

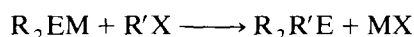
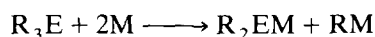
Annual review  
**Antimony**  
Annual review covering the year 1991

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Except for our annual survey covering the year 1989, no book or review devoted exclusively to organoantimony compounds was published in 1991. Wolfsberger [1] wrote an interesting review of the preparation of tertiary phosphines, arsines, stibines, and bismuthines by a procedure he termed the method of Müller, Hewertson, and Watson. This method involved the following types of sequential reactions:

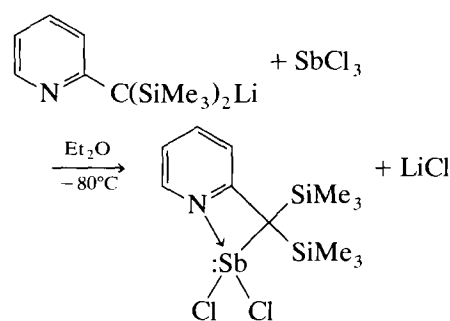


(where R and R' are alkyl or aryl; E = P, As, Sb, or Bi; M = Li, Na, or K; and X = Cl, Br, or I).

Some information about organoantimony compounds was included in a new textbook on organometallic chemistry [2] and in surveys of recent publications on the main-group elements [3] and on organic derivatives of arsenic, antimony, and bismuth [4]. Organoantimony compounds were briefly mentioned in reviews or annual surveys on the following subjects: organosilicon derivatives of phosphorus, arsenic, antimony, and bismuth [5], transition-metal fluoro compounds containing carbonyl, phosphine, arsine, or stibine ligands [6], conjugation and the periodic system [7], reactions of metal carbonyls with Group V or Group VI ligands [8], and the thermochemistry of organometallic compounds [9,10].

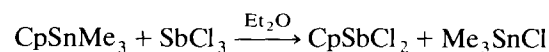
A monomeric dichlorostibine was prepared in 70%

yield by the interaction of an organolithium reagent and antimony trichloride [11]:



The resulting compound was stable enough to be sublimed at 200–210°C, ca. 0.2 mbar. It was studied by NMR (<sup>1</sup>H and <sup>13</sup>C) and by X-ray diffraction. The coordination environment around the antimony could be considered distorted trigonal–bipyramidal with a carbon atom, a chlorine atom, and a lone pair of electrons occupying the trigonal–planar positions. Most of the bond distances were unexceptional, but the Sb–N distance of 2.371 Å was unusually long. Attempts at dialkylating antimony trichloride with the organolithium reagent were unsuccessful and resulted in the rapid loss of trimethylchlorosilane and the formation of intractable oils.

Single crystals of colorless cyclopentadienyldichlorostibine were obtained by the interaction of cyclopentadienyltrimethylstannane and antimony trichloride at –35°C [12]:

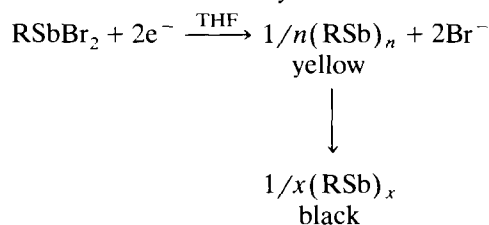


The compound was light-sensitive, thermolabile, and moderately soluble at room temperature in toluene and diethyl ether. When it was heated overnight under nitrogen at 80°C, it changed completely into a black

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powder. The latter substance appeared to be an amorphous modification of cyclopentadienyldichlorostibine. It was insoluble in hexane, toluene, diethyl ether, and tetrahydrofuran. Treatment with water led to hydrolysis and the formation of white, flocculent precipitate. X-ray crystal structure analysis of the colorless crystals of cyclopentadienyldichlorostibine showed molecules in which the cyclopentadienyl ligand was in an  $\eta^3$ -bonded state with a short Sb–C bond (227 pm) and two long Sb–C bonds (258 and 260 pm). Intermolecular interactions of the Menshutkin type resulted in additional Sb–Cp contacts and in a chain structure that was chiral. The Sb–C distances associated with this intermolecular bonding ranged from 341–358 pm.

Tetrastibetanes, pentastibolanes, and polymeric organoantimony(I) compounds were obtained by the electroreduction of alkyl dibromostibines [13]:



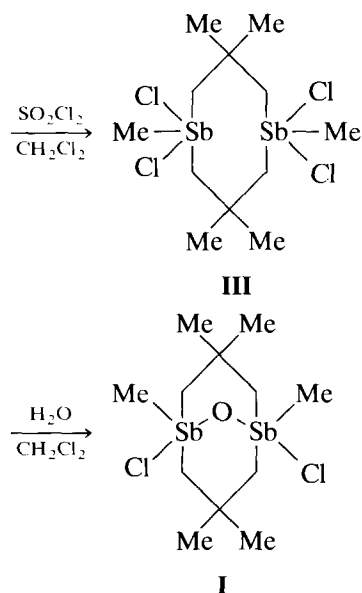
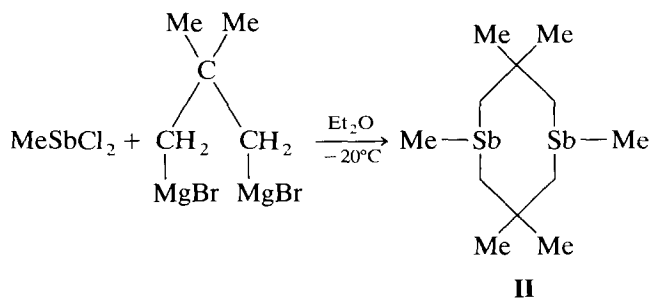
(where R is Et, Pr, or Bu;  $n = 4$  or  $5$ ; and  $x \gg 5$ ).

A green intermediate, referred to as “RSb”, was noted in the reduction, but no information about its structure was obtained. Oxidation of these species in the presence of bromide ion regenerated the alkyl dibromostibines:



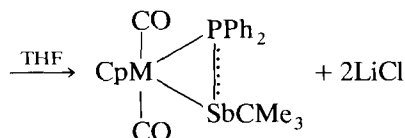
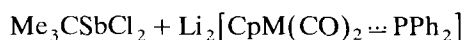
Previously the cyclic and polymeric substances were prepared by the dehalogenation of alkyl dibromostibines with magnesium in THF; in this study the cyclic compounds were identified by PMR and mass spectroscopy. The mass spectra of the polymeric substances were found to be identical with those of the polymers obtained by reduction with magnesium. When stored under argon, the yellow cyclic compounds became black and insoluble. The mechanistic aspects of the electrochemical reactions studied in this investigation were discussed in detail.

The 9-oxa-1,5-distibabicyclo [3.3.1.] nonane **I** was obtained as a hydrochloride by the following series of reactions [14]:



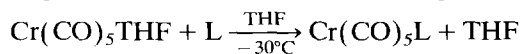
There was no evidence for the formation of the expected stibacyclobutane derivatives. The intermediate ditertiary stibine **II** was isolated as a white solid but was not further characterized. The tetrachloride **III**, which was also obtained as a white solid, appeared to be pure and was studied by PMR spectroscopy. The structure of the final product **I**·HCl was determined by X-ray diffraction. The two antimony atoms (which were described as pseudo trigonal-bipyramidally coordinated) shared an axial oxygen ligand, while the other axial position on each antimony atom was taken by a chlorine atom. All of the equatorial positions were occupied by carbon atoms, and the bridging oxygen was hydrogen bonded to a molecule of hydrogen chloride. All of the observed bond lengths were considered normal, and the equatorial planes were ideally planar. The bicyclononane skeleton had both six-membered rings in the normally less favored boat conformation.

Phosphametallacyclopropanes were obtained by the following type of reaction [15]:



(where Cp was  $\eta^5$ -cyclopentadienyl; and M = Cr or Mo).

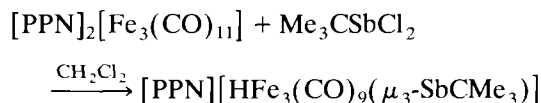
The antimony atom in the molybdenum-containing heterocycle exhibited Lewis basicity and was able to displace THF from a chromium complex:



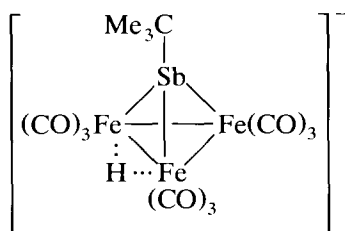
(where L was the heterocycle in which M = Mo). The heterocyclic ring was found to be kinetically stabilized by this reaction. A X-ray structural analysis indicated

that the ring skeleton underwent no change on coordination by the  $\text{Cr}(\text{CO})_5$  moiety.

The interaction of *tert*-butyldichlorostibine and a salt containing the anionic iron cluster  $\text{Fe}_3(\text{CO})_{11}^{2-}$  were found to yield an antimony-bridged anion [16]:

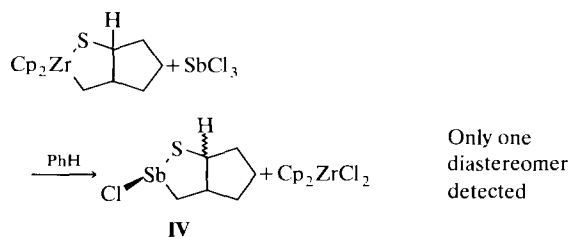
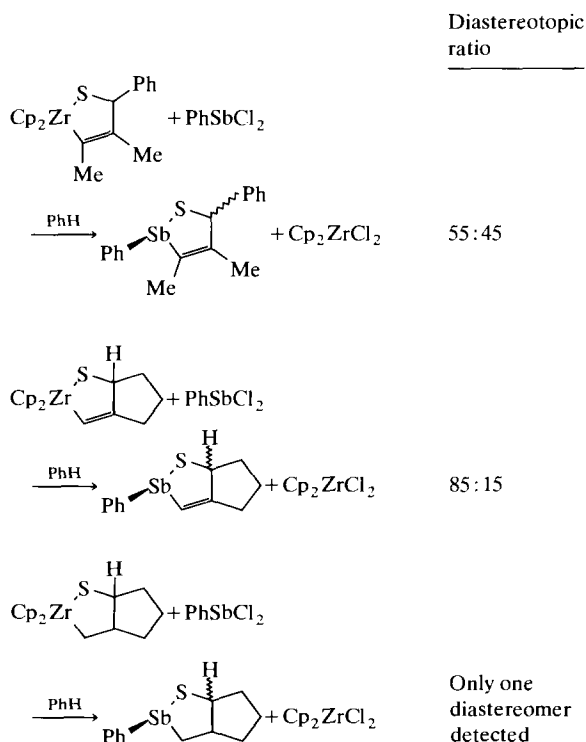


The stoichiometry of the above reaction was not elucidated. The following structure for this anion was suggested by a comparison of the IR and PMR spectra of the product with those of the corresponding phosphorus analog:

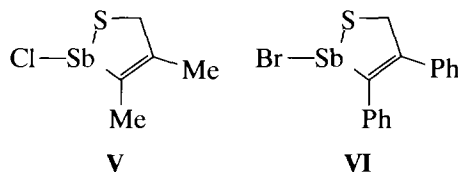


The interaction of trimethylantimony dibromide ( $\text{Me}_3\text{SbBr}_2$ ) and  $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$  or  $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$  in dichloromethane led to fragmentation of the anionic clusters and formation of the known iron complex  $\text{Me}_3\text{Sb-Fe}(\text{CO})_4$ .

Four new stibathiolanes were prepared by the reaction of zirconocene derivatives with either phenyldichlorostibine or antimony trichloride [17]:

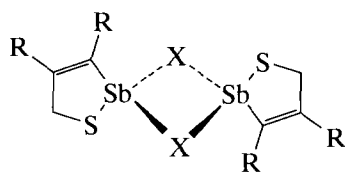


The compounds were relatively air-stable solids, but they were best stored under a dry atmosphere of nitrogen or argon. The diastereomeric ratios were determined by PMR analysis of the crude reaction mixtures. The diastereomers appeared to be stable to interconversion at  $80^\circ\text{C}$ . The X-ray crystal structure of the 1-chlorostibathiolane IV was determined and compared with the structures of the related compounds V and VI, which were prepared in an earlier investigation.



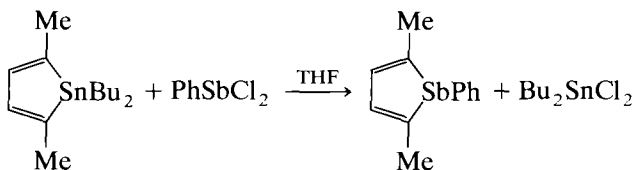
All three compounds were polymeric in the crystalline state. The antimony and sulfur atoms of each molecule were mutually bound to the sulfur and antimony atoms of the neighboring molecule in such a manner as to effect a see-saw geometry about the antimony atoms of each dimeric unit. In addition, each antimony atom was asymmetrically bridged by two halogen atoms to an antimony atom of another dimeric unit. Thus, close contacts between the antimony atoms and other heteroatoms of neighboring molecules produced interconnecting networks of antimony, sulfur, and halogen atoms. In the case of the 1-halostibathiolanes V and VI, the sulfur atom of each stibacycle was puckered out of the plane (by ca.  $0.26 \text{ \AA}$ ) of the ring in the direction of the second antimony atom to which it was bound. The saturated [3.0.3] ring system of the 1-chlorostibathiolane IV was found to be highly puckered. Each of the five-membered rings was composed of four nearly planar atoms and a tertiary carbon atom that was more than  $0.5 \text{ \AA}$  out of each plane. Molecular weight determinations of the stibathiolanes indicated that the compounds were monomeric in benzene solution. The PMR spectra of the 1-halostibathiolanes V and VI were dependent on both temperature and concentration. Under appropriate conditions of dilution or low temperature, the diastereotopic methylene protons gave rise to a pair of well-resolved doublets. When the temperature (or concentration) was increased, however, the signal became a singlet with a line width of ca. 50 Hz. The dynamic nature of the PMR spectra of these molecules was attributed to rapidly reversible halide-exchange reactions. A consequence of these exchange reactions

was the inversion of stereochemistry at antimony. This inversion appeared to involve intermediates of the following type:

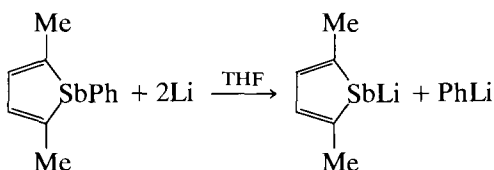


(where R = Me, X = Cl; or where R = Ph, and X = Br).

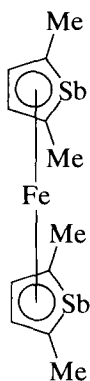
1-Phenyl-2,5-dimethylstibole was prepared by the following exchange reaction [18]:



Treatment of the stibole with lithium resulted in cleavage of the Ph–Sb bond and the formation of a deep red solution:



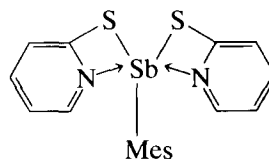
The addition of ferrous chloride to this solution at  $-78^{\circ}\text{C}$  gave deep red crystals of 2,2',5,5'-tetramethyl-1,1'-distibaferrocene:



X-ray diffraction showed that the molecule had a ferrocene-like arrangement. The iron atom was sandwiched between two  $\eta^5$ -bonded rings, which were completely eclipsed. Although the iron atom was  $\pi$ -bonded to all five atoms of each ring, it was slightly closer to the  $\beta$ -carbons (2.05–2.08 Å) than to the  $\alpha$ -carbons (2.08–2.14 Å), while the Sb–Fe distances were even greater (2.56, 2.57 Å). The intra-ring C–C bond distances were almost identical (1.41–1.43 Å); this fact was consistent with the conclusion that the rings were heteroaromatic. The intramolecular Sb  $\cdots$  Sb separation of 3.68 Å was significantly shorter than the sum of

the van der Waals radii (4.4 Å) and suggested that there was a direct inter-ring Sb  $\cdots$  Sb bond.

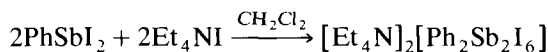
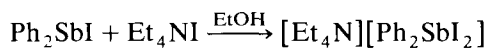
Mesitylbis(2-pyridinethiolato)stibine was obtained in 80% yield by the interaction of mesityldichlorostibine and sodium 2-pyridinethiolate in ethanol at 293 K [19]. An X-ray diffraction study of this substance showed that each antimony atom was a member of two chelate rings:



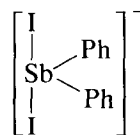
(where Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)

In the distorted tetragonal–pyramidal (pseudo-octahedral) coordination about the antimony atom, the two sulfur and the two nitrogen atoms were in *cis* positions, while the mesityl group occupied the apical position. The Sb–N distances were significantly longer than the sum of the covalent radii of antimony and nitrogen, whereas the Sb–C and Sb–S bond lengths agreed fairly well with the corresponding sums of the covalent radii. The intermolecular Sb  $\cdots$  Sb distance of 3.787 Å was somewhat shorter than the sum of the van der Waals radii (4.4 Å), and hence weak Sb  $\cdots$  Sb interactions were assumed. The Sb  $\cdots$  Sb contact was *trans* to the Sb–C bond and thus completed a distorted octahedron around the antimony atom.

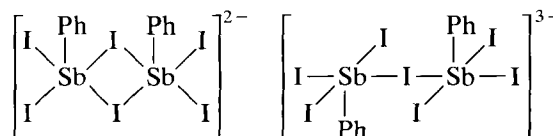
Three phenyliodoantimonates(III) were prepared by the following reactions [20]:



(where Hpy was pyridinium). The structures of these substances were established by X-ray structural analysis. The  $\text{Ph}_2\text{SbI}_2^-$  anion was found to display a  $\psi$ -trigonal–bipyramidal structure with axial Sb–I distances of 2.925 and 3.109 Å:



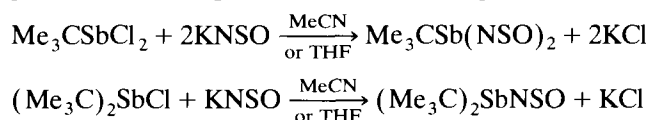
The antimony atoms in the dimeric anions, however, exhibited  $\psi$ -octahedral geometry:



The bridging Sb–I distances (3.185–3.305 Å) in the dinegative anion  $\text{Ph}_2\text{Sb}_2\text{I}_6^{2-}$  were significantly longer

than the terminal Sb–I distances (2.826–2.890 Å). The dihedral angle between the two basal  $\text{SbI}_4$  units in this anion was 106.4°. The trinegative anion  $\text{Ph}_2\text{Sb}_2\text{I}_7^{3-}$  exhibited  $C_i$  symmetry with the bridging iodine atom located at the center of inversion. The Sb–I distance involving the bridging atom was much longer (3.404 vs. 2.814 Å) than the Sb–I distance involving the iodines *trans* to the bridging atom. A structural correlation was presented for opposite Sb–X distances (where X = Cl, Br, or I) in linear three center X–Sb ··· X interactions. The sum of the bond distances in iodoantimonates(III) was found to be a minimum for symmetrical I–Sb–I three center bonds. This result was believed to reflect the antibonding influences of the  $\text{Sb}5s$  orbital. This influence was considerably smaller for bromoantimonates(III) and could be neglected for chloroantimonates(III).

The metathetical reaction of potassium thionylimide with *tert*-butyldichlorostibine or di-*tert*-butylchlorostibine was used to prepare two organoantimony compounds containing the Sb–N=S=O linkage [21]:

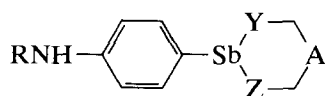


Both compounds were yellow oils, which were very moisture-sensitive. The IR spectrum of each substance exhibited an intense band that was attributed to the asymmetric stretching vibration of the NSO group and a medium-to-strong band attributed to the symmetric stretching vibration.

The icosahedral stibacarborane *closo*-1,2-CHSbB<sub>10</sub>H<sub>10</sub> and a number of related polyhedral heteroboranes were studied by <sup>11</sup>B and <sup>1</sup>H NMR spectroscopy [22]. The antimony atom was found to have a strong antipodal proton deshielding effect. There also appeared to be a deshielding effect for protons on positions  $\beta$  to the antimony atom, but this effect was not as significant. The assignment of the <sup>11</sup>B chemical shifts permitted a comparison of shielding trends among the isoelectronic *closo* compounds 1,2-CHCHB<sub>10</sub>H<sub>10</sub>, 1,2-CHSbB<sub>10</sub>H<sub>10</sub>, and 1,2-Sb<sub>2</sub>B<sub>10</sub>H<sub>10</sub>. The mean nuclear shielding was found to decrease when the CH group was replaced by an Sb atom.

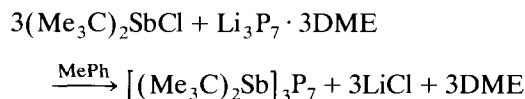
The IR and Raman spectra of the stibinediamine  $\text{MeSb}[\text{N}(\text{SiMe}_3)_2]_2$  were recorded in an article devoted mainly to bis(trimethylsilyl)amino derivatives of indium and tin [23]. The spectra of the antimony compound were compared with those of related substances containing Al–N, Ga–N, In–N, Sn–N, or As–N bonds.

A French patent application described the preparation of compounds of the following type [24]:

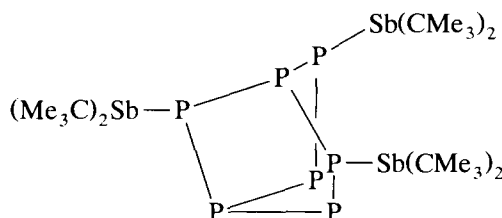


(where Y and Z = O or S; R is H or the 3,5-diamino-1-triazinyl group; and A is C<sub>1–18</sub> alkylene optionally substituted by OH). These substances were said to be parasiticides useful for the treatment of trypanosomiasis, leishmaniasis, and filariasis.

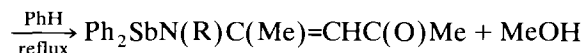
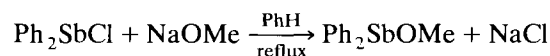
The interaction of di-*tert*-butylchlorostibine and trilithium heptaphosphide at –78°C was found to yield an antimony-substituted heptaphosphatricycloheptane [25]:



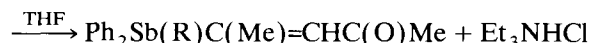
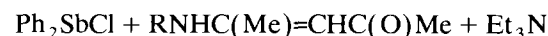
(where DME is 1,2-dimethoxyethane). Although this substance decomposed in toluene above –10°C, <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy suggested the following structure:



A series of diphenylantimony(III) derivatives containing the Sb–N bond was obtained by the interaction of diphenylmethoxystibine (prepared in situ) and a  $\beta$ -ketoamine [26]:

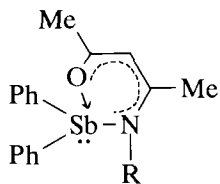


(where R = Me, Et, Pr, Me<sub>2</sub>CH, Bu, or Me<sub>2</sub>CHCH<sub>2</sub>). Two of these substances were also prepared by the triethylamine-promoted reaction of diphenylchlorostibine with the  $\beta$ -ketoamine:

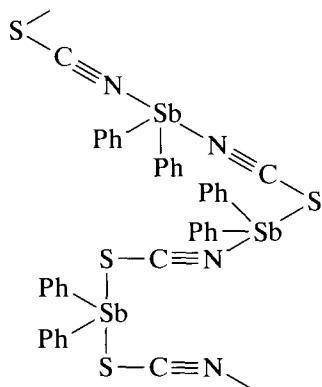


(where R = Me or Pr). All of the compounds were purified by dissolving in chloroform and then extracting with hexane. They were found to be dark brown viscous liquids, which were soluble in common organic solvents and monomeric in chloroform. Their IR spectra suggested that the ligands were chelating, and hence it was concluded that the antimony atom had a coordination number of four. The most plausible geometry on the basis of spectral studies (IR, PMR, and <sup>13</sup>C NMR) appeared to be trigonal-bipyramidal with a

coordinated oxygen atom and a lone pair of electrons occupying apical positions:

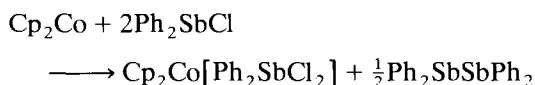


Diphenylthiocyanatostibine was prepared by the metathetical reaction between potassium thiocyanate and diphenylchlorostibine in acetonitrile solution [27]. The IR spectrum of this substance in chloroform suggested the presence of an *S*-bonded monomer, but the  $^{14}\text{N}$  NMR spectrum showed a single resonance at a chemical shift usually considered diagnostic of *N*-bonding. The X-ray structure revealed an infinite chain with a three molecule repeating unit:



Each antimony exhibited pseudo trigonal–bipyramidal coordination with two equatorial phenyl groups and two axial thiocyanates. Although the three independent thiocyanate groups in the repeating unit all bridged pairs of antimony atoms, they did so in different ways. Thus, one antimony atom was coordinated to two nitrogen atoms, the next antimony atom to one nitrogen and one sulfur atom, and the third antimony atom to two sulphur atoms. The thiocyanate groups were, as expected, effectively linear, while the angles at the coordinated nitrogen and sulfur atoms were such as to allow the development of an infinite “triangular spiral” structure in the solid state.

An ionic complex containing cobalt and antimony has been synthesized by the interaction of bis(cyclopentadienyl)cobalt(II) and diphenylchlorostibine [28]:

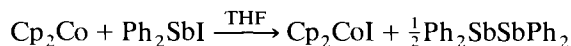


This salt could also be prepared by the following addition reaction:

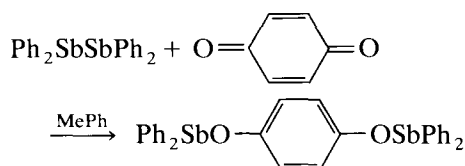
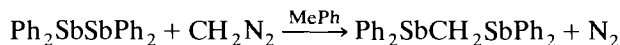
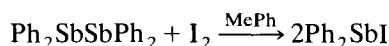


The yellow solid thus obtained was stable in air and, as a suspension in THF, was thermally stable up to about

100°C. It was practically insoluble in all common organic solvents. The solid-state structure of the salt was shown by X-ray diffraction to consist of the separated  $\text{Cp}_2\text{Co}^+$  and  $\text{Ph}_2\text{SbCl}_2^-$  ions. The cyclopentadienyl ligands in the cobalticinium cation were found to lie on two almost parallel planes. The cobalt atom was 1.65 and 1.62 Å away from the two centers of the pentagonal rings, which were almost exactly eclipsed. The structure of the diphenyldichloroantimonate(III) anion was described as distorted trigonal–bipyramidal with the phenyl groups occupying equatorial positions and the chlorines occupying the two axial sites. The C–Sb–C angle was 97.3°, a value much smaller than the 120° required for ideal trigonal–bipyramidal geometry. The Cl–Sb–Cl angle (177°), however, did not deviate greatly from the required linearity. Each ion in the crystal was surrounded by six ions of opposite charge. The interionic Sb···Co distances ranged between 5.68 and 7.30 Å. The shortest distance between ions of the same charge was 7.77 Å. Unlike diphenylchlorostibine, diphenyliodostibine did not react with bis(cyclopentadienyl)cobalt(II) to yield an ionic complex but instead was cleanly reduced to tetraphenyldistibine:

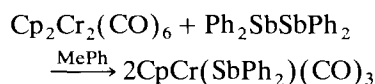


The cleavage of the Sb–Sb bond in the distibine was easily accomplished by iodine, *p*-benzoquinone, or diazomethane:



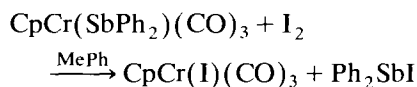
The IR spectra of the insertion products obtained by the last two reactions were similar to those previously reported for the analogous bismuth compounds. Further information about this study is given in the Annual Survey of Bismuth for 1991 [29].

A study was made of the exchange reactions between tetraphenyldiphosphine, -diarsine, -distibine, or -dibismuthine and dimeric complexes of chromium(I), molybdenum(I), or tungsten(I) of the general formula  $\text{Cp}_2\text{M}_2(\text{CO})_6$ , where Cp was  $\eta^5$ -cyclopentadienyl [30]. The rather weak chromium–chromium bond was readily cleaved in the dark by the distibine, and a red chromium(II) species was obtained:



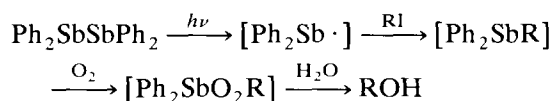
The IR spectrum of this tricarbonyl complex suggested that the geometry around the chromium atom was square–pyramidal. It reacted smoothly with iodine at

room temperature through the intermediacy of an unstable substance:

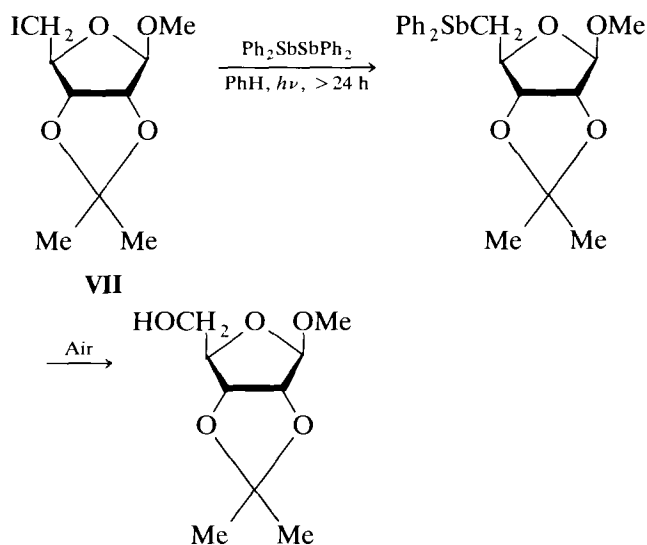


The yellow diphenyliodostibine was mechanically separated from the violet chromium complex. It was suggested that the unstable intermediate was the addition compound  $\text{CpCr}(\text{SbPh}_2\text{I}_2)(\text{CO})_3$ . Further information about this study is given in Ref. [29].

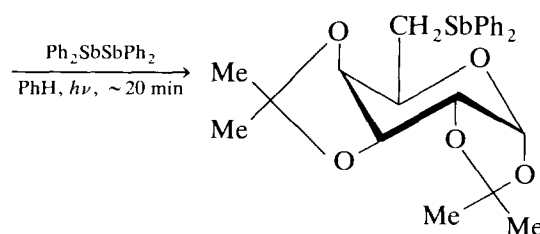
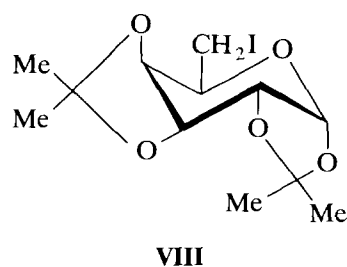
Tetraphenyldistibine was found to undergo homolysis on irradiation to produce the diphenylantimony(II) radical [31]. Reaction of this radical with alkyl iodides yielded alkyl diphenylstibines. In some cases, these stibines were air-sensitive and were converted by in situ air oxidation and hydrolysis into alcohols:



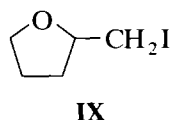
Thus, (tetrahydro-2-furanyl)methyl iodide reacted very slowly with the distibine on irradiation to give an air-sensitive intermediate that was readily oxidized to the expected alcohol. The D-ribofuranoside **VII** reacted in a similar manner:



Other alkyl iodides, however, reacted rapidly to produce air-stable tertiary stibines. For example, the D-galactopyranose **VIII** gave the corresponding stibine in 88% yield:

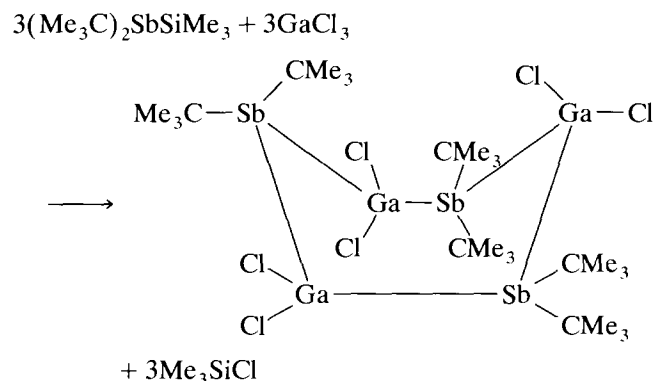


Although the stibine was not air-sensitive, it could be oxidized with basic hydrogen peroxide in acetone to give the expected alcohol in 84% yield. The tetrahydropyran derivative **IX** also reacted rapidly with tetraphenyldistibine to give an air-stable tertiary stibine.

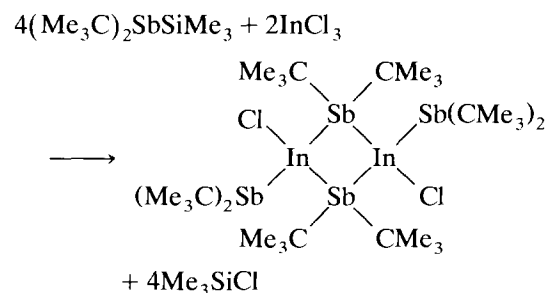


Lewis base coordination of the diphenylantimony(II) radical was proposed to account for the highly selective radical chemistry noted in this investigation.

An American patent described the synthesis of dialkylstibino complexes of gallium and indium that were said to be useful in metalorganic chemical vapor deposition (MOCVD) [32]. Thus, a trimer containing Ga–Sb bonds was prepared by the interaction of di-*tert*-butyl(trimethylsilyl)stibine and gallium chloride:

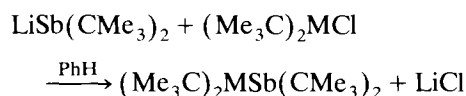


The boat-type conformation of the six-membered ring was established by X-ray diffraction. The reaction of di-*tert*-butyl(trimethylsilyl)stibine with indium chloride yielded a compound containing both bridged and terminal di-*tert*-butylstibino groups:



The structure of this substance was also determined by X-ray diffraction.

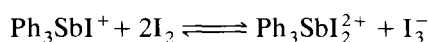
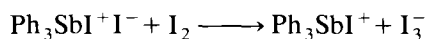
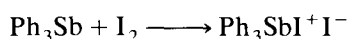
Another American patent described a number of volatile monomeric substances that could be pyrolyzed at relatively low temperatures to form essentially pure electronic grade metallic deposits or films [33]. Three organoantimony compounds were obtained by the following type of reaction:



(where M = Al, Ga, or In). Pyrolysis under a vacuum or in an inert atmosphere (e.g. He) resulted in the formation of crystalline AlSb, GaSb, or InSb.

The dithiophosphinate  $\text{Ph}_2\text{SbS}_2\text{PPh}_2$  and the dithiophosphate  $\text{Ph}_2\text{SbS}_2\text{P}(\text{OCHMe}_2)_2$  were tested in vivo in male AKR mice and in vitro against Ehrlich ascites tumor cells [34]. Both compounds exhibited dose-dependent inhibitory effects on in vivo tumor growth and on in vitro cell proliferation, cell viability, respiration, and protein synthesis. The inhibitory effects were related to the imbalance between ATP-producing and ATP-consuming processes in Ehrlich ascites tumor cells and also to their cell-cycle specificities.

An electrochemical technique was employed to study the ionization of the iodine complexes of triphenylstibine in 1,2-dichloroethane [35]. The cells were of the type  $\text{Pt}|\text{Ph}_3\text{Sb}, \text{I}_2||\text{Ph}_3\text{Sb}, \text{I}_2, \text{Et}_4\text{I}|\text{Pt}$ . At high concentrations of iodine relative to the stibine, the following reactions appeared to occur:

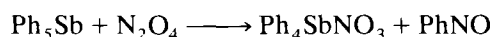


The cationic complex formed in the third reaction had not been proposed previously. The equilibrium constant for this reaction was estimated from the electrochemical data to be  $2.9 \times 10^{-2} \text{ M}^{-1}$ . Conductivity data supported the assumption that the triiodide complexes were completely ionized.

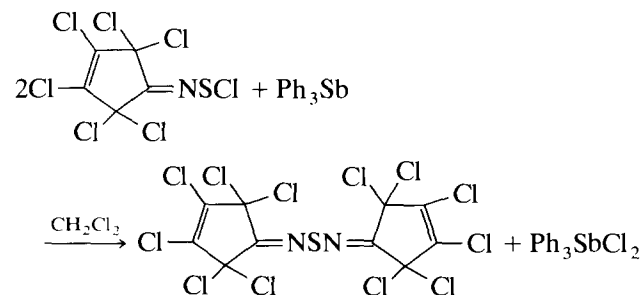
Triphenylstibine was included in a study that employed a conductometric titration technique for determining the stoichiometry of charge-transfer complexes that ionized in polar media [36]. Thus, conductometric titrations of iodine solutions against triphenylstibine were carried out at different concentrations (0.005, 0.01, and 0.02 M) in acetonitrile or acetonitrile–tetrachloromethane mixtures at 25, 30, 35, and 40°C. At a temperature of 25°C, the conductance maximum for the  $\text{Ph}_3\text{Sb}-\text{I}_2$  system in acetonitrile was found at a stoichiometry of about 1:4.

The oxidation of triphenylstibine with dinitrogen tetroxide was found to give the oxygen-bridged substance  $[\text{Ph}_3\text{Sb}(\text{ONO}_2)]_2\text{O}$  [37]. The interaction of pen-

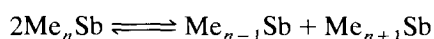
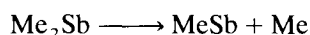
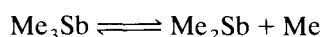
taphenylantimony and dinitrogen tetroxide resulted in cleavage of a Ph–Sb bond:



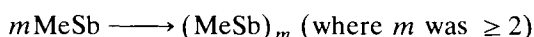
The use of triphenylstibine for the reductive dimerization of 2,2,3,4,5,5-hexachloro-3-cyclopentenylamidodisulfenyl chloride to a sulfoxylic diamide was reported [38]. Although the fate of the stibine was not elucidated, the oxidation–reduction presumably proceeded in accord with the following equation:



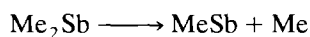
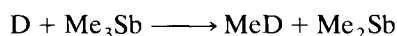
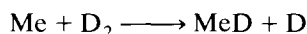
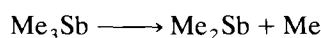
The importance of tertiary stibines as antimony sources for the production of Group III/V semiconductors by OMVPE (organometallic vapor-phase epitaxy) has prompted investigations of the decomposition mechanisms of trimethylstibine [39–41], trivinylstibine [40,42], triisopropylstibine [40,43], and triallylstibine [43]. In one study the pyrolysis of trimethylstibine in the temperature range 300–550°C was carried out with helium, hydrogen, or deuterium as the carrier gas [39]. The decomposition in helium appeared to be dominated by the following reactions:



(where  $n$  was 1 or 2)

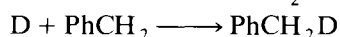
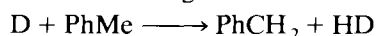


The addition of azomethane (which rapidly decomposed to nitrogen and methyl radicals) decreased the pyrolysis rate of the trimethylstibine. This effect was ascribed to the recombination of methyl and  $\text{Me}_2\text{Sb}$  radicals (see the first equation given above). When the helium atmosphere was used, there was no evidence for the abstraction of hydrogen atoms from the trimethylstibine. In a hydrogen or deuterium atmosphere, the pyrolysis occurred at much lower temperatures. In deuterium the main product was  $\text{MeD}$ . The following chain reaction was suggested:





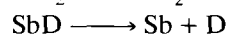
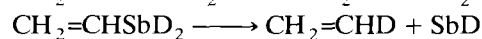
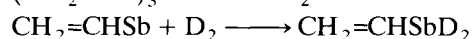
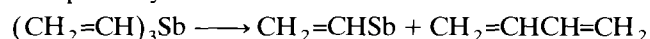
When toluene was added, small amounts of HD and PhCH<sub>2</sub>D were formed. These products were attributed to the following reactions:



The pyrolysis of a mixture of trimethylstibine and trimethylindium in a deuterium atmosphere was also studied. The decomposition rate of the stibine was found to increase, while the decomposition rate of the indium compound decreased. The effect of the latter substance was apparently indirect. It acted as a generator of deuterium atoms (via reaction of methyl radicals with the deuterium atmosphere), and these deuterium atoms then accelerated the decomposition rate of the trimethylstibine. The presence of the stibine, however, retarded the pyrolysis of the indium compound by depleting the concentration of deuterium atoms (which had already been shown to accelerate the pyrolysis of trimethylindium).

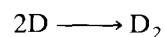
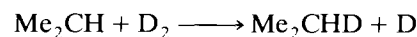
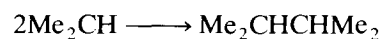
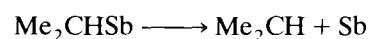
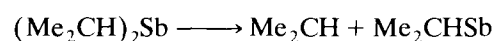
The vapor phase thermal decomposition of trimethylstibine, trimethylgallium, and mixtures of the two compounds in hydrogen or helium was investigated in another study with the aid of a hot-wall reactor and a mass spectrometer [41]. The disappearance curves of the starting materials and the appearance curves of stable gaseous products (methane and ethane) were determined as a function of temperature, residence time, and carrier flow. These results made it possible to deduce various kinetic parameters and to suggest the most likely reactions occurring in the vapor phase. When hydrogen was used as the carrier gas, it was found to take part in the reaction mechanisms with the formation of intermediate components. The decomposition of trimethylstibine in hydrogen appeared to involve the intermediacy of tetramethyldistibine. The latter substance was never found, however, when helium was used as the carrier gas. It was suggested that the bimetallic intermediate Me<sub>2</sub>SbGaMe<sub>2</sub> was formed during the thermal decomposition of mixtures of trimethylstibine and trimethylgallium, but this substance was not actually detected by the mass spectrometer.

The pyrolysis of trivinylstibine in the temperature range 300–550°C was studied in a reactor using helium or deuterium as the carrier gas [40,42]. The stibine was found to decompose at similar temperatures in both gases. Two alternative mechanisms for the pyrolysis in deuterium were proposed. One mechanism began with simple C–Sb bond homolysis to product vinyl radicals. The other mechanism (which was considered more likely) involved antimony-centered reductive elimination pathways:

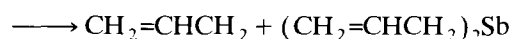


Addition of azomethane as a source of methyl radicals was found to accelerate the pyrolysis of the stibine in helium. This effect was ascribed to an attack of methyl radicals on the carbon atoms bonded to the antimony in the tertiary stibine. This attack was believed to cause cleavage of the C–Sb bond and the formation of propene. The addition of trimethylgallium was found to lower the decomposition temperature of the tertiary stibine in a deuterium atmosphere, presumably because the gallium compound was also a good source of methyl radicals. The decomposition of trivinylstibine alone or in a 1:1 ratio with trimethylgallium resulted in heavy carbonaceous deposits in the reactor. Decreasing the (CH<sub>2</sub>=CH)<sub>3</sub>Sb/Me<sub>3</sub>Ga ratio to 0.53, however, eliminated these deposits. At this lower ratio, therefore, trivinylstibine seemed potentially useful as a precursor for OMVPE.

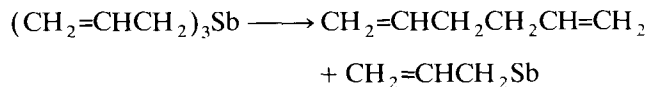
Pyrolysis reactions of triisopropylstibine [40,43] and triallylstibine [43] in an atmosphere of helium or deuterium were also investigated. The former compound was found to pyrolyze in the temperature range 250–350°C, while the latter pyrolyzed at 100–160°C. The ambient gas had no effect on the decomposition temperature of either tertiary stibine. The overall decomposition processes for both compounds were shown to be homogeneous and first order. The pyrolysis of triisopropylstibine in helium produced propene, propane, and 2,3-dimethylbutane; in a atmosphere of deuterium, a deuterated compound C<sub>3</sub>H<sub>7</sub>D was also formed. The decomposition of triisopropylstibine was believed to involve the following reactions:



The rate-determining step appeared to be the first reaction in the above series. Since the data obtained in the decomposition of triallylstibine were insufficient for establishing a unique mechanism, two possible schemes were suggested. One scheme began with homolytic cleavage of a C–Sb bond:



The other scheme involved reductive coupling:



Provided that homolysis was the rate-limiting step for the decomposition of both triisopropylstibine and triallylstibine, C–Sb bond strengths of 30.8 and 21.6 kcal mol<sup>-1</sup> for Me<sub>2</sub>CH–Sb and CH<sub>2</sub>=CHCH<sub>2</sub>–Sb, respectively, could be calculated from the experimental data. When either tertiary stibine was mixed with trimethylindium, a non-volatile liquid (probably an adduct) was obtained.

The highest mobility indium antimonide yet grown by OMVPE was obtained by using high purity trimethylstibine and trimethylindium as sources of the two metals, by carefully choosing the reactor geometry, and by taking care to control the flow of the organometallic compounds and the integrity of the reactor system [44]. Much of the work reported in this study involved growth optimization at 450°C. Growth at 425°C was also obtained but has not yet been optimized. Good morphology was not achieved at a growth temperature of 400°C. On a *p*-type indium antimonide substrate, an unintentionally doped layer was found to have a 77 K *n*-type carrier concentration of 1.4 × 10<sup>15</sup> cm<sup>-3</sup> and a mobility of 2.53 × 10<sup>5</sup> cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>. It was concluded that the epilayers prepared in this investigation possessed crystal quality, morphology, and cyclotron resonance characteristics comparable to state-of-the-art molecular beam epitaxy (MBE) layers.

Investigations have been reported of the effects of the ratio of trimethylstibine to triethylgallium on epilayer properties of gallium antimonide grown by low pressure metalorganic chemical vapor deposition (MOCVD) [45–48]. It was found that the surface morphology and the photoluminescence spectrum were strongly dependent on this ratio. A growth pressure of 100 torr was employed in these studies. Although the epilayers could be grown at temperatures ranging from 470 to 635°C, temperatures below 580°C appeared to be preferable.

Trimethylstibine was used as the antimony source in a study of epitaxial layers of the ternary substances In<sub>x</sub>Ga<sub>1-x</sub>Sb grown by MOCVD on gallium antimonide substrates at 600°C under pressures of 100 or 170 torr [49]. The variation of the indium composition in the solid with the vapor phase composition was studied with the aid of X-ray diffraction and photoluminescence (PL). The PL peak intensity was found to decrease rapidly with increasing lattice mismatch between the epilayers and the substrate.

Both trimethylstibine and triethylstibine were used as antimony sources for the low pressure (200 torr) MOCVD of indium antimonide [50]. The mobility of the indium antimonide was improved on the average by

70% as compared with samples grown under atmospheric pressure in the same reactor. All of the experiments were carried out at a temperature of 470°C in an atmosphere of hydrogen. The substitution of triethylstibine for trimethylstibine did not result in any improvement in the purity of the indium antimonide.

Trimethylstibine and triethylstibine were also employed as antimony sources for the preparation of InAs<sub>1-x</sub>Sb<sub>x</sub> strained-layer superlattices (SLS) and indium antimonide photodiodes by MOCVD [51]. The layers were grown at 470°C on indium antimonide substrates. Purified hydrogen was used as the carrier gas.

Triethylstibine was employed as the antimony source for the metalorganic molecular beam epitaxial (MOMBE) growth of gallium antimonide and ternary substances of the type InAs<sub>1-x</sub>Sb<sub>x</sub> [52]. The maximum growth rate for gallium antimonide was observed at a substrate temperature of 500°C. Precise control of the composition of the InAs<sub>1-x</sub>Sb<sub>x</sub> layers was accomplished in the temperature range from 400 to 500°C. No carrier gases were employed in these MOMBE growth experiments.

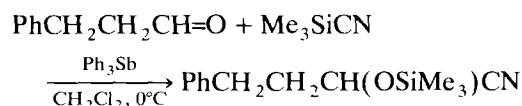
Triisopropylstibine was found to be an excellent antimony source for the production of thin films of indium antimonide by OMVPE [53,54]. Deposition temperatures as low as 300°C were successfully employed; this was the lowest temperature ever reported with a stable antimony source. Electronic transport measurements at 77 K on an unintentionally doped homoepitaxial layer of indium antimonide grown at 350°C yielded an *n*-type carrier concentration of 3.7 × 10<sup>16</sup> cm<sup>-3</sup> and a mobility of 6.3 × 10<sup>4</sup> cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>; the impurities responsible for the doping were believed to have come from the reagent grade chemicals used to prepare the tertiary stibine. Trimethylindium was employed as the indium source in this study.

In other investigations, triisopropylstibine was shown to be a viable antimony source for the OMVPE growth of both gallium antimonide and indium antimonide [55,56]. Trimethylgallium and trimethylindium were used as the sources of the Group III metals. The epilayers could be grown with good surface morphologies at temperatures between 430 and 600°C. The high growth efficiencies observed in this study suggested that there were few parasitic reactions between the stibine and trimethylgallium or trimethylindium. Hall-effect and photoluminescence measurements indicated that carbon contamination of the epilayers was minimal. The gallium antimonide layers grown at 500°C were *p*-type with a hole concentration at room temperature of 2 × 10<sup>16</sup> cm<sup>-3</sup>. Indium antimonide layers grown at 475°C were *n*-type with electron concentrations of approximately 5 × 10<sup>16</sup> cm<sup>-3</sup> at 77 K.

Tributylstibine was employed for the preparation of alumina-supported bimetallic catalysts of palladium al-

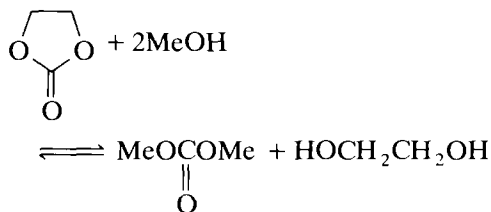
loyed with antimony [57]. A Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was first treated with hydrogen at 573 K, cooled in flowing hydrogen, and purged with nitrogen. It was then kept in contact (72 h at 363 K) with a solution of the tertiary stibine in heptane. Subsequently, the catalyst was dried at 393 K, and the tertiary stibine that had been deposited on the Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was reduced to metallic antimony in a hydrogen atmosphere at 573 or 773 K. The usefulness of these bimetallic catalysts for the gas-phase hydrogenation of 2-methyl-1-buten-3-yne (valylene) and 2-methyl-1,3-butadiene (isoprene) was then investigated.

Tributylphosphine, triphenylphosphine, triphenylarsine, triphenylstibine, and a number of amines were found to catalyze the facile formation of trimethylsilyl ethers of cyanohydrins by the addition of trimethylsilyl cyanide to aldehydes [58]. Thus, 10 mol% of triphenylstibine led to an 88% yield of the ether in the following case:



A mechanism was suggested that involved a hypervalent silicon derivative as the active cyanation intermediate.

Triphenylphosphine, -arsine, and -stibine were included in a study of catalysts for the transesterification of ethylene carbonate by methyl alcohol [59]:



The effectiveness of the three phenyl derivatives was in the order Ph<sub>3</sub>P ≫ Ph<sub>3</sub>As > Ph<sub>3</sub>Sb. The dimethyl carbonate formed in the above reaction was said to be useful as a gasoline octane enhancer, a methylating agent, and a urethane precursor.

The addition of triphenylstibine to molybdenum(V) chloride was shown to have a beneficial effect on the catalytic activity of the latter substance for the polymerization of 1-methylthio-1-alkynes of the type MeSC≡CR, where R was Et, Bu, Hex, or Oct [60]. In each case, the presence of the stibine increased both the yield and the molecular weight of the polymer.

Triphenylstibine has also been found to enhance the catalytic effect of tungsten(VI) chloride on the polymerization of (4-butyl-2,3,5,6-tetrafluorophenyl)acetylene and (pentafluorophenyl)acetylene [61]. In both cases, the yields of polymers were increased. The polymers were dark brown solids, and their main-chain structure consisted of alternating double bonds. Fur-

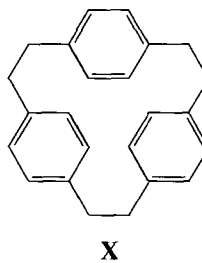
ther information about this study is given in the Annual Survey of Bismuth for 1991 [29].

Triethylstibine was found to inhibit the corrosion of iron exposed to 1 N HClO<sub>4</sub>, 1 N HCl, or 1 N H<sub>2</sub>SO<sub>4</sub> [62]. This effect was studied with the aid of polarization and impedance measurements. High inhibition efficiency (> 90%) was obtained at an extremely low concentration of the stibine (5 × 10<sup>-8</sup> M). This excellent result was attributed to the formation on the iron surface of a thin, highly persistent adhesive film that contained among other species the triethylstibonium (Et<sub>3</sub>SbH<sup>+</sup>) ion. The use of trialkyl- or triarylstibines for preventing the corrosion of iron alloys and steels in acidic solutions has also been reported in the Japanese patent literature [63].

A Japanese patent also described the use of trimethylstibine as the antimony source for obtaining a semiconducting crystal of gallium antimonide by atomic layer epitaxial growth [64]. Another Japanese patent claimed that triphenylstibine was effective as a catalyst in the manufacture of polycarbonates [65]. An American patent has reported that ceramic-metal intercalation compounds useful for dense cermet manufacture were prepared by exposing a ceramic to an organometallic compound (e.g. triphenylstibine) in a low dielectric solvent [66].

In addition to a paper already discussed [16], there have been a considerable number of other recent publications that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included cobalt [67,68], copper [69], iron [70–72], molybdenum [73–76], osmium [77], palladium [78], rhodium [79–81], ruthenium [82,83], silver [69], and tungsten [73,74].

The interaction of antimony trichloride and [2.2.2]paracyclophane (X) in benzene solution was found to yield the  $\pi$ -complex C<sub>24</sub>H<sub>24</sub> · 2SbCl<sub>3</sub> ·  $\frac{1}{2}$ PhH [84].

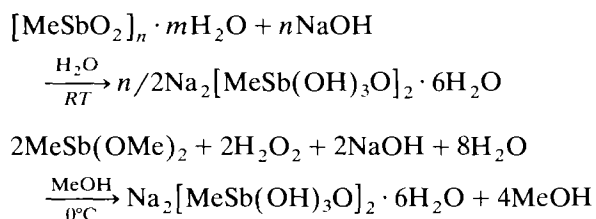


The complex melted in a sealed tube at 94°C. In a stream of nitrogen or in a vacuum, the crystals disintegrated with the evolution of the benzene of crystallization. The PMR spectrum of the complex in acetone-d<sub>6</sub> indicated extensive dissociation and/or fluxionality. X-ray crystallography showed SbCl<sub>3</sub> coordination to two of the benzene rings of the hydrocarbon in a quasi-centered  $\eta^6$  mode, while one of the benzene rings remained uncoordinated. The distances between the antimony atoms and the centers of the coordinated

benzene rings were 3.047 and 3.050 Å. Intermolecular chlorine-bridging between antimony atoms led to the presence of tetrameric units in the crystal lattice.

Raman spectroscopy at 77 K was employed to study the 2:1 Menshutkin complexes of antimony trichloride with benzene, biphenyl, or phenanthrene [85]. The experimentally observed spectra made it possible to perform a group theoretical analysis and a normal coordinate analysis of the antimony trichloride vibrations in the crystals. The interpretation of the observed vibrational frequencies in the intramolecular vibration region and in the lattice mode region was accomplished without the use of polarization measurements. The method of frequency calculation that was used to interpret the lattice modes did not require a knowledge of the intermolecular potential in an explicit form.

Wieber and Walz [86] described the preparation of methylstibonic acid and its sodium salt,  $\text{Na}_2[\text{MeSb}(\text{OH})_3\text{O}]_2 \cdot 6\text{H}_2\text{O}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, the IR spectrum, and the crystal structure of the sodium salt have now been reported [87]. Two synthetic methods for the preparation of this salt were employed:



The yields by either method were quantitative. Thermogravimetric analysis showed that 6 mol of water were lost in the temperature range 71–165°C, followed by a loss of 2 mol of methane in the temperature range 165–223°C. Further heating to 350°C resulted in further loss of water to give sodium antimonate  $\text{NaSbO}_3$ . The PMR spectrum gave two peaks centered at 1.28 ppm. The two peaks were very close together. The  $^{13}\text{C}$  NMR spectrum was a single peak at 15.87 ppm. From the IR spectral data, assignments were made for  $\nu\text{Sb}-\text{O}-\text{Sb}$  ( $780\text{ cm}^{-1}$ ),  $\nu\text{Sb}_2\text{O}_2$  ( $532\text{ cm}^{-1}$ ), and  $\nu\text{Sb}-\text{C}$  ( $388\text{ cm}^{-1}$ ). The crystal structure of the salt was determined by X-ray diffraction. Each antimony atom was a slightly distorted octahedron. The anion contained a four-membered ring with  $\text{Sb}-\text{O}-\text{Sb}$  bonds. The  $\text{O}-\text{Sb}-\text{O}$  angles were  $79.5^\circ$ ; the  $\text{Sb}-\text{O}-\text{Sb}$  angles were  $100.5^\circ$ . This structural feature was very similar to the four-membered ring found in  $(\text{Ph}_3\text{SbO})_2$ .

A US patent [88] described the preparation of a tungstate complex of phenylstibonic acid,  $(\text{CN}_3\text{H}_6)_6-(\text{PhSb})_2\text{W}_8\text{O}_{22} \cdot 3\text{H}_2\text{O}$ , (where  $\text{CN}_3\text{H}_6$  was the guanidinium cation) which was active against HIV in T4 lymphocytes with an  $\text{IC}_{50}$  value of  $22.4\text{ }\mu\text{g ml}^{-1}$ . The phenylstibonic acid was prepared by diazotizing aniline in isopropyl alcohol solution in the presence of antimony trichloride.

Zaitseva et al., in a series of papers, examined the effect of increasing the electron-donating properties of a ligand to an atom such as antimony on other ligands to the same central atom. In the first paper in this series [89] they prepared three compounds  $\text{Cs}[\text{PhSbCl}_5]$ ,  $\text{K}[\text{PhSbBr}_5]$ , and  $\text{Cs}[\text{SbCl}_6]$  and determined their crystal structures by X-ray diffraction. The geometry of the antimony atom in all three compounds was octahedral. Although  $\text{Cs}[\text{PhSbCl}_5]$  and  $\text{K}[\text{PhSbBr}_5]$  crystallized in different space groups, their atomic arrangements were similar. Each antimony atom was surrounded by five halogen atoms with a phenyl group and one halogen in *trans* positions of the slightly distorted octahedron. In  $\text{Cs}[\text{SbCl}_6]$ , however, the coordination polyhedron was an almost regular octahedron. The  $\text{Sb}-\text{Cl}$  and  $\text{Sb}-\text{Br}$  distances in  $\text{Cs}[\text{PhSbCl}_5]$  and  $\text{K}[\text{PhSbBr}_5]$  were longer than the  $\text{Sb}-\text{Cl}$  and  $\text{Sb}-\text{Br}$  distances in  $\text{Cs}[\text{SbCl}_6]$  and  $\text{Cs}[\text{SbBr}_6]$  (the latter from literature values). The lengthening averaged  $0.05\text{ }\text{\AA}$  for the Cl atom *cis* to the phenyl group and  $0.07\text{ }\text{\AA}$  for the atom *trans* to the phenyl group. For  $\text{K}[\text{SbBr}_5]$  the lengthening averaged  $0.01\text{ }\text{\AA}$  for the *cis* positions and was  $0.05\text{ }\text{\AA}$  for the *trans* position. This result was in contrast to the results previously reported for organohalogen compounds of Sn(IV) and Pb(IV) with similar structures where there was a *cis* lengthening and a *trans* contraction of the metal-halogen bonds.

In a second paper from Zaitseva's laboratory the three compounds  $\text{NH}_4[\text{PhSbCl}_5]$ ,  $\text{NH}_4[\text{PhSbBr}_5]$ , and  $\text{Me}_2\text{NH}_2[\text{PhSbCl}_5]$  were synthesized and their crystal structures determined by X-ray diffraction [90]. The  $\text{Sb}-\text{Cl}$  bonds in the two  $[\text{PhSbCl}_5]^-$  anions were lengthened in both *cis* and *trans* positions as compared with the  $[\text{SbCl}_6]^-$  anion. The lengthening averaged  $0.05\text{ }\text{\AA}$  for the *cis* positions for both compounds, and was  $0.06\text{ }\text{\AA}$  for the *trans* position in  $\text{NH}_4[\text{PhSbCl}_5]$  and was  $0.07\text{ }\text{\AA}$  for the *trans* position in  $\text{Me}_2\text{NH}_2[\text{PhSbCl}_5]$ . However, for the compound  $\text{NH}_4[\text{PhSbBr}_5]$ , the  $\text{Sb}-\text{Br}$  bond was contracted by  $0.04\text{ }\text{\AA}$  for the *trans*  $\text{Sb}-\text{Br}$  bond, while the *cis*  $\text{Sb}-\text{Br}$  bonds were practically identical with those in the  $[\text{SbBr}_6]^-$  anion. The authors pointed out, however, that anion-cation interactions could affect the structure of the  $[\text{PhSbX}_5]^-$  anion. Thus, in  $\text{Cs}[\text{PhSbCl}_5]$  and  $\text{K}[\text{PhSbBr}_5]$ , the cation could have a polarizing effect, while in  $\text{NH}_4[\text{PhSbCl}_5]$ ,  $\text{NH}_4[\text{PhSbBr}_5]$ , and  $\text{Me}_2\text{NH}_2[\text{PhSbCl}_5]$ , the cation could affect the anion as a result of hydrogen bonding.

Although there were indications that replacement of a halogen by a phenyl group in the anion  $[\text{SbX}_6]^-$  resulted in a lengthening of the other  $\text{Sb}-\text{X}$  bonds, the results were equivocal owing to either the polarizing effect of the cation or hydrogen bonding between the anion and cation. Accordingly, Zaitseva et al. [91] prepared the salts  $\text{PyH}[\text{PhSbCl}_5] \cdot \text{H}_2\text{O}$ ,  $\text{PyH}[\text{PhSbBr}_5] \cdot \text{H}_2\text{O}$ , and  $\text{QH}[\text{PhSbCl}_5]$ , where  $\text{PyH}$  was the pyridinium cation and  $\text{QH}$  was the quinolinium cation. The

authors stated that the pyridinium and quinolinium ions would have a much lower polarizing effect than  $\text{Cs}^+$  or  $\text{K}^+$  ions, and would have less tendency to hydrogen bond to the anion. The crystal structures of the three new compounds were determined by X-ray diffraction. The geometry of the antimony atom was octahedral in all three compounds, with the phenyl group and one halogen in *trans* positions. The N–O distances in the two pyridinium compounds were less than the sum of the covalent radii for these elements which indicated hydrogen bonding between the water molecule of crystallization and the pyridinium nitrogen atom. There were no hydrogen bonds between the cation and the  $[\text{PhSbX}_5]^-$  anions, but there was hydrogen bonding in the quinolinium salt. The crystal structure determinations revealed a lengthening of the Sb–X bonds in  $[\text{PhSbX}_5]^-$  compared with  $[\text{SbX}_6]^-$  for the *cis* halogen bonds. The average increase in lengths were 0.044 Å for  $\text{PyH}[\text{PhSbCl}_5]$ , 0.038 Å for  $\text{PyH}[\text{PhSbBr}_5]$ , and 0.054 Å for  $\text{H}[\text{PhSbCl}_5]$ . The lengths of the *trans* Sb–X bonds were the same, within standard deviations, as the Sb–X distances in the  $[\text{SbX}_6]^-$  ions.

Zaitseva et al. [92] also prepared the salt pyridinium tetrachlorodiphenylantimonate(V) by two different methods. Both methods involved the decomposition of the so-called May's salt,  $[\text{PhN}_2][\text{SbCl}_4]$ . In one method iron powder was added to the May's salt in acetone at 0°C; in the other method zinc powder was added to the May's salt in ethyl acetate at 60°C. Both products were crystallized from a 1:1:1 mixture of water–concentrated hydrochloric acid–ethanol. By the first method colorless prisms were obtained, by the second method matte needles. The structures of both modifications were determined by X-ray diffraction. The geometry of the antimony atom in both modifications was a distorted octahedron with four chlorines forming the equatorial plane and with the two phenyl groups at right angles to this plane. The phenyl groups in the first modification were oriented in parallel planes, but in the second modification the phenyl groups were mutually perpendicular. The Sb–Cl distance was 2.46 Å, which was 0.05 Å greater than the *cis* Sb–Cl distance in  $[\text{PhSbCl}_5]^-$  and 0.10 Å greater than the Sb–Cl average distance in  $[\text{SbCl}_6]^-$ . In neither modification were there any cation–anion contacts less than or equal to the sum of the van der Waals radii of the Cl and N atoms. These results confirmed the successive *cis* extension of the Sb–Cl bond by 0.05 increments in the stepwise replacement of the Cl ligand by phenyl groups in going from  $[\text{SbCl}_6]^-$  to  $[\text{PhSbCl}_5]^-$  to  $[\text{Ph}_2\text{SbCl}_4]^-$ . In another paper from Zaitseva's laboratory [93], the salt  $\text{NH}_4[\text{PhSbF}_5] \cdot \text{NH}_4[\text{HF}_2]$  was prepared from phenylstibonic acid and excess ammonium fluoride in hydrofluoric acid. It was recrystallized from 1:1 hydrofluoric acid/ethanol. The antimony atom in the anion was a distorted octahedron with the phenyl

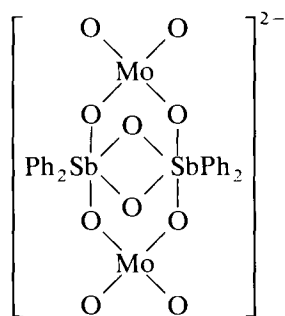
group and one fluorine atom in apical positions. Several cation–anion contacts were less than the sum of the van der Waals radii of the nitrogen and fluorine atoms which indicated  $\text{NH} \cdots \text{F}$  hydrogen bonds. However, owing to the poor crystal quality, unequivocal conclusions concerning interactions between the ions could not be reached.

Alonzo et al. [94] prepared the interesting compound 1,10-phenanthroline tetrachloromethoxyphenylantimonate(V) by the reaction between ammonium pentachlorophenylantimonate(V) and phenanthroline in methanol solution. The product crystallized from solution as a white crystalline solid, mp 145°C (decomp.). It was characterized by elemental analyses, IR and Mössbauer spectroscopy, and by X-ray diffraction. The crystal structure contained two independent anionic  $[\text{PhCl}_4\text{SbOCH}_3]^-$  groups and two independent cationic phenanthroline groups. The coordination around each antimony atom was octahedral with four chlorine atoms forming a plane and with the phenyl and methoxy groups perpendicular to this plane. The Sb–Cl, Sb–C, and Sb–O distances were comparable with those found in similar compounds. The N–O distances between the oxygens of the methoxy groups and the protonated nitrogens of the phenanthroline cations suggested  $\text{NH} \cdots \text{O}$  hydrogen bonding between these two ions. Assignments for  $\nu\text{Sb–Cl}$  and  $\nu\text{Sb–O}$  in the IR spectrum were made by comparison with the spectra of  $[\text{PhSbCl}_5]^-$  and  $[\text{Sb}(\text{OMe})_6]^-$  ions. The  $^{121}\text{Sb}$  Mössbauer spectrum was compared with published data for the  $[\text{PhSbCl}_5]^-$  ion and rationalized by taking into account the substitution of Cl for MeO ligands in a position *trans* to the organic residue.

Raj and Misra [95] prepared a number of 1:1 adducts of diaryltrichloroantimony compounds with a variety of Lewis bases containing oxygen or nitrogen donors. The antimony compounds used were  $\text{Ph}_2\text{SbCl}_3$ ,  $(4\text{-MeC}_6\text{H}_4)_2\text{SbCl}_3$ ,  $(4\text{-ClC}_6\text{H}_4)_2\text{SbCl}_3$ ,  $(4\text{-MeOC}_6\text{H}_4)_2\text{SbCl}_3$ , and  $(4\text{-FC}_6\text{H}_4)_2\text{SbCl}_3$ , and the Lewis bases used were dibenzyl sulfoxide, dibutyl sulfoxide, triphenylarsine oxide, pyridine 1-oxide, triphenylphosphine oxide, pyridine,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -picoline, DMF, HMPA, and thiourea. The adducts were prepared by stirring equimolar amounts of the two reactants in methanol solution for 1 h at room temperature, then refluxing for 0.5 h. After removal of the solvent, the resulting white solids were recrystallized from dichloromethane-petroleum ether. They possessed sharp melting points and were characterized by IR and PMR spectroscopy. They were monomolecular by cryoscopic determinations in nitrobenzene. Conductivity measurements in methanol and nitrobenzene showed the adducts to be non-ionic. With oxygen donor ligands (S–O, P–O, N–O, and As–O), the values of the above stretching bands in the IR spectra appeared at lower frequencies as compared with the free ligands,

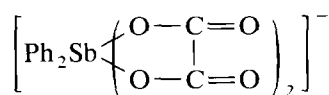
whereas with nitrogen donor ligands the values of the  $\nu_{\text{C=N}}$  bands appeared at higher frequencies. The PMR spectra of the two complexes  $(4\text{-MeC}_6\text{H}_4)_2\text{SbCl}_3 \cdot \text{DMSO}$  and  $(4\text{-MeC}_6\text{H}_4)_2\text{SbCl}_3 \cdot \text{HMPA}$  showed sharp singlets for the methyl protons of the tolyl groups and the donor ligands. On the basis of the IR and PMR results, and the monomeric and non-ionic nature of the complexes, the authors suggested that the configuration of the antimony atoms in each compound was octahedral, with the aryl groups in *trans* positions.

Liu et al. prepared the quadruply bridged dianion **XI** by the reaction of diiodotriphenylantimony and bis(tetrabutylammonium) molybdate [96].



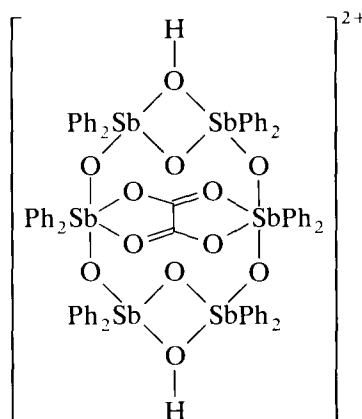
**XI**

Southerington et al. [97], in a paper from Sowerby's laboratory, suggested that the same compound could be readily prepared from bis(bromo- $\mu$ -oxodiphenylantimony),  $(\text{Ph}_2\text{SbBrO})_2$ , and bis(tetrabutylammonium) molybdate, and indeed they did obtain the expected compound from the two reactants in chloroform solution. They then treated the same antimony compound with one molar equivalent of silver oxalate in chloroform solution expecting to obtain the neutral mono-oxalate triply-bridged analog of **XI**. Instead, they obtained an ionic compound with a doubly charged cation and two singly charged dioxalato-diphenylantimony anions. The compound was characterized by IR spectroscopy and X-ray diffraction. The anion was the *cis* isomer with one phenyl group and an oxalato oxygen in *trans* position:



The complex cation contained a 12-membered planar ring with six antimony atoms and two four-membered  $\text{Sb}_2\text{O}_2$  rings. One oxygen atom on each of these rings carried a hydrogen atom that was hydrogen bonded to an oxalato oxygen of the anion. The two center antimony atoms were connected by a single tetradentate

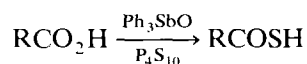
oxalato group. Thus, the cation possessed the following structure:



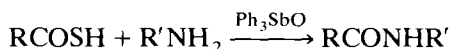
The doubly-bridged antimony atoms possessed distorted trigonal-bipyramidal geometry while the two center antimony atoms, bridged by the tetradentate oxalato group, possessed distorted octahedral geometry. The anion contained one molecule each of chloroform and acetonitrile of crystallization.

Nomura et al. [98] recently reported that a mixture of triphenylstibine oxide and tetraphosphorus decasulfide was an excellent reagent mixture for converting carboxylic acids into the corresponding thioic acids. These authors have now reported that carboxylic acids can be readily esterified under very mild conditions with catalytic amounts of  $\text{Ph}_3\text{SbO}$  and  $\text{P}_4\text{S}_{10}$  [99]. Thus, acetic acid and 1-butanol gave a 91% yield of butyl acetate by using catalytic amounts of  $\text{Ph}_3\text{SbO}$  and  $\text{P}_4\text{S}_{10}$ , and allowing the mixture to stand for 5 h at 25°C. Both components of the catalytic mixture were required to effect the esterification. The reaction was then extended to the preparation of a number of esters. Both aromatic and aliphatic acids were esterified under mild conditions in large yields. Benzoic acid and phenol gave phenyl benzoate in 55% yield when the reactants were warmed to 50°C for 24 h in the presence of the catalyst. Pivalic acid and 1-hexanol gave the ester in 69% yield after heating to 80°C for 24 h, but the same acid and *tert*-butyl alcohol gave the ester in only 10% yield. Adipic acid gave diethyl adipate, and *N*-carbobenzyloxyglycine gave the ethyl ester in 90% yield. The authors suggested that the use of  $\text{Ph}_3\text{SbO}/\text{P}_4\text{S}_{10}$  for the esterification of carboxylic acids was superior to all other direct esterification methods.

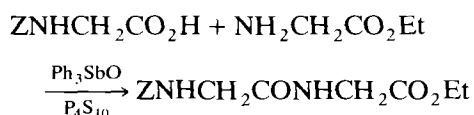
As noted in the above paragraph, Nomura et al. showed that a mixture of triphenylstibine oxide and tetraphosphorus decasulfide could be used for the conversion of carboxylic acids to the corresponding thioic acids:



Triphenylstibine oxide was also found to be a catalyst for converting thiolic acids to amides:



The Japanese authors have now combined the two reactions to produce amides by a one pot synthetic procedure [100]. Thus, *N*-hexylacetamide was prepared in 90% yield from acetic acid, hexylamine, tetraphosphorus decasulfide, and triphenylstibine oxide. A number of other amides RCONHR', where R and R' were aliphatic or aromatic groups, were similarly obtained. Ethanolamine gave *N*-(2-hydroxyethyl)acetamide in 95% yield. The method was also successful for the preparation of dipeptide esters from *N*-protected amino acids and amino acid esters:



(where Z was a group such as benzyloxycarbonyl).

Shi, Basolo, and coworkers published several papers on the kinetics and mechanism of oxygen atom transfer from  $\text{Me}_3\text{NO}$  to metal carbonyls. These authors [101] then extended their studies to the oxygen atom transfer of the bases  $(4\text{-MeOC}_6\text{H}_4)_2\text{EO}$  (where E = Se or Te) and  $\text{Ph}_3\text{EO}$  (where E is arsenic or antimony). Some data were also listed for the bases  $\text{Me}_3\text{NO}$ ,  $\text{PhIO}$ ,  $\text{Ph}_3\text{PO}$ ,  $\text{Ph}_2\text{SO}$ , and pyridine *N*-oxide. The base strengths of the oxides were determined by the IR shifts of the O–H stretching frequency ( $\Delta\nu_{\text{O-H}}$ ) on the addition of the base to a solution of methanol in carbon tetrachloride. The base strengths were in the order  $\text{R}_3\text{NO} > \text{R}_2\text{TeO} \sim \text{R}_3\text{AsO} \sim \text{R}_3\text{SbO} > \text{R}_2\text{SeO} > \text{pyridine } N\text{-oxide} > \text{R}_3\text{PO} > \text{R}_2\text{SO}$ . The reactions of the bases listed above with the metal carbonyls  $\text{Cr}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$  were studied. Neither  $\text{Ph}_3\text{PO}$  nor  $\text{Ph}_2\text{SO}$  reacted with either carbonyl compound.  $\text{Ph}_3\text{SbO}$  did not react with  $\text{Cr}(\text{CO})_6$  under the experimental conditions used, but did react with  $\text{Fe}(\text{CO})_5$  to give the known compound  $\text{Fe}(\text{CO})_4\text{SbPh}_3$ . The reaction was carried out under heterogeneous conditions, i.e. adding solid  $\text{Ph}_3\text{SbO}$  to a solution of  $\text{Fe}(\text{CO})_5$  in THF. A second order rate constant  $\geq 4 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  was calculated. This rate constant was compared with the rate constant obtained by the reaction of  $\text{Ph}_3\text{AsO}$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Bu}_3\text{P}$  to give  $\text{Fe}(\text{CO})_4\text{PBu}_3$ , and with the rate constants obtained by the reaction of  $(4\text{-MeOC}_6\text{H}_4)_2\text{SeO}$  or  $(4\text{-MeOC}_6\text{H}_4)_2\text{TeO}$  with  $\text{Cr}(\text{CO})_6$  to give relative rates of oxygen transfer in the order  $\text{TeO} > \text{SeO} > \text{SbO} > \text{AsO}$ . It was concluded that no quantitative assessment was possible of each of the factors believed to contribute to the rates of oxygen atom transfer in these reactions.

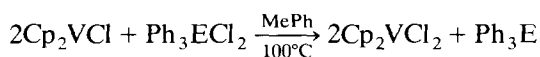
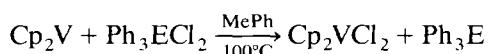
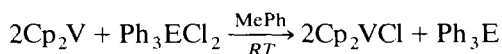
Ferguson et al. [102] prepared bis(trifluoroacetato)-triphenylantimony and the corresponding bismuth compound, and determined their structures by X-ray diffraction. The antimony compound was a slightly distorted trigonal bipyramid with equatorial phenyl groups and axial trifluoroacetato groups. In contrast to the bismuth compound, where there was considerable interaction between the carbonyl oxygens and the bismuth atom, there was essentially no carbonyl oxygen–antimony interaction. The Sb–O (carbonyl) distances were considerably longer than the Sb–O (bonding oxygen) distances with ratios of 1.50 and 1.52 for the two trifluoroacetato groups. This paper is discussed in greater detail in the Annual Survey of Bismuth for 1991 [29].

Dwivedi et al. [103] prepared a series of organoantimony xanthates of the type  $\text{Ph}_3\text{Sb}[\text{SC}(\text{S})\text{OR}]_2$  (where R = Me, Et, Pr,  $\text{Me}_2\text{CH}$ , Bu,  $\text{Me}_2\text{CHCH}_2$ ,  $\text{Me}(\text{CH}_2)_3\text{CH}_2$ , or  $\text{PhCH}_2$ ) by the reaction of  $\text{Ph}_3\text{SbBr}_2$  with the corresponding potassium xanthate. The IR spectra of the products showed that the antimony–xanthate linkage was unidentate and the antimony atom was penta-coordinate. In addition to the IR data, the compounds were characterized by molecular weight and conductivity determinations (both in nitrobenzene), but the actual data were not given. The compounds were said to be monomolecular and nonelectrolytes.

In a previous paper, Yanaga et al. [104] reported the Mössbauer spectra of four inorganic antimony compounds ( $\text{SbCl}_3$ ,  $\text{SbBr}_3$ ,  $\text{SbI}_3$ , and  $\text{SbCl}_5$ ) and one organic antimony compound ( $\text{Me}_3\text{SbCl}_2$ ) in dichloroethane solutions at 20 K. The isomer shifts were compared with the electron densities at the antimony nuclei calculated by Hartree-Fock molecular orbital calculations. From the data obtained a value for  $\Delta R/R = -(11 \pm 2) \times 10^{-4}$  for the 37.15 keV M1 transition of  $^{121}\text{Sb}$  was calculated (where  $\Delta R/R$  was the relative change of the effective charge radius between the excited and the ground state of the Mössbauer nucleus). These same authors then expanded their results to include Mössbauer data on  $\text{Me}_3\text{SbF}_2$  both in frozen solution and in the crystalline state [105]. The value of  $\Delta R/R = -(10.2 \pm 1.0) \times 10^{-4}$  for the 37.15 keV transition of  $^{121}\text{Sb}$  was calculated. Some computations of the electron density at the tin nucleus for several inorganic tin compounds were also obtained. By comparing valence electron contact densities with isomer shifts obtained from Mössbauer spectroscopy, a value for  $\Delta R/R$  for the 23.87 keV M1 transition of  $^{119}\text{Sn}$  was estimated. Contact densities of isoelectronic pairs of Sb and Sn compounds were plotted against each other. In a similar manner, isomer shifts of isoelectronic pairs of Sb and Sn compounds were plotted against each other.

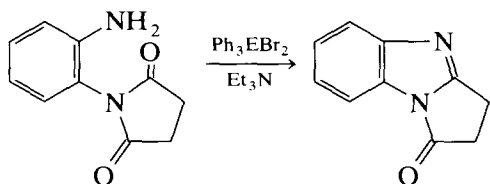
Sharutin and Bychkov [106] found that both vanadocene and cobaltocene reduced dichlorotriphenyl-

lantimony (or dichlorotriphenylbismuth) to triphenylstibine (or triphenylbismuthine):



(where E = Sb or Bi). In a similar manner cobaltocene and dichlorotriphenylantimony in toluene solution at 100°C gave chlorodicyclopentadienylcobalt and triphenylstibine. The reactions were carried out in sealed glass ampoules.

In a paper devoted to the effect of Group 15 organometallic compounds of the type  $\text{R}_3\text{EBr}_2$  (where R was an alkyl or aryl group; and E = P, As, or Sb) on the following cyclization reaction, dibromotriphenylantimony was found to be ineffective, whereas the corresponding phosphorus and arsenic compounds gave the product in 58% and 52% yields, respectively [107]:



It was suggested that the mechanism of the cyclization involved a nucleophilic attack of the amino group on the cation  $[\text{Ph}_3\text{EBr}]^+$ , and that the inability of the antimony compound  $\text{Ph}_3\text{SbBr}_2$  to ionize in solution was the reason why it was ineffective as a catalyst for the cyclization reaction.

A mixture of organic tin halides (e.g.  $\text{Me}_2\text{SnI}_2$ ) and organic antimony(V) halides (e.g.  $\text{Ph}_3\text{SbI}_2$ ) served as a catalyst for the preparation of thermosetting polyisocyanate-polyepoxide heat-resisting moldings [108].

Naoshima and Carraher [109] described the condensation of dichlorotriphenylantimony with the polysaccharide xylan to produce a water-insoluble precipitate. This work is essentially a repeat of a previous paper [110] which was summarized in the Annual Survey of Antimony for 1990 [111].

In a paper largely devoted to the polar effect of substituents on the Ni–O bond in compounds of the type  $(2\text{-FC}_6\text{H}_4)(\text{Ph}_3\text{P})_2\text{NiO}_2\text{CC}_6\text{H}_4\text{R}$ , a comparison of the polarity of the Ni–O bond with the polarity of the Sb–O bond in compounds of the type  $\text{Ph}_4\text{SbO}_2\text{CC}_6\text{H}_4\text{R}$  was made [112]. The polarity of the Ni–O bond significantly exceeded the polarity of the Sb–O bond in a number of substituted benzoic acid compounds studied.

In a preliminary communication [113], Huang et al. reported that benzyltributylantimony bromide, when treated with an alkyl- or phenyllithium reagent, followed by treatment with an aldehyde, gave, after hy-

drolisis, homobenzylic alcohols. In this manner, 1,2-diphenylethanol was obtained from benzyltributylantimony bromide and benzaldehyde. The authors suggested that the reaction involved the formation of a pentaalkyl- or tetraalkylphenylantimony compound  $\text{Bu}_3\text{SbR}(\text{CH}_2\text{Ph})$  (where R is phenyl or an alkyl group) which, by nucleophilic attack on the aldehyde  $\text{R}'\text{CHO}$ , gave the intermediate  $\text{R}'\text{CH}(\text{CH}_2\text{Ph})\text{OSbR}_3$ . Hydrolysis then gave the homobenzylic alcohol  $\text{R}'\text{CH}(\text{CH}_2\text{Ph})\text{OH}$ . Huang and Liao [114] then extended this reaction to the preparation, not only of homobenzylic alcohols, but also to the preparation of homoallylic alcohols, hydroxyesters, and hydroxynitriles. Thus, from the aldehydes  $\text{R}'\text{CHO}$  (where  $\text{R}'$  is Ph, 4- $\text{ClC}_6\text{H}_4$ , 4- $\text{MeC}_6\text{H}_4$ ,  $\text{PhCH}=\text{CH}$ , or 2-pyridyl) the corresponding homobenzylic alcohols  $\text{R}'\text{CH}(\text{OH})\text{CH}_2\text{Ph}$  were obtained in yields which varied from 77–98% (based on the aldehyde used). In all but one reaction, where  $\text{Et}_3(\text{CH}_2\text{Ph})\text{SbBr}$  was used, the starting antimony compound was  $\text{Bu}_3(\text{CH}_2\text{Ph})\text{SbBr}$ . Three different organolithium compounds  $\text{BuLi}$ ,  $\text{PhLi}$ , and  $\text{Me}_3\text{CLi}$  were used; all three gave essentially the same yields. The reactions were carried out in THF solution at  $-78^\circ\text{C}$ , and the products were purified by column chromatography. The reaction failed with the ketones acetophenone and benzophenone.

If, instead of benzyltributylantimony bromide, allyltributylantimony bromide was used, homoallylic alcohols  $\text{R}'\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$  were obtained in yields of 68–92%. In these reactions  $\text{R}'$  was the same as in the preparation of the homobenzylic alcohols. In addition, in one reaction  $\text{R}'\text{CHO}$  was citral which gave the homoallylic alcohol in 72% yield. Another series of reactions employed the carboethoxyallyl compound  $[\text{Bu}_3(\text{CH}_2\text{CH}=\text{CHCO}_2\text{Et})\text{Sb}]\text{BPh}_4$  and yielded the ethyl 5-aryl-5-hydroxypent-2-enoates,  $\text{R}'\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CHCO}_2\text{Et}$ , where  $\text{R}'$  was Ph, 4- $\text{ClC}_6\text{H}_4$ , 4- $\text{BrC}_6\text{H}_4$ , 4- $\text{FC}_6\text{H}_4$ , 4- $\text{MeC}_6\text{H}_4$ , or 4- $\text{O}_2\text{NC}_6\text{H}_4$ . The yields varied from 55% ( $\text{R}' = 4\text{-FC}_6\text{H}_4$ ) to 98% ( $\text{R}' = 4\text{-ClC}_6\text{H}_4$ ). Another series of reactions led to the preparation of  $\beta$ -hydroxypropionates,  $\text{R}'\text{CH}(\text{OH})\text{CH}_2\text{CO}_2\text{R}$ , when the antimony compound used was  $\text{Bu}_3\text{Sb}(\text{CH}_2\text{CO}_2\text{R})\text{Br}$ . In these reactions  $\text{R}'$  was Ph, 4- $\text{ClC}_6\text{H}_4$ , 4- $\text{MeC}_6\text{H}_4$ , or 4- $\text{MeOC}_6\text{H}_4$ , and, in all but one case, R was Et.

In the reaction where  $\text{Bu}_3\text{Sb}(\text{CH}_2\text{CO}_2\text{Me})\text{Br}$  was used, a mixture of the propionate  $\text{PhCH}(\text{OH})\text{CH}_2\text{CO}_2\text{Me}$  (65%) and the acrylate  $\text{PhCH}=\text{CHCO}_2\text{Me}$  was obtained. Substitution of the tetraphenylborate anion for the bromide gave the propionate in 97% yield. The authors pointed out that the  $\beta$ - and  $\delta$ -hydroxy esters described here are usually prepared by the Reformatsky reaction, and that this new method was a novel alternative, often giving larger yields than the Reformatsky reaction.

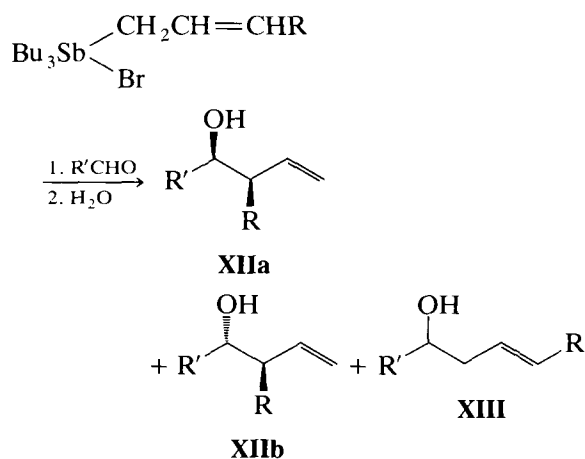
Finally, the authors prepared a series of  $\beta$ -aryl- $\beta$ -



hydroxypropionitriles  $\text{RCH}(\text{OH})\text{CH}_2\text{CN}$  from  $\text{Bu}_3\text{Sb}(\text{CH}_2\text{CN})\text{Br}$  and aryl aldehydes (where  $\text{R} = \text{Ph}$ , 4- $\text{Cl}-\text{C}_6\text{H}_4$ , 4- $\text{MeOC}_6\text{H}_4$ , 3,4- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$ , or 3,4- $(\text{CH}_2\text{O}_2)\text{C}_6\text{H}_3$ ). In addition to the  $\beta$ -hydroxypropionitriles produced in each reaction, small amounts of the acrylonitriles (3–18%)  $\text{RCH}=\text{CHCN}$  were isolated.

Four of the starting antimony compounds,  $[\text{R}_3\text{Sb}(\text{CH}_2\text{Ph})]\text{X}$  (where  $\text{R} = \text{Bu}$  or  $\text{Et}$ ; and  $\text{X} = \text{Br}$ ) and the compounds  $[\text{Bu}_3\text{SbCH}_2\text{CH}=\text{CHCO}_2\text{Et}]\text{X}$  and  $[\text{Bu}_3\text{SbCH}_2\text{CO}_2\text{Me}]\text{X}$  (where  $\text{X} = \text{Ph}_4\text{B}$ ) were isolated and characterized by elemental analysis, PMR, IR, and mass spectrometry. The other tetraalkylantimony halides ( $\text{Br}$  and, in one case,  $\text{I}$ ) were used in situ without isolation. All of the reaction products were characterized by PMR and IR and in most cases by mass spectroscopy. The authors offered several suggestions for the mechanisms involved in the reactions they studied.

In their 93rd paper on the use of organometallic compounds of Groups 15 and 16 as reagents in organic synthesis, Huang et al. [115] reported on the stereoselective addition of tetraalkylantimony bromides (where one of the alkyl groups was allylic and the other three groups were butyl) to aldehydes to produce, after hydrolysis, homoallylic alcohols:

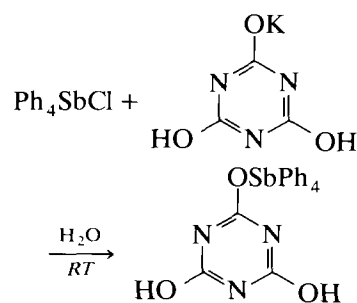


(where  $\text{R} = \text{Me}$ ,  $\text{Pr}$ , or  $\text{Me}_2\text{CH}$ ; and  $\text{R}'$  is an alkyl, alkenyl, phenyl, or substituted phenyl group). The total yields were large (90–97%). The principal products were mixtures of the *erythro* **XIIa** and *threo* **XIIb** alcohols ( $\gamma$ -addition) with much smaller amounts of alcohol formed by  $\alpha$ -addition (**XIII**). The ratio of *erythro* to *threo* products depended greatly on the substituent  $\text{R}$ . Thus, when  $\text{R} = \text{Me}$  the *erythro*:*threo* ratio was always about 2:1; whereas when  $\text{R} = \text{Me}_2\text{CH}$  the *threo* isomer predominated (70–98%). When  $\text{R} = \text{Bu}$ , the *erythro*:*threo* ratio was close to 1:1 (except for the case where  $\text{R}' = \text{Pr}$  when the *erythro*:*threo* ratio was 35:65). The ratio between the isomers was determined on the reaction mixtures by comparison of their PMR spectra (and/or capillary GC behavior) with authentic materials. In addition to PMR data, IR and mass

spectral data and, in some cases, elemental analyses of the reaction products were reported.

Feher and Weller previously published a number of papers on the synthesis of polyhedral aluminosilsesquioxanes as models for aluminosilicates. Thus, they described polysilicate anions in which the cation was  $\text{Me}_4\text{Sb}^+$  [116]. In a more recent paper, these authors described the reactions of bridged oxygen compounds,  $\text{Me}_3\text{SiOSbMe}_4$ ,  $\text{Me}_3\text{SiOSnMe}_3$ ,  $\text{Me}_3\text{SnOSnMe}_3$ ,  $\text{Me}_3\text{COSbMe}_4$ , and  $\text{Ph}_4\text{SbOSbPh}_4$ , with the hydridosilsesquioxane  $\text{H}_8\text{Si}_8\text{O}_{12}$  [117]. The substances prepared were those in which all hydrogens were replaced by  $\text{OSiMe}_3$ ,  $\text{OSnMe}_3$ , or  $\text{OSbMe}_4$  groups. However, the reaction of  $\text{H}_8\text{Si}_8\text{O}_{12}$  with  $\text{Me}_3\text{SiOSnMe}_3$  or  $\text{Ph}_4\text{SbOSbPh}_4$  produced complex mixtures of inseparable Si–H oxidation products. The compound  $\text{Si}_8\text{O}_{12}(\text{OSbMe}_4)_8$  was prepared by the reaction of the tin compound  $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$  (prepared from  $\text{H}_8\text{Si}_8\text{O}_{12}$  and  $\text{Me}_3\text{SnOSnMe}_3$ ) with  $\text{Me}_3\text{COSbMe}_4$  or  $\text{Me}_3\text{SiOSbMe}_4$ . All of the compounds prepared, except for  $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ , were volatile and were removed in vacuo to give spectroscopically pure products.

Sharutin et al. [118] prepared derivatives of cyanuric acid containing one, two, or three tetraphenylantimony groups by the reaction between the mono-, di-, or tripotassium salts of cyanuric acid and tetraphenylantimony chloride. Thus, the mono tetraphenylantimony compound was obtained as follows:



This same compound resulted from the reaction of pentaphenylantimony with cyanuric acid in a sealed ampoule at 200°C. Only one hydrogen was replaced in this reaction, even though an excess of pentaphenylantimony was used. The new compounds were characterized by IR spectroscopy and by elemental analyses. In the IR spectra of the compounds containing one or two tetraphenylantimony groups, absorption bands for both carbonyl and hydroxyl groups were observed. The two compounds reacted with potassium iodide in aqueous solution to give tetraphenylantimony iodide and the mono- or dipotassium salts of cyanuric acid, respectively.

The rotational excitations of a methyl group were previously studied at very low temperatures and at high temperatures as a simple example of motional processes in the solid state. In the present paper [119] parameters describing the  $\text{Me}_4\text{Sb}^+$  cation tumbling

and the methyl group reorientation at high temperatures were determined from the proton spin-lattice relaxation time  $T_1$  in the NMR spectrum at two different Larmor frequencies over the temperature range  $7.2 \leq T/K \leq 417$ . Inelastic neutron scattering techniques (INS) were used to study rotational motions at 4 K. Quantum mechanical tunneling of the methyl groups at this low temperature were determined. The results from the INS and NMR experiments at low temperature were explained in terms of two crystallographically inequivalent methyl groups. These results were in accordance with the previously determined crystal structure determination. Activation energies derived from NMR spin-lattice relaxation times for the two inequivalent methyl groups were reported as 1.50 kJ and 3.81 kJ mol<sup>-1</sup>, respectively.

Solid-solid phase-transition temperatures, entropies of transition, and room-temperature lattice parameters of 16 compounds of the type [Me<sub>4</sub>E]<sub>2</sub>[MX<sub>4</sub>] (where E = P, As, or Sb; M = Co, Cu, or Zn, and X = Cl, Br, or I) were determined [120]. The antimony compounds studied in this investigation were [Me<sub>4</sub>Sb]<sub>2</sub>[MX<sub>4</sub>] (where MX<sub>4</sub> = CoCl<sub>4</sub>, CuCl<sub>4</sub>, ZnCl<sub>4</sub>, CoBr<sub>4</sub>, CuBr<sub>4</sub>, or ZnBr<sub>4</sub>). They were prepared by mixing an alcoholic solution of Me<sub>4</sub>SbX with an alcoholic solution of the metal halide (where X = Cl or Br). Crystal growth of salts of the type [Me<sub>4</sub>Sb]<sub>2</sub>[MI<sub>4</sub>] (where M = Co or Zn) was unsuccessful. The chloride and bromide salts were recrystallized from acetonitrile. The compounds were analyzed for the M<sup>2+</sup> ions spectrophotometrically and the [Me<sub>4</sub>E]<sup>+</sup> cations were characterized by their IR spectra. Single crystal X-ray diffraction studies of all of the compounds were carried out. The compounds were divided into two types. One type was [Me<sub>4</sub>P]<sub>2</sub>[MX<sub>4</sub>] (where MX<sub>4</sub> = CoBr<sub>4</sub>, CoI<sub>4</sub>, ZnBr<sub>4</sub>, or ZnI<sub>4</sub>) and [Me<sub>4</sub>As]<sub>2</sub>[MX<sub>4</sub>] (where MX<sub>4</sub> = CuBr<sub>4</sub>, CoI<sub>4</sub>, or ZnI<sub>4</sub>). All had the β-K<sub>2</sub>SO<sub>4</sub> type structure, analogous to the [Me<sub>4</sub>N]<sub>2</sub>[MX<sub>4</sub>] type compounds. The other type of compounds had larger cation to anion radii and were grouped into a [Me<sub>4</sub>As]<sub>2</sub>[CoCl<sub>4</sub>] structural type, characterized by an apparent association with a cubic unit cell having ca. 12.7 Å axes.

## References

- [1] W. Wolfsberger, *Chem.-Ztg.*, 115 (1991) 7.
- [2] R.C. Mehrotra and A. Singh, *Organometallic Chemistry*, Wiley, New York, 1991.
- [3] P.D. Lickiss, *Annu. Rep. Prog. Chem., Sect. B: Org. Chem.*, 86 (1991) 261; 87 (1991) 271.
- [4] J.L. Wardell, *Organomet. Chem.*, 20 (1991) 130; *Chem. Abstr.*, 116 (1992) 151836s.
- [5] D.A. Armitage, *Silicon-Heteroat. Bond.* (1991) 151.
- [6] N.M. Doherty and N.W. Hoffman, *Chem. Rev.*, 91 (1991) 553.
- [7] P.P. Shorygin and K. Ya. Burshtein, *Usp. Khim.*, 60 (1991) 3.
- [8] M.A. Beckett, *Organomet. Chem.*, 20 (1991) 180; *Chem. Abstr.*, 116 (1992) 174195w.
- [9] H.A. Skinner, *NATO ASI Ser., Ser. C*, 367 (1991) 1.
- [10] G. Pilcher, *NATO ASI Ser., Ser. C*, 367 (1991) 9.
- [11] C. Jones, L.M. Engelhardt, P.C. Junk, D.S. Hutchings, W.C. Patalinghug, C.L. Raston and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1991) 1560.
- [12] W. Frank, *J. Organomet. Chem.*, 406 (1991) 331.
- [13] Y. Mourad, Y. Mugnier, H.J. Breunig and M. Ates, *J. Organomet. Chem.*, 406 (1991) 323.
- [14] M.A.G.M. Tinga, M.K. Groeneveld, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets and A.L. Spek, *Recl. Trav. Chim. Pays-Bas*, 110 (1991) 290.
- [15] E. Lindner, M. Heckmann, R. Fawzi and W. Hiller, *Chem. Ber.*, 124 (1991) 2171.
- [16] W. Deck and H. Vahrenkamp, *Z. Anorg. Allg. Chem.*, 598/599 (1991) 83.
- [17] R.A. Fisher, R.B. Nielsen, W.M. Davis and S.L. Buchwald, *J. Am. Chem. Soc.*, 113 (1991) 165.
- [18] A.J. Ashe III, T.R. Diephouse, J.W. Kampf and S.M. Al-Taweel, *Organometallics*, 10 (1991) 2068.
- [19] K.-H. Hengstmann, F. Huber and H. Preut, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, C47 (1991) 2029.
- [20] W.S. Sheldrick and C. Martin, *Z. Naturforsch., B: Chem. Sci.*, 46 (1991) 639.
- [21] M. Herberhold, T. Triebner, T. Chivers and S.S. Kumaravel, *Z. Naturforsch., B: Chem. Sci.*, 46 (1991) 169.
- [22] X.L.R. Fontaine, J.D. Kennedy, M. McGrath and T.R. Spalding, *Magn. Reson. Chem.*, 29 (1991) 711.
- [23] M. Rannenber, J. Weidlein and A. Obermeyer, *Z. Naturforsch., B: Chem. Sci.*, 46 (1991) 459.
- [24] L. Maes, R. Hamers and E. Bajyana-Songa, *Fr. Demande FR 2640269; Chem. Abstr.*, 114 (1991) 247542c.
- [25] G. Fritz, E. Layher, H. Goesmann, D. Hanke and C. Persau, *Z. Anorg. Allg. Chem.*, 594 (1991) 36.
- [26] R. Gupta, Y.P. Singh and A.K. Rai, *Indian J. Chem., Sect. A: Inorg., Bioinorg., Phys., Theor. Anal. Chem.*, 30A (1991) 541.
- [27] G.E. Forster, I.G. Southerington, M.J. Begley and D.B. Sowerby, *J. Chem. Soc., Chem. Commun.*, (1991) 54.
- [28] F. Calderazzo, F. Marchetti, F. Ungari and M. Wieber, *Gazz. Chim. Ital.*, 121 (1991) 93.
- [29] G.O. Doak and L.D. Freedman, *J. Organomet. Chem.*, in press.
- [30] F. Calderazzo, A. Juris, R. Poli and F. Ungari, *Inorg. Chem.*, 30 (1991) 1274.
- [31] A.G.M. Barrett and L.M. Melcher, *J. Am. Chem. Soc.*, 113 (1991) 8177.
- [32] R.A. Jones, A.H. Cowley, and J.G. Ekerdt, US Patent no. US 5047565; *Chem. Abstr.*, 116 (1992) 59639g.
- [33] K.T. Higa, US Patent no. US 5068370; *Chem. Abstr.*, 116 (1992) 59625z.
- [34] C. Socaciu, A. Bara, C. Silvestru and I. Haiduc, *In Vivo*, 5 (1991) 425; *Chem. Abstr.*, 116 (1992) 75826w.
- [35] Y.R. Zhang, I. Solomon and S. Aronson, *Can. J. Chem.*, 69 (1991) 606.
- [36] B. Bhattacharjee and S.N. Bhat, *Proc.-Indian Acad. Sci., Chem. Sci.*, 103 (1991) 69.
- [37] V.V. Sharutin and V.T. Bychkov, *Metalloorg. Khim.*, 4 (1991) 1191; *Chem. Abstr.*, 115 (1991) 280160v.
- [38] A. Apblett, T. Chivers, J.F. Fait and R. Vollmerhaus, *Can. J. Chem.*, 69 (1991) 1022.
- [39] C.A. Larsen, S.H. Li and G.B. Stringfellow, *Chem. Mater.*, 3 (1991) 39.
- [40] C.A. Larsen, R.W. Gedridge, Jr., S.H. Li and G.B. Stringfellow, *Mater. Res. Soc. Symp. Proc.*, 204 (1991) 129.
- [41] A. Salesse, A. Giani, P. Grosse and G. Bougnot, *J. Phys. III*, 1 (1991) 1267; *Chem. Abstr.*, 116 (1992) 72561v.
- [42] C.A. Larsen, R.W. Gedridge, Jr. and G.B. Stringfellow, *Chem. Mater.*, 3 (1991) 96.

- [43] S.H. Li, C.A. Larsen, G.B. Stringfellow and R.W. Gedridge, Jr., *J. Electron. Mater.*, **20** (1991) 457.
- [44] D.K. Gaskill, G.T. Stauf and N. Bottka, *Appl. Phys. Lett.*, **58** (1991) 1905.
- [45] T.S. Wu, Y.K. Su, F.S. Juang, N.Y. Li and K.J. Gan, *Proc. SPIE – Int. Soc. Opt. Eng.*, **1361** (1991) 23; *Chem. Abstr.*, **115** (1991) 38839m.
- [46] Y.K. Su, F.S. Juang, N.Y. Li, K.J. Gan and T.S. Wu, *Solid-State Electron.*, **34** (1991) 815; *Chem. Abstr.*, **115** (1991) 124610m.
- [47] H.Y. Ueng, S.M. Chen, Y.K. Su and F.S. Juang, *Mater. Res. Soc. Symp. Proc.*, **216** (1991) 265.
- [48] Y.K. Su and F.S. Juang, *Mater. Res. Soc. Symp. Proc.*, **216** (1991) 269.
- [49] Y.K. Su, F.S. Juang and T.S. Wu, *Jpn. J. Appl. Phys., Part 1*, **30** (1991) 1609; *Chem. Abstr.*, **115** (1991) 245023f.
- [50] B.T. Cunningham, R.P. Schneider, Jr. and R.M. Biefeld, *Mater. Res. Soc. Symp. Proc.*, **216** (1991) 233.
- [51] R.M. Biefeld, B.T. Cunningham, S.R. Kurtz and J.R. Wendt, *Mater. Res. Soc. Symp. Proc.*, **216** (1991) 175.
- [52] T. Kaneko, H. Asahi, Y. Itani, Y. Okuno and S. Gonda, *J. Cryst. Growth*, **111** (1991) 638.
- [53] G.T. Stauf, D.K. Gaskill, N. Bottka and R.W. Gedridge, Jr., *Appl. Phys. Lett.*, **58** (1991) 1311.
- [54] G.T. Stauf, D.K. Gaskill, N. Bottka and R.W. Gedridge, Jr., *Mater. Res. Soc. Symp. Proc.*, **216** (1991) 239.
- [55] C.H. Chen, Z.M. Fang, G.B. Stringfellow and R.W. Gedridge, Jr., *Appl. Phys. Lett.*, **58** (1991) 2532.
- [56] C.H. Chen, Z.M. Fang, G.B. Stringfellow and R.W. Gedridge, Jr., *J. Appl. Phys.*, **69** (1991) 7605.
- [57] H.R. Aduriz, P. Bodnariuk, B. Coq and F. Figueras, *J. Catal.*, **129** (1991) 47.
- [58] S. Kobayashi, Y. Tsuchiya and T. Mukaiyama, *Chem. Lett.*, (1991) 537.
- [59] J.F. Knifton and R.G. Duranleau, *J. Mol. Catal.*, **67** (1991) 389.
- [60] T. Matsumoto, T. Masuda and T. Higashimura, *J. Polym. Sci., Part A: Polym. Chem.*, **29** (1991) 295.
- [61] T. Yoshimura, T. Masuda, T. Higashimura, K. Okuhara and T. Ueda, *Macromolecules*, **24** (1991) 6053.
- [62] N. Saito, H. Nishihara and K. Aramaki, *Corros. Sci.*, **32** (1991) 577.
- [63] H. Nishihara, K. Aramaki and N. Usuki, Japanese Kokai Tokkyo Koho, JP 03120388 [91,120,388]; *Chem. Abstr.*, **115** (1991) 187583a.
- [64] N. Ootsuka and M. Ozeki, Japanese Kokai Tokkyo Koho, JP 03185716 [91,185,716]; *Chem. Abstr.*, **115** (1991) 244652y.
- [65] T. Sugano and Y. Oshino, Japanese Kokai Tokkyo Koho, JP 03149221 [91,149,221]; *Chem. Abstr.*, **115** (1991) 280852x.
- [66] R.J. Hoffman and C.S. Hart, US Patent no. US 5021368; *Chem. Abstr.*, **115** (1991) 237630m.
- [67] Y. Wang, Z. Lei, H. Feng and Y. Liu, *Appl. Organomet. Chem.*, **5** (1991) 517; *Chem. Abstr.*, **116** (1992) 129228y.
- [68] T. Bartik, T. Krümmling, C. Krüger, L. Markó, R. Boese, G. Schmid, P. Vivarelli and G. Pályi, *J. Organomet. Chem.*, **421** (1991) 323.
- [69] A. Baiada, F.H. Jardin, R.D. Willett and K. Emerson, *Inorg. Chem.*, **30** (1991) 1365.
- [70] J.A.S. Howell, G. Walton, M.-C. Tirvengadam, A.D. Squibb, M.G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. Gottlieb and G. Strul, *J. Organomet. Chem.*, **401** (1991) 91.
- [71] H. Schumann and L. Eguren, *J. Organomet. Chem.*, **403** (1991) 183.
- [72] H. Schumann, L. Eguren and J.W. Ziller, *J. Organomet. Chem.*, **408** (1991) 361.
- [73] P.K. Baker, S.G. Fraser and D. Ap Kendrick, *J. Chem. Soc. Dalton Trans.*, (1991) 131.
- [74] J. Seth and U.C. Agarwala, *Adv. Organomet., Proc. 1st Indo – Sov. Symp. "Organomet. Chem."*, 1988, Published 1989, 272; *Chem. Abstr.*, **115** (1991) 173298z.
- [75] H. Schumann, J.H. Enemark, M.J. Labarre, M. Bruck and P. Wexler, *Polyhedron*, **10** (1991) 665.
- [76] P.K. Baker and D. Ap Kendrick, *Inorg. Chem. Acta*, **188** (1991) 5.
- [77] B.F.G. Johnson, J. Lewis, M.-A. Pearsall and L.G. Scott, *J. Organomet. Chem.*, **413** (1991) 337.
- [78] V. Farina and B. Krishnan, *J. Am. Chem. Soc.*, **113** (1991) 9585.
- [79] K. Sünkel, *Chem. Ber.*, **124** (1991) 2449.
- [80] S.P. Best, A.J. Nightingale and D.A. Tocher, *Inorg. Chim. Acta*, **181** (1991) 7.
- [81] R. Cini, G. Giorgi and E. Periccioli, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **C47** (1991) 716.
- [82] D.S. Pandey, R.L. Mishra and U.C. Agarwala, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, **30A** (1991) 41.
- [83] R. Prasad, L. Mishra and U.C. Agarwala, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, **30A** (1991) 45.
- [84] T. Probst, O. Steigelmann, J. Riede and H. Schmidbaur, *Chem. Ber.*, **124** (1991) 1089.
- [85] A.V. Kondyurin, S.N. Mikov and A.T. Kozulin, *J. Raman Spectrosc.*, **22** (1991) 249.
- [86] M. Wieber and J. Walz, *Z. Naturforsch. B: Chem. Sci.*, **45** (1990) 1615.
- [87] M. Wieber, U. Simonis and D. Kraft, *Z. Naturforsch., B: Chem. Sci.*, **46** (1991) 139.
- [88] S.H. Wasfi, US Patent no. US 5041576; *Chem. Abstr.*, **115** (1991) 280296u.
- [89] E.G. Zaitseva, S.V. Medvedev and L.A. Aslanov, *Zh. Strukt. Khim.*, **31** (1) (1990) 104.
- [90] E.G. Zaitseva, S.V. Medvedev and L.A. Aslanov, *Zh. Strukt. Khim.*, **31** (1) (1990) 110.
- [91] E.G. Zaitseva, S.V. Medvedev and L.A. Aslanov, *Zh. Strukt. Khim.*, **31** (2) (1990) 92.
- [92] E.G. Zaitseva, S.V. Medvedev and L.A. Aslanov, *Zh. Strukt. Khim.*, **31** (5) (1990) 133.
- [93] E.G. Zaitseva, S.V. Medvedev and L.A. Aslanov, *Zh. Strukt. Khim.*, **31** (5) (1990) 138.
- [94] G. Alonzo, N. Bertazzi, G. Bombieri, G. Bruno and F. Nicolo, *J. Crystallogr. Spectrosc. Res.*, **21** (1991) 635.
- [95] P. Raj and N. Misra, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys. Theor. Anal. Chem.*, **30A** (1991) 901.
- [96] B. Liu, Y. Ku, M. Wang, B. Wang and P. Zheng, *J. Chem. Soc., Chem. Commun.*, (1989) 651.
- [97] I.G. Southerington, M.J. Begley and D.B. Sowerby, *J. Chem. Soc., Chem. Commun.*, (1991) 1555.
- [98] R. Nomura, S.-I. Miyazaki, T. Nakano and H. Matsuda, *Chem. Ber.*, **123** (1990) 2081.
- [99] R. Nomura, S.-I. Miyazaki, T. Nakano and H. Matsuda, *Appl. Organomet. Chem.*, **5** (1991) 513.
- [100] R. Nomura, T. Nakano, Y. Yamada and H. Matsuda, *J. Org. Chem.*, **56** (1991) 4076.
- [101] J.-K. Shen, Y.-C. Gao, Q.-Z. Shi, A.L. Rheingold and F. Basolo, *Inorg. Chem.*, **30** (1991) 1868.
- [102] G. Ferguson, B. Kaitner, C. Glidewell and S. Smith, *J. Organomet. Chem.*, **419** (1991) 283.
- [103] B.K. Dwivedi, H.N. Mehrotra and D. Mehrotra, *Asian J. Chem.*, **3** (1991) 58.
- [104] M. Yanaga, K. Endo, H. Nakahara, S. Ikuta, T. Miura, M. Takahashi and M. Takeda, *Hyperfine Interact.*, **52** (1989) 147.
- [105] M. Yanaga, K. Endo, H. Nakahara, S. Ikuta, T. Miura, M. Takahashi and M. Takeda, *Hyperfine Interact.*, **62** (1990) 359.

- [106] V.V. Sharutin and V.T. Bychkov, *Zh. Obshch. Khim.*, 61 (1991) 1357.
- [107] H.Z. Alkhatlan and H.A. Al-Lohedan, *Phosphorus, Sulfur Silicon Relat. Elem.*, 61 (1991) 367.
- [108] N. Iwamoto, Eur. Patent Application EP 412759; *Chem. Abstr.*, 114 (1991) 248572z.
- [109] Y. Naoshima and C.E. Carraher, Jr., *Inorg. Met.-Containing Polym. Mater.*, (Proc. Am. Chem. Soc. Int. Symp.), (1990) 327.
- [110] Y. Naoshima and C.E. Carraher, Jr., *Polym. Mater. Sci. Eng.*, 61 (1989) 442.
- [111] L.D. Freedman and G.O. Doak, *J. Organomet. Chem.*, 442 (1992) 1.
- [112] A.S. Peregudov, G.I. Drogunova, L.S. Isaeva, E.I. Fedin and D.N. Kravtsov, *Metalloorg. Khim.*, 4 (1991) 90; *Chem. Abstr.*, 114 (1991) 207480z.
- [113] Y.-Z. Huang, Y. Laio and C. Chen, *J. Chem. Soc., Chem. Commun.*, (1990) 85.
- [114] Y.-Z. Huang and Y. Liao, *J. Org. Chem.*, 56 (1991) 1381.
- [115] Y.-Z. Huang, L.-J. Zhang, C. Chen and G.-Z. Guo, *J. Organomet. Chem.*, 412 (1991) 47.
- [116] F.J. Feher and K.J. Weller, *Organometallics*, 9 (1990) 2638.
- [117] F.J. Feher and K.J. Weller, *Inorg. Chem.*, 30 (1991) 880.
- [118] V.V. Sharutin, V.T. Bychkov and R.P. Zakharova, *Zh. Obshch. Khim.*, 61 (1991) 1359.
- [119] G. Burbach and A. Weiss, *Z. Naturforsch., A: Phys. Sci.*, 46 (1991) 759.
- [120] M.R. Pressprich, M.R. Bond and R.D. Willett, *Phys. Rev. B: Condens. Matter*, 43 (1991) 13549.