in acetonitrile at room temperature on stirring for 24 h [311].



Scheme 124.

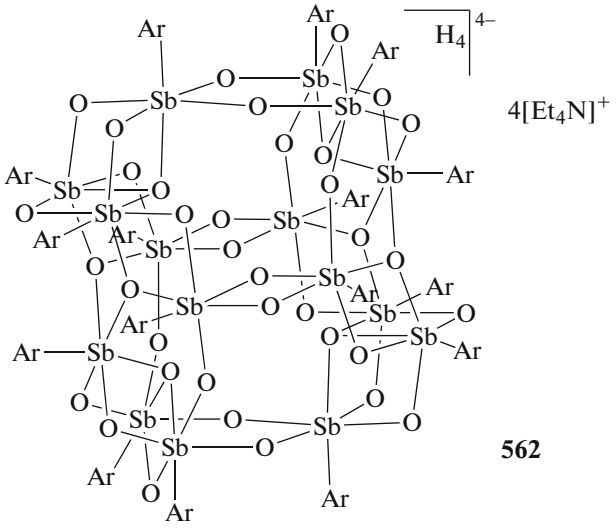
When binuclear (2,6-dimesitylphenyl)antimony oxide is treated with sulfuric acid, it is transformed into binuclear complex **559** with the bridging sulfate ligand. The treatment of the oxide with

an aqueous solution of sodium hydroxide affords tetranuclear organoantimony derivative **560** (Scheme 125) containing the hydrated sodium cations [312].



Scheme 125.

Three polynuclear tetrabutylammonium arylstibonates $[(p\text{-Cl}{-}C_6H_4Sb)_{16}(\mu_3\text{-O})_8(\mu_2\text{-OH})_5(\mu_2\text{-O})_{23}]^{3-}[Et_4N]_3^+$ (**561**) and $[(p\text{-Cl}{-}C_6H_4Sb)_{16}(\mu_3\text{-O})_8(\mu_2\text{-OH})_6(\mu_2\text{-O})_{22}]^{4-}[Et_4N]_4^+$ (**562**) (Scheme 126), as well as $[Na_2(p\text{-Cl}{-}C_6H_4Sb)_{12}(\mu_4\text{-O})_3(\mu_3\text{-O})_{12}(\mu_2\text{-O})_9(OH)_6(H_2O)_3]^{4-}[Et_4N]_3^+$ (**563**) containing solvate water and acetonitrile molecules were synthesized from *para*-chlorophenylstibonic acid and tetrabutylammonium hydroxide [313].



Scheme 126.

The reaction of diphenyltellurium oxide with organostibonic acid or polymeric triphenylantimony oxide affords the 14-nuclear (**564**) and octanuclear (**565**) organoantimony clusters (Scheme 127) [314].

$$ArSbO(OH)_2(H_2O)_n \xrightarrow[\text{Toluene, } \Delta, 12\text{ h}]{Ph_2TeO} [Ph_3Te]_2[Na_2(H_2O)_2(ArSb^{V})_{10}(Sb^{III})_4(Ph_2Te)_4(O)_{30}(OH)_4]$$

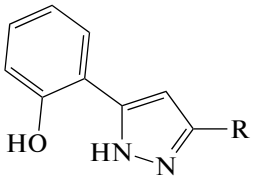
564 Ar = *p*-Br–C_6H_4

$$[Ph_3SbO]_n \xrightarrow[\text{Toluene, } \Delta, 12\text{ h}]{Ph_2TeO} [Ph_3Te]_4[(Ph_2Sb^{V})_4(Sb^{III})_4(O)_{12}(OH)_4]$$

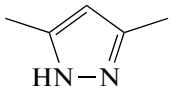
565

Scheme 127.

Tetranuclear and 16-nuclear antimony clusters **566**–**571** were synthesized from the pyrazolyl ligands H_2L^R and HL and arylstibonic acids (Scheme 128). These clusters contain the Sb–O bonds and coordination of the nitrogen atoms with the metal atom determined, in authors' opinion, by the volume of the pyrazolyl ligand [315].



H_2L^R: R = Ph, ^{t}Bu, H

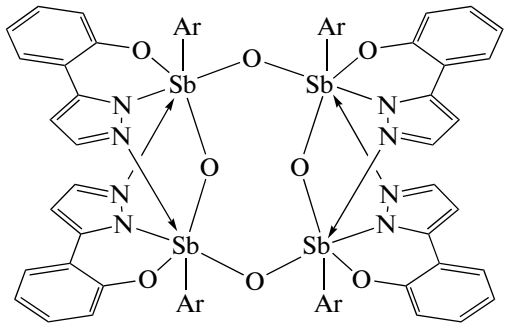


HL

$[(ArSb)_4(O)_5(OH)_2(HL^{Ph})_4]$
Ar = *p*-Cl–C_6H_4 **566**
Ar = *p*-Br–C_6H_4 **567**
$[(ArSb)_4(O)_5(OH)_2(HL^{tBu})_4]$
Ar = *p*-Br–C_6H_4 **568**

$[(ArSb)_4(O)_4(L^H)_4]$
Ar = *p*-Br–C_6H_4 **569**

$[(ArSb)_{16}(O)_{28}(OH)_8(HL)_6]$
Ar = *p*-Cl–C_6H_4 **570**
Ar = *p*-Br–C_6H_4 **571**

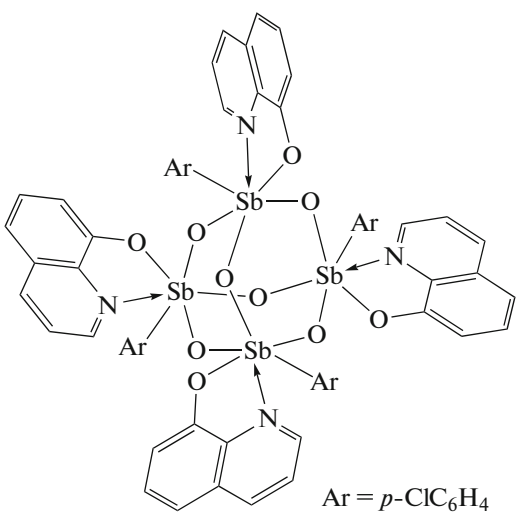


Ar = *p*-Br–C_6H_4 **569**

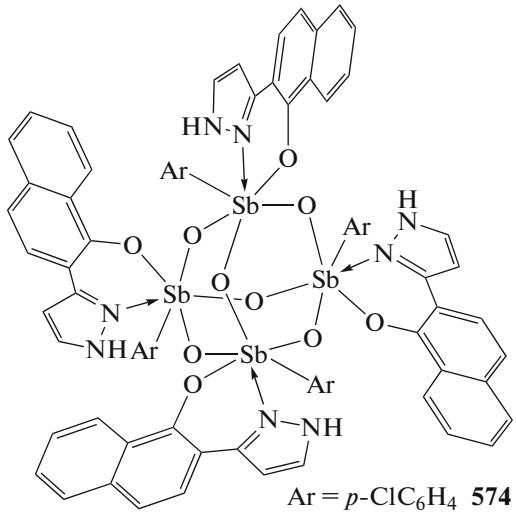
Scheme 128.

The reactions of arylstibonic acids with 8-hydroxyquinoline (HL^1) or 2-(pyrazol-5-yl)-α-naphthol (HL^2) taken in equimolar amounts in toluene on reflux make it possible to obtain adamantane-like clusters of the $L_4(RSb)_4O_6$ type (Scheme 129): $[(p\text{-X}–C_6H_4Sb)_4(\mu_2\text{-O})_6(L^1)_4]$, where X = Cl (**572**), Br (**573**)), $[(p\text{-Cl}–C_6H_4Sb)_4(\mu_2\text{-O})_6(L^2)_4] \cdot HL^2$ (**574**) and $[(p\text{-Br}–C_6H_4Sb)_4(\mu_2\text{-O})_6(L^2)_4]_2 \cdot HL^2$ (**575**) [316]. Interestingly, the structures of compounds **572**–**575** resemble the dimeric form of antimony oxide Sb_2O_3. The tetramer $[(p\text{-Cl}–C_6H_4Sb)_4(\mu_2\text{-O})_4(L^2\text{-H})_4]$ (**576**), whose structure is similar to that of tetranuclear antimony complex **569**, was also isolated as a by-product. In this com-

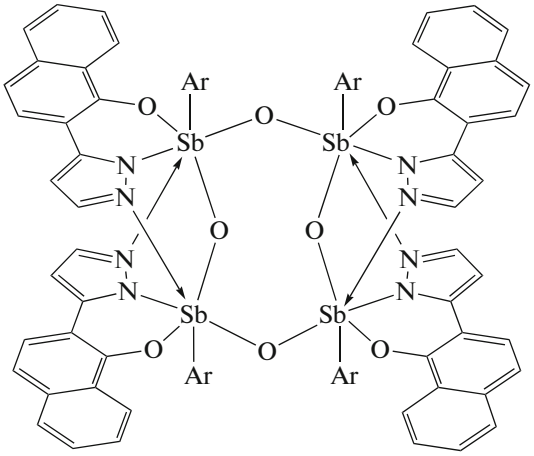
plex, the naphthol ligand is deprotonated not only at the hydroxyl group but also at the nitrogen atom of the pyrazolyl group, and an additional covalent interaction of this nitrogen atom with the adjacent antimony atom is observed in tetranuclear cluster **576** (Scheme 129).



Ar = *p*-ClC_6H_4 **572**
Ar = *p*-BrC_6H_4 **573**



Ar = *p*-ClC_6H_4 **574**
Ar = *p*-BrC_6H_4 **575**



Ar = *p*-ClC_6H_4 **576**

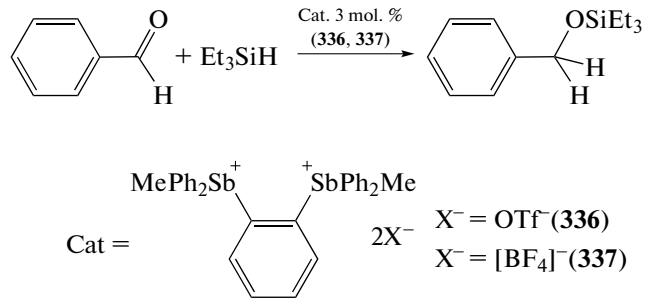
Scheme 129.

PRACTICAL USE OF ANTIMONY(V) ARYL COMPOUNDS

Although the antimony derivatives are fairly toxic, they are widely used for nearly a century in therapy as antiparasitic drugs, especially in the treatment of leishmaniosis [317]. On the whole, the works devoted to the practical use and study of potential possibilities of using the aryl derivatives of pentavalent antimony are scarce. Some triarylantimony dicarboxylates **259**–**266** (Scheme 56) and **284**–**291** (Scheme 58) were shown to be biologically active substances [129, 134], and organoantimony lapachol derivative **215** inhibits the growth of chronic leukemia cells [108]. Organoantimony derivatives of acetylsalicylic and 3-acetoxybenzoic acids (compounds **223** and **224** [113]), triphenyl- and tri-*para*-tolylantimony diacrylates (**227**–**236** (Scheme 49) [116], and compounds **279** and **280** [131]) are characterized by antibacterial activity and efficient in the treatment of leishmaniosis and staphylococcus. Some aryl compounds of pentavalent antimony are characterized by anticancer activity: compounds **213**, **124** [107], **218**, **219** [111], **237**–**241** (Scheme 51) [117], **255**–**258** (Scheme 55) [128], **281**, triarylantimony(V) bis(*N*-phenylglycinates) [132], and **403** [195]. Triphenylantimony bis(*N*-oxyphthalimide) and bis(*N*-oxysuccinimide) complexes **213** and **214** (Scheme 47) [107] should specially be distinguished, since they are more active anticancer agents than cisplatin.

The high catalytic activity of the arylantimony compounds was described for triflate **321**, which catalyzes aldol condensation (Scheme 69) [148], and com-

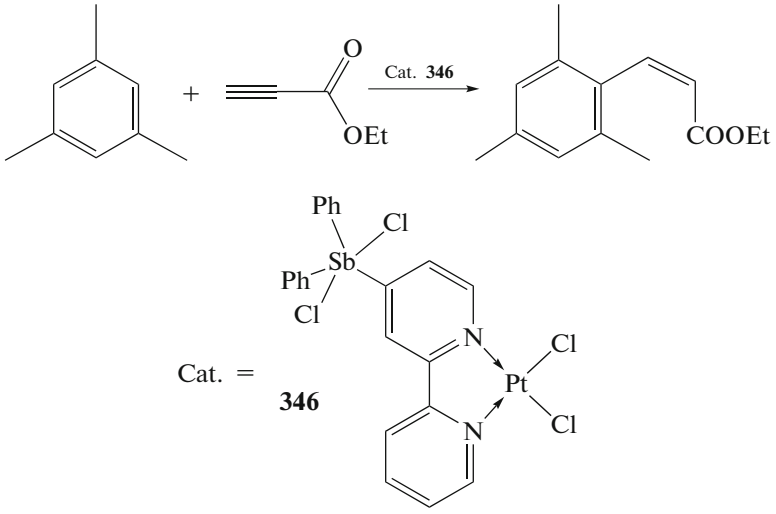
plexes **336** and **337**, the latter being an efficient catalyst in the hydrosilylation of benzaldehyde using triethylsilane (Scheme 130) [156].



Scheme 130.

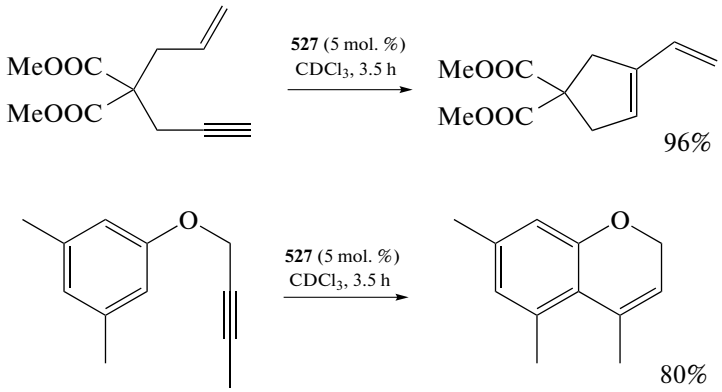
The catalytic properties of these stibonium compounds were studied in the hydrosilylation of benzaldehyde using triethylsilane in $CDCl_3$ (Scheme 130). Although $[Ph_3MeSb]^+[OTf]^-$ and $[Ph_3MeSb]^+[BF_4]^-$ (3 mol %) do not favor the reaction at room temperature, some catalytic activity of compound **336** was observed (1.5 mol %) with a conversion of 11% in 8 h. A surprising contrast behavior was observed for compound **337** (1.5 mol %), which turned out to be much more active when benzaldehyde hydrosilylation occurs to the complete conversion within 8 h.

The platinum-containing complex of triarylantimony dichloride (**346**) (Scheme 81) catalyzes the addition of mesitylene to ethyl acetylenecarboxylate (Scheme 131) [159].



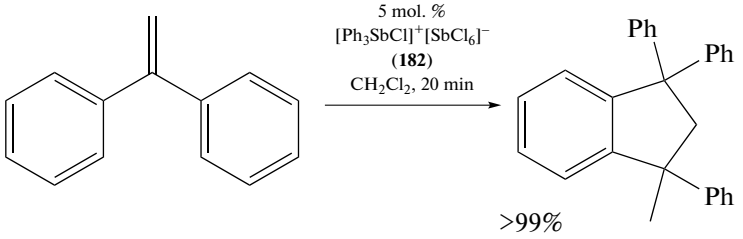
Scheme 131.

Another platinum-containing triflate complex **527** (Scheme 118) is an efficient catalyst for the cycloaddition reactions (Scheme 132) [300].



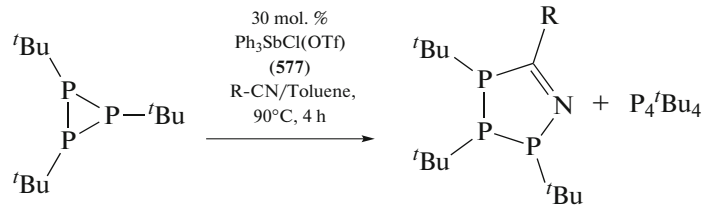
Scheme 132.

Complex **182** is an example of the active catalyst in the dimerization of 1,1-diphenylethylene (Scheme 133), and the yield of the condensation product reaches 99% [90].



Scheme 133.

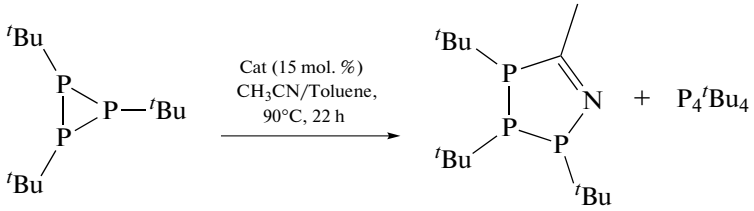
Chlorotriphenylantimony trifluoromethanesulfonate $Ph_3SbCl(OTf)$ (**577**) was shown to catalyze the cycloaddition of nitriles with cyclotriphosphines (Scheme 134) forming 1-aza-2,3,4-triphospholenes in the yield up to 90% [318]. Triphenylantimony bis(triflate) **308** also possesses a similar activity in this reaction (Scheme 135).



R = Me, Et, *n*Pr, *n*Bu, *i*-Pr, ^{t}Bu, Ph

Yield = 90, 88, 88, 85, 50, 3, 20%

Scheme 134.



Cat = $Ph_3SbCl(OTf)$ (**577**)	84%	16%
Cat = $Ph_3Sb(OTf)_2$ (**308**)	80%	20%

Scheme 135.

CONCLUSIONS

The chemistry of the organometallic and coordination compounds of antimony(V) is presently developed rather intensively, and many diverse mono-, bi-, and polynuclear compounds were revealed during the recent 10–15 years. These antimony compounds demonstrate a high variety of structural types and exhibit reactivity in the very diverse processes. The study of these compounds showed a high catalytic activity in a series of interesting and promising catalytic processes (aldol condensation, hydrosilylation, formation of new carbon—carbon bonds, cycloaddition, and others) and a possibility of the selective fixation of fluoride anions. The possibility of stabilization of the tricoordinated carbon compound was established, and the possibility of reversible binding of molecular oxygen by the complexes of metals of the main groups was demonstrated for the first time. Several organoantimony derivatives are biologically active substances and have antibacterial, antifungal, and anticancer activity. Organoantimony and coordination compounds remain at present to be significantly poorly studied compared to the phosphorus- and arsenic-containing compounds. However, an analysis of publications on the topic suggests that interest in these compounds increases permanently, since the antimony(V) derivatives are very perspective as catalysts of the very diverse reactions of fine organic synthesis, biochemically active substances and drug components, carriers of small molecules, sensors to various anions and molecular groups, and many other applications.

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