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Organoantimony compounds with element–element bonds

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Contents

Abstract

In this article an overview is given on recent developments in the chemistry of organometallic compounds with antimony–antimony bonds or bonds between antimony atoms and elements of the groups 14 and 16. © 1997 Elsevier Science S.A.

Keywords: Organo antimony compounds; Sb–group 14 element bond; Sb–group 16 element bond; Sb–Sb bond

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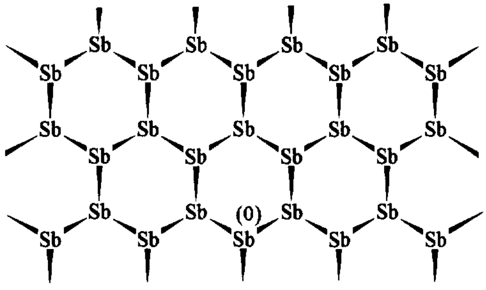
1. Introduction

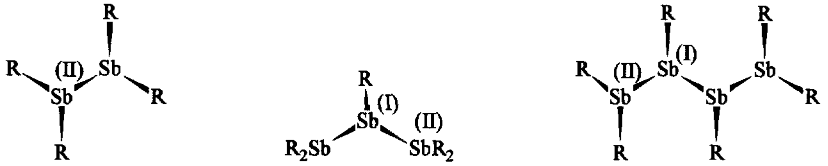
Developments in the field of organo antimony chemistry dealing with homonuclear bonds or heteronuclear bonds between Sb and elements of the groups 14 and 15 are discussed in this article.

A simple approach for the existence of compounds with the Sb–Sb bond and *tert.*-stibines is to consider the structure of elemental antimony and to formally saturate the valences with organic substituents. The structure of antimony consists of layers of puckered six-membered rings with three short Sb–Sb bonds and three inter layer Sb···Sb contacts per antimony atom. The structures of a layer of the element and of organic derivatives with Sb–Sb bonds are depicted in Fig. 1.

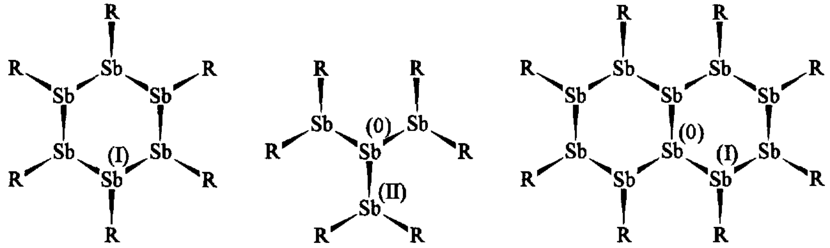
In the most trivial case, when one antimony atom is cut out of the lattice by adding three substituents R, a *tert.*-stibine, R_3Sb results, and pyramidal environment



elemental antimony



distibine **catena-tristibine** **catena-tetrastibine**



cyclo-hexastibine **stibinostibine** **bicyclic decastibine**

Fig. 1. Structures of elemental antimony and of organic derivatives containing Sb(0), Sb(I) or Sb(II).

of the antimony atom is preserved. Since 1850, when the synthesis of triethylstibine was reported by Löwig and Schweizer, about 200 *tert.*-stibines with alkyl or aryl substituents have been reported. Only stibines with heavier group 14 or group 16 element bonds will be discussed here.

The number of known compounds decreases dramatically when Sb_2 units are considered. The resulting structures are distibines, $R_2Sb–SbR_2$ that have been studied since the first decades of this century. About 25 derivatives with organic or organometallic groups R have now been synthesized. In recent years there has been considerable interest in this class of compounds mainly because some of the derivatives which are named thermochromic distibines, display unusual color changes on phase transitions. E.g. tetramethyldistibine is colorless in the gas phase, yellow in fluid states but red in the solid state close to the melting point of 18.5 °C. Cooling with liquid nitrogen brings the yellow color back. All the thermochromic distibines that have been characterized by X-ray analysis in the crystalline state, have structures where the substituents around the pyramidal antimony atoms adopt the *anti* conformation and where the distibine molecules are aligned to antimony chains through short intermolecular Sb···Sb contact distances. It is of interest to compare the known structures of the distibines with the environment of diantimony units in the lattice of elemental antimony. In both cases the conformation is all *trans* and the interlayer contacts in the element correspond to the intermolecular contacts that are characteristic for thermochromic distibines.

Other structures that may be derived from elemental antimony and that have been realized as organoantimony derivatives are tristibines, $R_2SbSb(R)SbR_2$, tetrastibines, $R_2SbSb(R)Sb(R)SbR_2$ and longer organoantimony chain compounds. However, the knowledge of these chain compounds is limited because they only exist in equilibria and have not been obtained in a crystalline state. More comprehensively characterized are the cyclohexastibines, $(RSb)_6$ that reflect the structure of the element with respect to the chair conformation and the presence of short Sb···Sb contacts between the rings. Sections of the antimony lattice that have not yet been reproduced in organoantimony compounds are the antimony skeletons of stibinostibines, $(R_2Sb)_3Sb$ or bicyclic derivatives.

A way to differentiate the antimony atoms of the distibines and polystibines depicted in Fig. 1 is to consider the formal oxidation numbers. They are calculated with the usual formalism where Sb is the electropositive partner and Sb–Sb bonds are not considered in the electron counting. Following this formalism distibines are Sb(II) compounds, cyclostibines are Sb(I) compounds, stibinostibines contain Sb(II) and Sb(0) whereas in bicyclic stibines Sb(I) and Sb(0) are incorporated.

A consequence of the fact that all these compounds are derived from elemental antimony is that they all have the same type of central bonds, i.e. sigma single bonds between two antimony atoms bearing each a lone pair of electrons. For the bonding, sp^3 orbitals or 5p-orbitals with the lone pair in the 5s orbital may be used. This is the most common but not the only way of Sb–Sb-bonding. As in phosphorus chemistry [1] there are many more possibilities when three-, four- and five-coordinate (σ) compounds of tri-, tetra- or penta- valent (λ) antimony are considered. Selected structural skeletons (A–H) are given in Fig. 2.

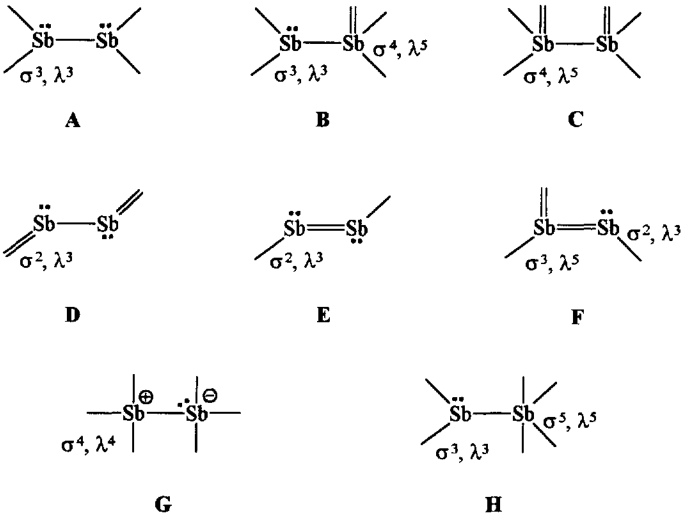


Fig. 2. Types of compounds with antimony–antimony bonds

The type A corresponds to distibines. The types B and C have been realized in complexes like $[Cr(CO)_5]_n(Me_2Sb\text{–}SbMe_2)$ ($n = 1, 2$) where the antimony atoms act as donors to 16 electron fragments of transition metal complexes. An example of type D is the very remarkable distibabutadiene that has been recently reported. Type E considers the structure of a distibene. A related molecule, a stibaphosphene $RSb{=}PR'$ has been prepared. Distibenes have been stabilized in transition metal complexes that may be described as compounds belonging to type F. Type G is present in structures containing Sb(III) both as a donor and as an acceptor. The reaction of Ph_2SbLi with Me_3SbBr_2 has been reported to give a compound of type H. But no structural data have been given.

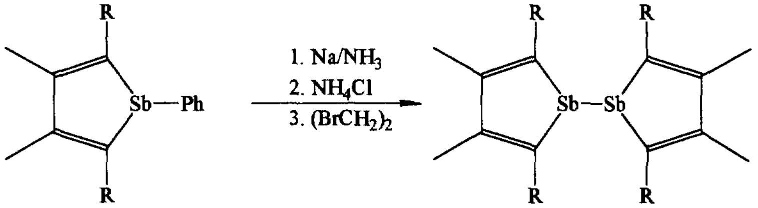
2. Organometallic compounds with bonds between antimony atoms

2.1. Distibines

The chemistry of thermochromic and non thermochromic distibines has been reviewed [2,3] a few years ago and therefore only recent developments since then are considered here. Tetramethyldistibine was the object of a study on the gas phase structure by UV photoelectron spectroscopy [4]. The spectra give evidence for the existence of *gauche* (12%) and *anti* conformers (88%) in the gas phase.

Buchwald et al. [5] have reported the synthesis of octamethylbistibole and 2,2′,5,5′-

tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbistibole (Eq. (1)).



(1)

R = Me, Me$_3$Si

Both derivatives show the typical colors of non thermochromic distibines. They are orange solids that melt to give identically colored liquids and orange/yellow solutions.

Another recent development is the synthesis of R_2SbSbR_2, ($R = Me_3SiCH_2$) [6] by dehalogenation of R_2SbBr according to Eq. (2).

$$2(Me_3SiCH_2)_2SbBr + Mg \rightarrow (Me_3SiCH_2)_2Sb-Sb(Me_3SiCH_2)_2 + MgBr_2 \quad (2)$$

The novel distibine is non thermochromic. At ambient temperatures it is a yellow, air sensitive oil that preserves this color on phase transition. The ^1H-NMR spectrum at 25 °C in C_6D_6 shows an AB spin system for the methylene protons of the organo substituent. This pattern indicates that the pyramidal structure is stable towards inversion.

Another development with respect to thermochromism is the formation of the first distibine with organolead substituents [7] (Eq. (3), Eq. (4)). Elimination of Me_3SiCl from $(Me_3Si)_3Sb$ and Me_3PbCl gives $(Me_3Pb)_3Sb$ as an intermediate that decomposes with formation of $(Me_3Pb)_2Sb$–$Sb(PbMe_3)_2$ and Me_3Pb–$PbMe_3$. The dilead compound was not isolated, instead Me_4Pb and Pb were detected as decomposition products.

$$(Me_3Si)_3Sb + 3Me_3PbCl \rightarrow (Me_3Pb)_3Sb + 3Me_3SiCl \quad (3)$$

$$2(Me_3Pb)_3Sb \rightarrow (Me_3Pb)_4Sb_2 + (Me_3Pb)_2 \quad (4)$$

The novel distibine is red in the solid state but yellow in hydrocarbon solutions. It is remarkably stable as a solid but decomposes rapidly in solution. Similar solid state properties have also been observed for the lighter homologues of the type $(Me_3M)_4Sb_2$ (M = Si, Ge, Sn), however these thermochromic distibines are much more stable in solution. The low stability of the lead analogue in solution makes the characterization difficult, and the solid state structure could not be determined. By analogy with the Si-, Ge- and Sn homologues [2,3] it is assumed that $(Me_3Pb)_4Sb_2$ adopts the *anti* conformation and is associated to linear chains through short intermolecular Sb–Sb contacts

2.2. Catena-polystibines

Catena-polystibines, i.e. chain compounds with R_2Sb end groups and RSb chain members form in equilibria mixtures of distibines and cyclostibines [8] (Eq. (5), Eq. (6)).

$$R_2Sb-SbR_2+1/n(R'Sb)_n \rightleftharpoons R_2Sb-Sb(R')-SbR_2 \tag{5}$$

R = Me, Et, Ph; R′ = Et, *n*Pr, $n=5$; R′ = *t*Bu, $(Me_3Si)_2CH$, Mes, $n=4$

$$Ph_2Sb-Sb(Et)-SbPh_2+1/5(EtSb)_5 \rightleftharpoons Ph_2Sb-Sb(Et)-Sb(Et)-SbPh_2 \tag{6}$$

The catena tristibine $Me_2Sb–Sb(Me)–SbMe_2$ was first obtained by reduction of Me_2SbBr and $MeSbBr_2$ with Mg in THF [8]. It only exists in presence of a large excess of $Me_2SbSbMe_2$. When the distibine is removed a longer chain compound, $Me_2Sb(SbMe)_{13}SbMe_2$ is formed as a black shining solid [9]. The process is reversible, i.e. action of the distibine on the black chain compound gives the tristibine back (Eq. (7)).

$$12Me_2SbSbMe_2+Me_2Sb(SbMe)_{13}SbMe_2 \rightleftharpoons 13Me_2SbSb(Me)SbMe_2 \tag{7}$$

A combination of ^{1}H-NMR-spectroscopy and mass spectrometry could be used for the identification of the novel catena stibines in the respective equilibria. None of them could be isolated in a pure crystalline state.

2.3. Cyclostibines

The most recent reviews in the field of monocyclostibines $(RSb)_n$ [10,11] comprise reports on rings with the ring size $n=3$–6. Trimeric ions $R_3Sb_3^+$ (R = alkyl) have been detected by mass spectrometry. A trimer $(RSb)_3$ has not yet been isolated and characterized by crystallography. However, the tricyclic tristibine RSb_3 ($R=CH_3C(CH_2)_3$) is known and fully characterized [12]. Tetramers protected by bulky substituents are known as all *trans* $(RSb)_4$ (R = *t*Bu, Mes, $(Me_3Si)_2CH$) molecules. Pentamers $(RSb)_5$ (with R = Et, *n*Pr, *n*Bu) exist in hydrocarbon solutions but polymerize in the absence of solvent. Examples of hexamers are the known solvates of phenyl antimony such as $(PhSb)_6 \cdot$ benzene and the tolylantimony derivatives. The syntheses of the series of crystalline samples of tolylantimony rings [13] was performed by oxidation of solutions of $RSb(SiMe_3)_2$ in toluene in the air (Eq. (8)).

$$RSb(SiMe_3)_2+1/2O_2 \rightarrow 1/6(RSb)_6+(Me_3Si)_2O \tag{8}$$

R = *o*-, *m*-, *p*-Tol

An analogous procedure had also been used for the syntheses of crystalline samples of $(PhSb)_6$ and hence it appears that the oxidation of silylstibines is a general method for aryl antimony ring syntheses. The *o*-tolyl and *p*-tolyl derivatives have been characterized by X-ray crystallography. The structures contain stacks of antimony six rings in the chair conformation with equatorial tolyl substituents. It has been mentioned above that the principal features of the ring geometry are analogous to the rings in the layers of elemental antimony. However, the bond lengths and the bond angles of the organoantimony rings are smaller than the corresponding parameters in the element. The interlayer contact distances in elemental antimony are considerably shorter than intermolecular Sb···Sb separations between ring molecules (see Table 1).

Table 1
Structural data of Sb_6 rings

	Sb–Sb (pm)	Sb...Sb (pm)	Sb–Sb–Sb (deg)	Sb–Sb–C (deg)	Ref.
Element	291	336	95.6	–	[73]
$(PhSb)_6 \cdot C_7H_8$	283.1–284.0(1)	419	86.4–93.9(1)	92.1–100.3(3)	[44]
$(m\text{-TolSb})_6$	282.8–283.4(1)	420	83.2–96.0(1)	89.8–99.6(3)	[13]
$(o\text{-TolSb})_6$	281.8–283.6(1)	>440	85.5–99.4(1)	91.1–100.3(3)	[13]

The study of the ^{1}H-NMR spectra of benzene solutions that had been obtained from crystals of hexamers revealed that the hexameric structures are not preserved in solution but equilibrium mixtures of pentamers and tetramers result (Eq. (9)).

$$1/6(RSb)_6(s) \rightleftharpoons 1/5(RSb)_5(solv) \rightleftharpoons 1/4(RSb)_4(solv) \quad (9)$$

R = Ph, *o*-, *m*-, *p*-Tol; s = solid, solv = in solution

The synthesis of red crystals of $(Me_3SiCH_2Sb)_n$ was achieved by dehalogenation of $Me_3SiCH_2SbCl_2$ with Mg in THF [14].

$$RSbCl_2 + Mg \rightarrow 1/n(RSb)_n + MgCl_2 \quad (10)$$

$R = Me_3SiCH_2$, $n = 4, 5$

The pattern of the ^{1}H-NMR spectra in solution corresponds to an equilibrium between the tetramer and the pentamer. The pentamer had been previously detected among the decomposition products of $Me_3SiCH_2SbH_2$ [15]. A black solid product of the composition $(Me_3SiCH_2Sb)_x$ also formed in this process or by reducing the corresponding dichloride with Cp_2Co.

The first reductive method for the synthesis of aryl antimony rings is the reaction of arylantimony dichlorides with cobaltocene (Eq. (11)) [16].

$$3RSbCl_2 + 2Cp_2Co \rightarrow 1/n(RSb)_n + 2[CpCo_2][RSbCl_3] \quad (11)$$

(R = Ph, *o*-, *m*-, *p*-Tolyl, $n = 4, 5$ in solution)

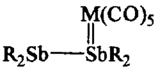
This result is of interest because other reductive methods, e.g. the reaction of $PhSbBr_2$ with Mg failed to give arylantimony rings and polymers formed instead [17].

For the characterization of the organoantimony rings and chains by ^{121}Sb Mössbauer spectroscopy [18], the well defined crystalline cycles $(PhSb)_6$ and $(tBuSb)_4$, the crystals of *p*-tolylantimony that very likely consist of $(p\text{-}TolSb)_6$, and black solid $(EtSb)_x$ of unknown stucture were studied. $(EtSb)_x$ is reversibly formed from solutions containing $(EtSb)_4$ and $(EtSb)_5$ when the solvent is removed. It is believed that this solid polymeric form of ethyl antimony consists of very large rings ($x \gg 6$). The Mössbauer parameters of the antimony rings were measured and compared with the data of distibines, *tert.*-stibines and organo antimony(III) halides. All of the antimony ring compounds show similar parameters that are typical for the $RSbSb_2$-type of coordination. Mössbauer spectroscopy appears to be a useful method for characterization, even of those organoantimony rings that cannot be analyzed by X-ray diffractometry.

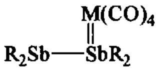
2.4. Complexes with Sb–Sb bonded ligands

The basic chemistry of distibines as ligands in the coordination sphere of transition metal carbonyl complexes was studied twenty years ago. More recently also crystal structures reveal three different types of coordination. Distibines may act as monodentate or as bidentate bridging ligands towards 16 electron metal carbonyl fragments. The third possibility, the fission of the Sb–Sb bond with formation of complexes containing bridging diorganoantimonido groups will not be discussed here.

Complexes with the monodentate distibine ligand (1:1 complexes) represent Type B of Sb–Sb bonded species (cf. Fig. 2) with a σ^3, λ^3 Sb combined with a σ^4, λ^5 Sb. The 16 electron ML_n fragments are isolobal with chalcogen atoms.


$R_2Sb{-}\overset{M(CO)_5}{\overset{\|}{Sb}}R_2$

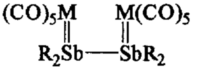
R = Me, Et, Ph; M= Cr, W [19]


$R_2Sb{-}\overset{M(CO)_4}{\overset{\|}{Sb}}R_2$

R = Et, *t*Bu; M= Fe [20]

The corresponding distibine oxides or sulfides of the type $R_2Sb\text{–}Sb(E)R_2$ (E = O, S), are however unknown. Addition of chalcogens to distibanes leads to the formation of insertion products.

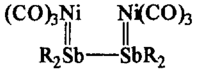
Complexes of bidentate distibine ligands (1:2 complexes) are also known.


$\overset{(CO)_5M}{\overset{\|}{R_2Sb}}{-}\overset{M(CO)_5}{\overset{\|}{Sb}}R_2$

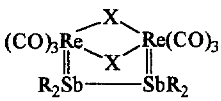
R = *t*Bu, Ph; M = Cr, W [19]

R = Me, Et; M = Cr, W [22]

R = Me, Ph; M = Mo [23]


$\overset{(CO)_3Ni}{\overset{\|}{R_2Sb}}{-}\overset{Ni(CO)_3}{\overset{\|}{Sb}}R_2$

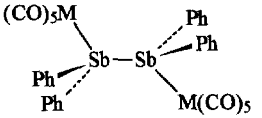
R = Me [20]



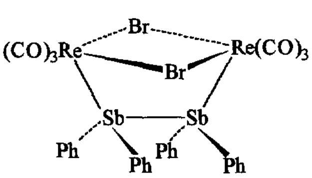
R = Ph; X = Br, I [21]

The synthesis of these derivatives is straightforward. Photochemically generated solutions of $M(CO)_5(THF)$ ($M = Cr$, Mo, W) in THF react with the solutions of the distibines in the appropriate molar ratio to give the corresponding 1:1 or 1:2 complexes. For the formation of the iron or nickel carbonyl complexes, $Fe_2(CO)_9$ or $Ni(CO)_4$ was reacted with the distibine.

$Re_2Br_2(CO)_6(Sb_2Ph_4)$ was formed from tetraphenyldistibine and $Re_2Br_2(CO)_6(THF)_2$. The complexes $(CO)_5M–Ph_2SbSbPh_2–M(CO)_5$ ($M = Cr$ [24], W [25]) have been characterized by X-ray crystallography. In the crystal there are centrosymmetric μ-2-distibine pentacarbonyl-metalcomplexes in the *anti* conformation. The structural parameters of the ligand including the conformation are similar to the geometry of solid distibine. On the contrary in $Re_2Br_2(CO)_6(Sb_2Ph_4)$ the distibine ligand adopts the *syn* structure as a consequence of the positions of the coordination sites in the bridged $((Re(CO)_3Br)_2$ fragment. Structural data of complexes with the tetraphenyldistibine ligand are given in Table 2.



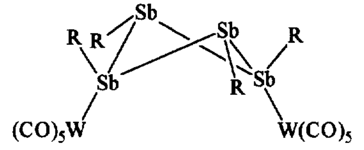
M = Cr, W



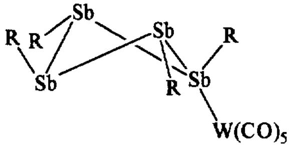
The first complexes with a cyclostibine ligand have been obtained by reactions between $(THF)W(CO)_5$ and $(tBuSb)_4$. The 1:2 complex has been characterized by X-ray diffraction [25]. The geometry of the $(tBuSb)_4$ ligand is essentially preserved on complexation. The mean Sb–Sb and Sb–W bond lengths are 283.7 and 283.5 pm respectively.

Table 2
Structural parameters of tetraphenyldistibine complexes

	Sb–Sb (pm)	Sb–M (pm)	C–Sb–C (deg)	Sb–Sb–C (deg)	Ref.
$Ph_2SbSbPh_2$	283.7(1)	–	94.4(2)	96.5,93.8	[27]
$[SbPh_2Cr(CO)_5]_2$	286.6(1)	262.6(1)	101.0(3)	98.7(2)	[24]
$[SbPh_2W(CO)_5]_2$	286.1(1)	274.9(1)	100.8(3)	99.2(2)	[25]
$[SbPh_2Re(CO)_3Br]_2$	282.6(4)	272.6(3)	102.1(1)	104.2(7)	[21]



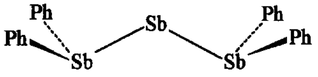
R = *t*Bu, 1:2 complex



1:1 complex

2.5. Organometallic anions with Sb–Sb bonds

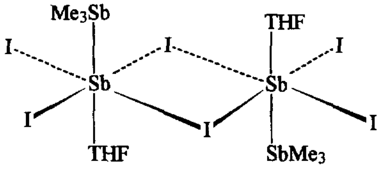
A remarkable salt, Li(12-crown-4)$_2$(Sb$_3$Ph$_4$)·THF [26], containing the first trinuclear organoantimony anion, has been obtained as a side product of the reaction of Ph$_3$Sb with Li powder in THF. The salt is a dark red crystalline product. The crystal structure contains a bent Sb$_3$ chain with two diphenyl antimony groups coordinated to a central antimony atom. The Sb–Sb bond length is 276.1(1) pm. This distance is very short for a Sb–Sb single bond (cf. Ph$_2$Sb–SbPh$_2$: Sb–Sb-distance = 283.7 pm [27]). The Sb–Sb–Sb bond angle of 88.8(1)° is surprisingly small too, bringing Ph$_2$Sb groups to a Sb···Sb contact distance of 386.4(1) pm. Neither the reaction path leading to the formation of the anion nor the structural features are well understood. Further research in this field appears to be promising.



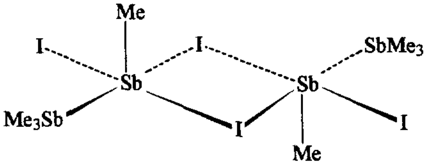
2.6. Compounds with dative Sb–Sb bonds

Tert.-stibines, R$_3$Sb are donor molecules that coordinate easily to acceptors like transition metal carbonyls or halides. When stibines coordinate to antimony halides compounds with dative Sb→Sb bonds result. The term dative bond [28] implies that the formation of the donor acceptor complex is reversible and species with paired electrons result on dissociation. In contrast, the dissociation of a "normal" Sb–Sb sigma bond would result in the formation of a R$_2$Sb· radical. As a general trend it was assumed that dative bonds have often less than half of the bond strength of covalent bonds for the same pair of atoms. Stable adducts between Sb-donor and Sb-acceptor molecules have been reported by Summers and Sisler [29] in 1969. The reaction of Me$_3$Sb with SbI$_3$ gave SbI$_3$·SbMe$_3$ (m.p. 91–92 °C).

Recently the structure of the related adduct, Me$_3$Sb·SbI$_3$·THF [30] has been investigated by X-ray diffractommetry. The adduct forms centrosymmetric dimers. The acceptor antimony atoms have octahedral coordination with trimethylstibine and THF in *trans* positions and iodine atoms in *cis* positions. The two octahedra share an edge formed by two bridging iodine atoms. The length of the coordinative Sb–Sb bond is very close to the normal single bond distance (cf. Me$_2$SbSbMe$_2$, Sb–Sb 283.8(1) pm [31]). A related adduct is Me$_3$Sb·SbMeI$_2$ [32]. The structure is described as a centrosymmetric dimer of tetragonal pyramids (ψ octahedra) with iodine atoms in bridging positions. Again the coordinative Sb–Sb bond compares well with the Sb–Sb single bond length in $Me_2SbSbMe_2$. The adducts are not stable in solution or in the gas phase [33].



Sb-Sb 284.30(10) Sb-I 279.6 - 355.8 Sb-O(THF) 285.0 pm

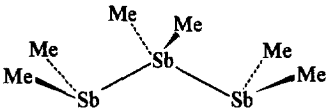


Sb-Sb 285.9(1) Sb-I 291-348 pm

Not only monostibines but also distibines may act as donors in reactions with organoantimony halide acceptors forming trinuclear adducts containing two Sb–Sb bonds. The ionic compound $[Me_2Sb–SbMe_2–SbMe_2]$ $[Me_2SbBr_2]$ [34] is formed from dimethylantimony bromide and tetramethyldistibine (Eq. (12)) as the first example of such a trinuclear adduct.

$$Me_2SbSbMe_2 + 2Me_2SbBr \rightarrow [Me_2Sb-SbMe_2-SbMe_2][Me_2SbBr_2] \qquad (12)$$

In the solid state the adduct is sufficiently stable for X-ray analysis. The cation is a bent symmetric chain of Me_2Sb units with a tetrahedral coordination of the central antimony atom. The Sb–Sb distances are shorter than the Sb–Sb single bond lengths in tetramethyldistibine. The formation of $[Me_2Sb–SbMe_2–SbMe_2][Me_2SbBr_2]$ in solution is reversible. NMR spectra of a mixture of tetramethyldistibine and dimethylantimony bromide do not show the two singlet peaks of the components but a broad signal in between. This result indicates a rapid migration of the Me_2Sb groups between the adduct components.

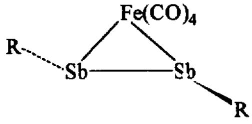


Sb-Sb 282.03(4) pm Sb-Sb-Sb 116.18(2)°

2.7. Compounds with two coordinate Sb

In recent years two types of compounds containing bonds between two coordinate antimony atoms have been examined, namely distibenes RSb = SbR and a distibabutadiene R′RC = Sb–Sb = CR′R.

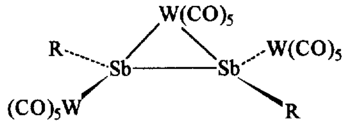
Attempts to obtain distibenes RSb = SbR by dehalogenation of organoantimony dihalides $RSbCl_2$ with bulky substituents ($R = (Me_3Si)_2CH$, $(Me_3Si)_3C$, 2,4,6-$t$$Bu_3C_6H_4$) have not been successful. However the related phosphastibene RSb = PR′ ($R = (Me_3Si)_2CH$, R′ = 2,4,6-$t$$Bu_3C_6H_4$) has been obtained. It is unstable in solution and decomposes with formation of the corresponding diphosphene [35]. Complexes that may be viewed to contain distibene ligands have however been prepared. $[Fe(\eta^2\text{-}R_2Sb_2)(CO)_4]$ $R = (Me_3Si)_2CH$ [36] is a product of the reaction of $RSbCl_2$ with $Na_2[Fe(CO)_4]$.



$R = (Me_3Si)_2CH$

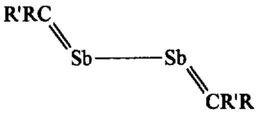
Sb-Sb 277.4(1) pm Fe-Sb-C(R) 107.5(1)° Sb-Sb-C(R) 101.9°

Another structurally characterized distibene complex is $[W(\eta^2\text{-}R_2Sb_2)(CO)_5][W(CO)_5]_2$ [37], a red crystalline air stable product (m.p. 110 °C dec.) from the reaction of $PhSbCl_2$ with $Na_2[W_2(CO)_{10}]$.



$R = C_6H_5$, Sb–Sb 270.6 pm

A remarkable development is the synthesis of the distibabutadiene R′RC = Sb–Sb = CR′R ($R = Me_3SiO$, R′ = 2,4,6-$t$$Bu_3C_6H_2$) by reaction of R′COCl with $Li[Sb(SiMe_3)_2[DME)]$ [38].



$R = Me_3SiO$, R′ = 2,4,6-$t$$Bu_3C_6H_2$

Sb-Sb 277.4(1) pm Sb=C 205.6(10) pm C-Sb-Sb 94.7(3)°

The distibabutadiene is a stable red crystalline compound with little air sensitivity. The Sb–Sb distance is shorter than in $Ph_2Sb–SbPh_2$ (283.7(1) pm). This may be a consequence of a delocalisation of the π bonds leading to a partial double bond character of the central antimony-antimony bond and/or it may indicate that the radii of sp^2 antimony atoms are smaller than of sp^3 antimony atoms.

2.8. Compounds with five coordinate Sb

Several trinuclear organoantimony compounds of the type $R_2Sb–Sb(R'_3)–SbR_2$, $R = Ph$, Tol; $R' = Ph$, Tol, Me have been reported from reaction of R_2SbLi with R'_3SbBr_2 in a 2:1 molar ratio [39]. The result is surprising because the formation of a mixture of R_3Sb and R_2SbSbR_2 could have been expected. The novel tristibines have been characterized by molecular weight determination. Crystallographic data have not been reported.

3. Compounds with bonds between Sb and Si, Ge, Sn, or Pb

Known types of compounds with bonds between Sb and the heavier group 14 elements are:

$(R_3M)_3Sb$ $R'(R_3M)_2Sb$ $R_2(R_3M)Sb$
$(R_3M)_2Sb–Sb(MR_3)_2$ $Li(R_3M)_2Sb$
$M = Si, Ge, Sn, Pb$

The reactions leading to these derivatives have been covered in 1988 [40]. A comprehensive review dates back as far as 1969 [41].

3.1. Syntheses

A method that has been used frequently in our laboratory for the synthesis of $(Me_3Si)_3Sb$ is the reaction of Li_3Sb with Me_3SiCl in diethylether. The yield of 76% as reported by Amberger and Salazar [42] has been obtained when the original prescription was carefully followed. The corresponding Ge, Sn or Pb compounds form [7] in good yield by the exchange reaction (Eq. (13). The lead compound is however unstable at ambient temperature.

$$(Me_3Si)_3Sb + 3Me_3MCl \rightarrow (Me_3M)_3Sb + 3Me_3SiCl \qquad (13)$$

$M = Ge, Sn, Pb$

Recently $(Me_2PhSi)_3Sb$ has been prepared [43] in 35% yield by the reaction of "Na_3Sb" (generated in situ) and chlorodimethylphenylsilane in tetrahydrofuran at reflux temperature. Compounds of the type $RSb(SiMe_3)_2$ ($R = Ph$ [44], *o*-, *m*-, *p*-Tol [13]) are formed in 65% yield in the reaction of $RSbBr_2$ with Mg and

Me_3SiCl in THF.

$$RSbBr_2 + Mg + 2Me_3SiCl \rightarrow RSb(SiMe_3)_2 + 2MgBrCl \qquad (14)$$

R = Ph, *o*-, *m*-, *p*-Tol

Exchange reactions of *p*-$TolSb(SiMe_3)_2$ with Me_3MCl (M = Ge, Sn) give the corresponding Ge or Sn derivatives [45].

$$R(Me_3Si)_2Sb + 2Me_3MCl \rightarrow R(Me_3M)_2Sb + 2Me_3SiCl \qquad (15)$$

M = Ge, Sn; R = *p*-Tol

Derivatives of the type R_2SbMMe_3 (M = Si, Ge, Sn) [46] have been prepared 20 years ago by reaction of a solution of Ph_2SbLi in THF with Me_3MCl.

$$Ph_2SbLi + Me_3MCl \rightarrow Ph_2SbMMe_3 + LiCl \qquad (16)$$

M = Si, Ge, Sn

3.2. Reactions of tert.⁻ organometalstibines

All the *tert.*-organometalstibines are air sensitive compounds. $(Me_3Si)_3Sb$ is self-igniting when exposed to the atmosphere on paper. Air oxidation in solution gives $(Me_3SiO)_3Sb$ [44]. The formation of distibines of the type $(Me_3M)_2Sb{-}Sb(MMe_3)_2$ is achieved when excess *tert.*-organometalstibines react with air in absence of solvent.

$$2(Me_3M)_3Sb + 1/2O_2 \rightarrow (Me_3M)_2Sb-Sb(MMe_3)_2 + (Me_3M)_2O \qquad (17)$$

M = Si [47], Ge [47], Sn [48].

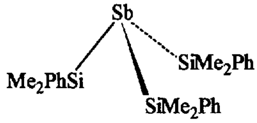
The reaction of $(Me_3Si)_3Sb$ with MeLi in 1,2-dimethoxyethane gives $(Me_3Si)_2SbLi \cdot DME$ and Me_4Si [49]. $(Me_3Si)_2SbSb(SiMe_3)_2$ is obtained in excellent yield by reaction of $(Me_3Si)_2SbLi \cdot 2THF$ and $BrCH_2CH_2Br$ [50]. The coordination chemistry of $(Me_3M)_3Sb$ has been studied in the seventies and complexes of the type $(Me_3M)_3SbM'(CO)_n$ (M = Si, Ge, Sn, M' = Cr, Mo, W, $n = 5$ [51], [52]; M = Si, Ge, M' = Fe, $n = 4$ [53]; M = Si, Ge, Sn, M' = Ni, $n = 3$ [54]) have been synthesized. The silylstibine complexes $(Me_3Si)_3SbM(CO)_5$ initiate the polymerization of tetrahydrofuran [52] and cannot be prepared by the usual exchange reaction between $(THF)M(CO)_5$ and the silylstibine ligand in THF. Photolyses of $M(CO)_6$ in petroleum ether in the presence of $(Me_3Si)_3Sb$ gave however the expected 1:1 complexes. An unusual result had the reaction of $(Me_3Sn)_3Sb$ with $Fe_2(CO)_9$ giving $(Me_3Sn)_2Fe(CO)_4$ and Sb instead of the expected stannylstibine complex [53].

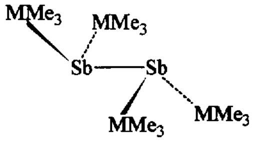
Reactions of $RSb(MMe_3)_2$ (R = Ph, Tol; M = Si, Ge, Sn) with air give $(Me_3M)_2O$ and organoantimony rings $(RSb)_n$. However, the analogous reaction of tBuSb$(SiMe_3)_2$ with air fails to give the known $(t\text{BuSb})_n$ ring. Instead tBuOOtBu and $(Me_3Si)_2SbSb(SiMe_3)_2$ are formed [17].

3.3. Structures

Little is known about the structures of organometalstibine derivatives. Although the vibrational data of $(H_3Si)_3Sb$ had initially been assigned to a planar arrangement [55] it was demonstrated that these data are also in accordance with a pyramidal $SbSi_3$ framework [56]. The structure of $(H_3Si)_3Sb$ has not yet been proven unambiguously from the gas phase parameters determined by electron diffraction [43]. However the vibrational data for $(Me_3M)_3Sb$ (M = Si [56], Ge, Sn [51]) have been interpreted in favor of a pyramidal structure.

There are very few single crystal X-ray diffraction data available for organometalstibines. The structure of the first *tert.*-organometalstibine $(Me_2PhSi)_3Sb$ [43] has been reported very recently, and Si_3Sb skeleton is pyramidal. The crystalline organometaldistibines $[(Me_3M)_2Sb]_2$ (M = Si, Ge, Sn) adopt the *anti* conformation with a pyramidal environment at the antimony atom. The structure of $(Me_3Si)_2SbLi \cdot DME$ contains $(SbLi)_x$ chains with the antimony atoms in the center of a distorted tedrahedron formed from two Si and two lithium atoms. Structural parameters of organometal stibines are listed in Table 3.





M = Si, Ge, Sn

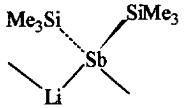


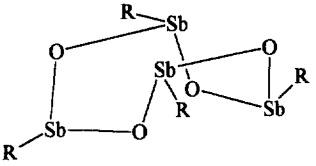
Table 3
Distances and angles in structures of organometalstibine derivatives

Compound	M	Sb–M (pm)	M–Sb–M (deg)	Ref.
$(Me_2PhM)_3Sb$	Si	255.43(8)–256.19(8)	99.81(3)–100.76(3)	[43]
$(Me_3M)_2SbLi \cdot DME$	Si	253.2(1)	94.2(1)	[49]
$(Me_3M)_4Sb_2$	Ge	259.4	94.46(3)	[50]
$(Me_3M)_4Sb_2$	Ge	262.4(1)–263.6(1)	93.23(4)	[47]
$(Me_3M)_4Sb_2$	Sn	278.9(1)–280.5(1)	91.9(1)	[74,75]

4. Organometallic compounds with bonds between Sb and O, S, Se, Te

The following types of compounds are discussed here:
$(RSbE)_n$, $(R_2Sb)_2E$, $[(R_2Sb)_2E_3]_2$
$Sb(ER)_3$, R_2SbER, $RSb(ER)_2$
E = Chalcogen

Some of these derivatives are cyclic, and have recently been reviewed [11]. Since then progress has been achieved in the field of $(RSbE)_n$ derivatives. The hydrolysis of $RSbCl_2$ [R = $(Me_3Si)_2CH$] with aqueous KOH gave $[(R)SbO]_n$. In the crystal, this oxide adopts a tetrameric structure ($n=4$) containing a boat shaped eight membered Sb_4O_4 ring. The tetrameric unit is not preserved in benzene solution. The ^{1}H-NMR data support a trimeric structure with a Sb_3O_3 ring and the substituents in *cis–trans* positions [57]. The analogous $(RSbE)_n$ (E = S, Se, Te) compounds have been synthesized by the reaction of the corresponding sodium chalcogenides with $RSbCl_2$ [R = $(Me_3Si)_2CH$]. However, the crystal structures of these derivatives are not known. The ^{1}H-NMR data suggest the presence of dimers and trimers in solution [58].



Compounds of the type $R_2Sb–E–SbR_2$ are formed by oxidation of distibines (Eq. (18)),

$$R_2SbSbR_2 + E \rightarrow R_2SbESbR_2 \qquad (18)$$

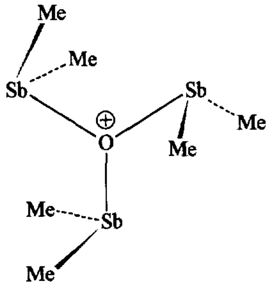
$$E = 1/2O_2,\ 1/8S_8,\ 1/xSe_x,\ 1/xTe_x$$

or by hydrolysis of R_2SbX compounds. Some of these compounds show thermochromic behavior. For a recent review see Ref. [59].

The electroreduction of $(Ph_2Sb)_2O$ gives Ph_2Sb^-. However, the other product of reduction, namely Ph_2SbO^-, was not detected by voltammetry [60].

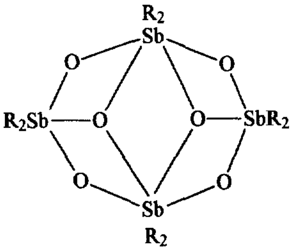
$$Ph_2SbOSbPh_2 + 2e^- \rightarrow Ph_2Sb^- + Ph_2SbO^- \qquad (19)$$

A recent result features the reactivity of $Me_2SbOSbMe_2$. This monoxide reacts with Me_2SbBr with formation of colorless crystals of $[(Me_2Sb)_3O]Br$ [61]. The crystal structure contains an oxonium salt with trigonal planar geometry around oxygen.

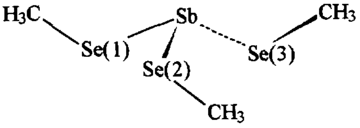


Sb-O 211.6(1) Sb-O-Sb 119.9(1)°

Derivatives of the type $[(R_2Sb)_2E_3]_2$ (R = Ph, *o,p*-Tol) have been obtained by air oxidation of distibines or by a rearrangement process during the oxidation of $RSb(SiMe_3)_2$ [62]. The crystal structure consists of polynuclear molecules: The analogous phenyl compound has been obtained before by the reaction of Ph_3Sb with H_2O_2 [63].

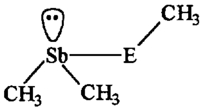


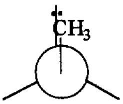
A compound of the type $Sb(ER)_3$ has been prepared by reaction of elemental antimony with dimethyldiselenide. In the crystals of $Sb(SeMe)_3$ [64] the molecules have a trigonal pyramidal skeleton formed by the heavy atoms. They are associated through short intermolecular Sb···Se contacts with distances of 355–366 pm.



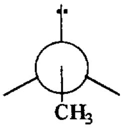
Sb-Se 256.8(1) - 258.8(1) pm Se-Sb-Se 82.5(1)-102.1(1)°

Compounds of the type Me_2SbEMe (E = S, Se, Te) are formed by exchange reaction of MeEEMe with $Me_2SbSbMe_2$. The molecular structure of two of these derivatives (E = S, Se) has been determined by gas phase electron diffraction [65]. The data show that the predominant conformer is one where the dihedral angle ϕ defined by the E–C bond, the Sb–E bond and the presumed direction of the lone pair at the Sb atom falls in the range −45 to +45° (*syn*-conformer: $\phi = 0°$). The presence of the *anti* conformer ($\phi = 180°$) has been excluded. The Sb–S and Sb–Se bond distances are 241.4(8) and 255.5(3) pm, respectively. The reaction of $Me_2SbSbMe_2$ with RSSR ($R = P(S)Me_2$) gives $Me_2SbSP(S)Me_2$ [66]. The crystal structure contains molecules with an arrangement of the $Me_2Sb–S–P$ unit that is also close to *syn* conformation ($\phi = 34.3(4)°$). The molecules build polymeric chains through intermolecular Sb···S contacts. The related compound *p*-$Tol_2Sb–SP(S)Et_2$ was obtained from *p*-Tol_2SbCl and $NaSP(S)Et_2$ [67]. The crystals contain molecules in the *syn* conformation that are associated to dimers trough Sb···S contacts. The phenyl derivative $Ph_2SbSP(S)Ph_2$ [68] possesses a related structure with association of the molecules to dimers. The dihedral angles ϕ of some derivatives $R_2Sb–E–R'$ are given in Table 4. Despite the differences in structures and phases that lead to different intra or intermolecular interactions, it appears that with one exception the molecules or molecular fragments adopt conformations close to a *syn* arrangement. However, the available data are too limited to establish a general trend and more analytical and theoretical work seems to be necessary in this field.

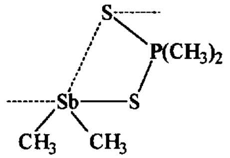




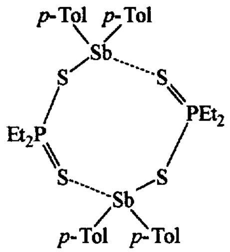
syn
φ = 0°



anti
φ = 180°



Sb-S 255.5(2) Sb···S 382.2(2) Sb···S' 315.8(2) pm



Sb-S 248.5(3), 250.9(3) Sb···S 331.8(3), 355.6(3) pm

Table 4
Conformations of derivatives $R_2Sb–E–R'$

R	E	R′	ϕ^a (deg)	Phase	Ref.
Ph	O	$SbPh_2$	43.3,6.8	Crystal	[76]
Me	S	Me	$17(10)^b$	Gas	[65]
Me	Se	Me	$21(9)^c$	Gas	[65]
MeSe	Se	Me	31.5(1), 73.2(1), 169.6(1)	Crystal	[64]
p-Tol	S	$P(S)Et_2$	13.5(4), 21.0(4)	Crystal	[67]
Me	S	$P(S)Me_2$	34.3(4)	Crystal	[66]

[a] For a definition of ϕ see text.
[b] Syn conformer, mole fraction 79(11)%.
[c] Syn conformer, mole fraction 97(6)%.

Compounds of the type $RSb(ER)_2$ have been obtained by rearrangement processes of R_2SbER type compounds at elevated temperature [69].

$$2R_2SbER \rightarrow R_3Sb + RSb(ER)_2 \tag{20}$$

R = Me, Et; E = S, Se, Te

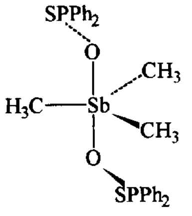
Another way is the reaction of a cyclostibine, $(RSb)_n$ with a dichalcogenide.

$$(RSb)_n + R'EER' \rightarrow RSb(ER')_2 \tag{21}$$

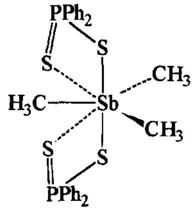
R = Et, R′ = Me, Ph, *p*-Tol, E = Se, Te [70]; R = Me_3SiCH_2, R′ = *p*-Tol, E = Te [13]

Attempts to determine the solid state structure of these derivatives have not been successful.

On the contrary the structures of compounds of the type $R_3Sb(ER')_2$ E=O [71], S [72]; R = CH_3, R′ = $P(S)Ph_2$ have been determined by X-ray diffractommetry. The coordination at antimony is trigonal bipyramidal in the case of the oxo derivative with the methyl carbon atoms in equatorial and the oxygen atoms in apical positions. The sulfur compound displays a different coordination mode. When the weak intramolecular Sb···S interactions are considered, the coordination number at the antimony atom increases from five to seven. [19,20,22,23]



Sb-O 211.4(5), 210.7(5)



Sb-S 261.1(5) Sb···S 374.4(8), 383.9(8) pm

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