

Annual review

Antimony: annual survey covering the year 1993

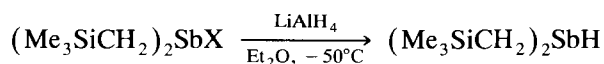
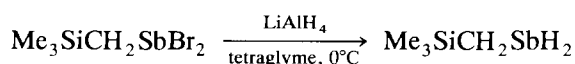
Leon D. Freedman, G.O. Doak

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

Keywords: Antimony

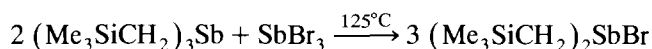
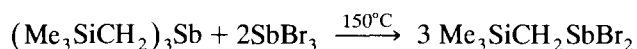
No book or review devoted exclusively to organoantimony compounds was published in 1993. Professor Breunig, however, has written an interesting account of recent developments in the field of inorganic and organic antimony homocycles and heterocycles [1]. The use of tertiary stibines as antimony sources for the growth of semiconductor materials has been discussed in two reviews on novel precursors for organometallic vapor phase epitaxy (OMVPE) [2,3]. Organoantimony compounds have also been included in a review on the use of allylic organometallic reagents in organic synthesis [4] and in a chapter on the metabolism of alkyl arsenic and antimony compounds [5]. A critical review has been published of the possible mechanisms for the production of thermodynamically unstable organic and inorganic species of arsenic, antimony, and selenium in sea water and for their transformation into stable forms [6]. In addition, information about organoantimony compounds has been given in surveys of recent publications on the Group 15 elements [7] and on organic derivatives of arsenic, antimony, and bismuth [8]. Organoantimony compounds have also been very briefly mentioned in review articles on organometallic aromaticity [9], on organometallic complexes of five-membered heterocycles [10], and on bioalkylation of the heavy elements [11].

Primary and secondary trimethylsilylmethylstibines have been prepared in moderate yields by the lithium aluminum hydride reduction of a dihalo- or halostibine [12]:



(where X was Br or I)

The dibromo- and bromostibines used in these syntheses were obtained by the following redistribution reactions:



Both the primary and secondary stibines were colorless, reactive liquids and were soluble in hydrocarbons and ethers. The vapor pressure of the primary stibine was 2.0 Torr at 0°C; the secondary stibine was much less volatile but could be distilled under dynamic vacuum (10^{-6} Torr) at ambient temperature. When exposed to air, both species were rapidly oxidized to white solids. Like their neopentyl counterparts, the trimethylsilylmethylstibines exhibited reasonable thermal stability in the absence of light. Thus, the primary stibine showed no signs of decomposition when stored in a hydrogen atmosphere for three months. After longer standing, however, a decomposition product believed to be $(\text{Me}_3\text{SiCH}_2\text{Sb})_5$ was isolated. The primary and secondary stibines were characterized by IR and NMR (^1H and ^{13}C) spectroscopy. The IR spectrum of each compound was dominated by a very intense absorption associated with the Sb–H stretch (1865 cm^{-1} for the primary stibine in the gas phase and 1835 cm^{-1} for the secondary stibine as a neat liquid). The NMR results were for the most part similar to those previously reported for the neopentyl compounds. In the case of bis(trimethylsilylmethyl)stibine, however, the coupling of the methylene hydrogens to the hydrogen of the Sb–H bond was not equivalent. This difference was manifested by the Sb–H resonance becoming a triplet of triplets rather than a simple quintet. A preliminary evaluation was reported of the potential of trimethylsi-

lylmethylstibine as a metal organic chemical vapor deposition (MOCVD) precursor. This study showed that this compound could be used with trimethylindium to deposit thin films of indium antimonide (InSb) at 450°C. The thin films grown in these experiments were characterized by Auger electron spectroscopy and X-ray diffraction.

Diisopropylstibine has been obtained in 56% yield by the reduction of diisopropylbromostibine with lithium aluminum hydride [13,14]. The bromostibine was dissolved in ether and added to an ether slurry of the reducing agent at -78°C ; the mixture was then slowly warmed to room temperature. The secondary stibine was isolated by fractional distillation at $32\text{--}33^{\circ}\text{C}$ (6 Torr) as an extremely air-sensitive and photosensitive colorless liquid. Although it showed no evidence of decomposition after 4 days in the dark at 0°C , it started to decompose within minutes after exposure to sunlight. The onset of pyrolysis of diisopropylstibine in hydrogen was found to occur above 100°C . Complete pyrolysis was observed just above 350°C . The onset of pyrolysis in argon also occurred above 100°C , but the pyrolysis was complete around 300°C . Analyses of the pyrolysis products were performed, but it remained unclear whether free-radical, β -hydrogen elimination, reductive elimination, or some combination of these processes dominated the pyrolysis. Diisopropylstibine was employed in an atmospheric pressure chemical vapor deposition (CVD) reactor to grow polycrystalline antimony films on silicon substrates at temperatures as low as 200°C . Hydrogen and argon were used as carrier gases. Auger electron spectroscopy of these films showed no detectable carbon impurities. The films were also studied by X-ray diffraction.

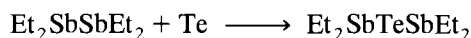
Diisopropylstibine has been employed for the OMVPE of InSb at temperatures as low as 275°C [15,16]. The epilayers were grown with trimethylindium as the indium source and hydrogen as the carrier gas. It was concluded that diisopropylstibine was an excellent precursor for the low temperature OMVPE growth of InSb. The vapor pressure of this secondary stibine was convenient, and its pyrolysis temperature was much lower than for other precursors such as trimethylstibine, triisopropylstibine, or *tert*-butyldimethylstibine. The morphology and crystallographic quality of the epitaxial layers were believed to be acceptable for semiconductor applications. The sole drawback of diisopropylstibine as a precursor was the high n-type doping level observed in layers grown at low temperatures. Thus, layers grown at 300°C were found to have donor densities in excess of 10^{19} cm^{-3} . SIMS analysis of the InSb layers indicated that carbon was the principal impurity present.

Treatment of tetraethylstibine with cadmium iodide in THF (and subsequent removal of the solvent) has been found to yield a stable, crystalline polymeric adduct of composition $[\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2]_n$ [17]. X-ray diffraction

showed that the structure consisted of iodide-bridged $\text{Et}_4\text{Sb}_2 \cdot \text{CdI}_2$ units in which a cadmium atom was bonded to each antimony atom. An antimony atom and two iodine atoms formed a trigonal-planar arrangement around each cadmium atom. Two weak axial bonds to the iodides of adjacent units resulted in distorted trigonal-bipyramidal coordination to cadmium. The Sb–Sb distance of 2.784 \AA was shorter than that found in the metal (2.90 \AA) or in closely related molecules such as tetramethyldistibine. The ease with which tetraethylstibine formed an adduct with cadmium iodide prompted an investigation of the reactivity of the distibine with species that might be encountered in the gas mixing channel or reactor cell of a MOCVD reactor. Thus, a 1:1 adduct was formed by the interaction of the distibine and neat dimethylcadmium in the liquid phase. The insoluble air-sensitive product thus obtained was probably polymeric with a backbone of $[-\text{Cd}-\text{Sb}-\text{Sb}-]_n$ chains. A slow reaction occurred when liquid samples of the distibine and diethyltelluride were mixed. Even after a month, substantial amounts of starting materials were still present. The major products were triethylstibine, $\text{Et}_2\text{SbTeSbEt}_2$, and Et_2SbTeEt . The latter tellurium compound could easily be obtained by the following reaction:



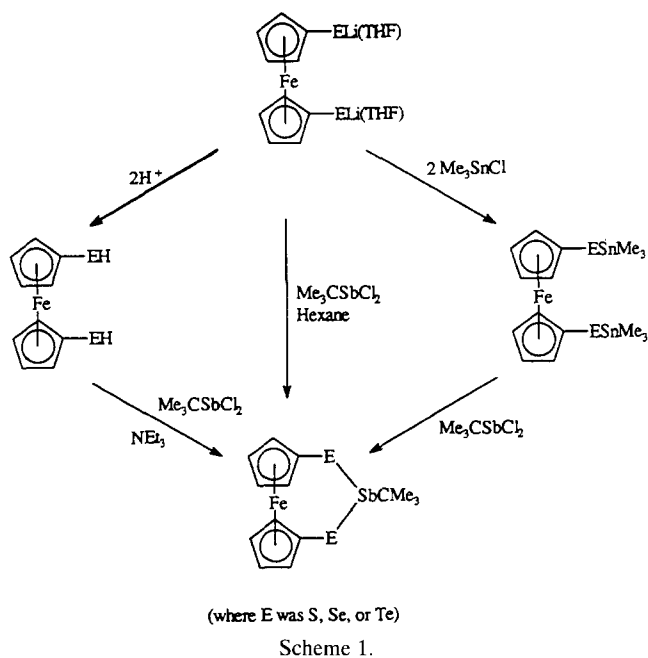
The interaction of the distibine and tellurium metal resulted in formation of the former tellurium compound in 82% yield:



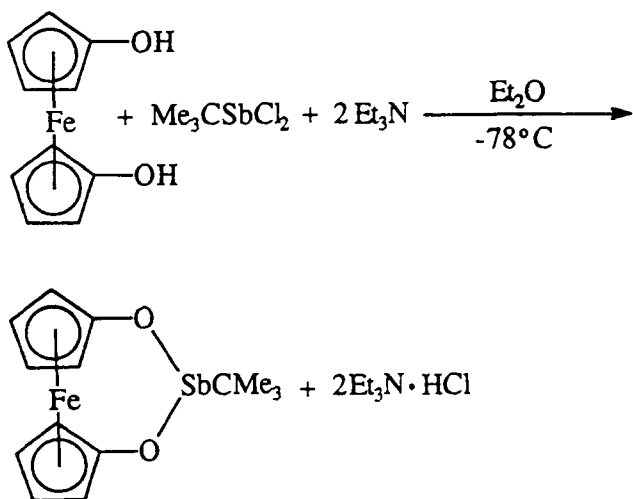
No reaction occurred, however, when the distibine was stirred with mercury or cadmium at room temperature. The distibine was shown to be a useful and safe dopant feedstock for the low temperature growth of p-type $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ by MOCVD. Dimethylcadmium, diethyltelluride, and elemental mercury were used in the MOCVD reactor with hydrogen at atmospheric pressure as the carrier gas. Tetraethylstibine was also employed to grow epitaxial InSb by MOCVD. Growth was achieved at temperatures as low as 330°C with 1:1 doses of trimethylindium and the distibine. Pyrolysis of both tetraethylstibine and tetramethylstibine was also studied. In both cases, decomposition at 300°C in a hydrogen atmosphere yielded a thin film of antimony metal. Analysis of these films by XPS revealed no detectable impurities.

As shown in Scheme 1, three methods have been employed for the synthesis of 1,3-dithia-, 1,3-diselena-, and 1,3-ditellura-[3]ferrocenophanes containing antimony in the central bridge position [18].

The ^1H and ^{13}C NMR solution spectra of the [3]ferrocenophanes at room temperature suggested that these compounds possessed rigid structures.



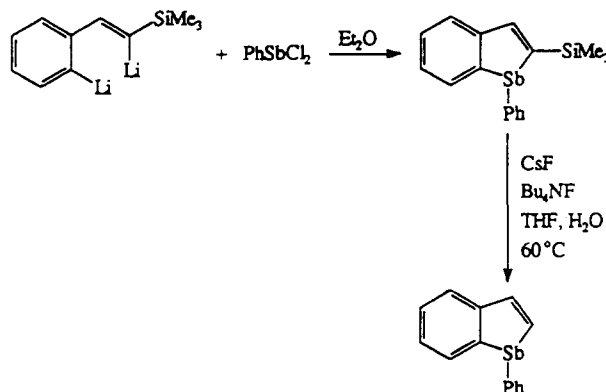
The analogous 1,3-dioxa-[3]ferrocenophane has been prepared by one of the three methods mentioned in the above paragraph [19]:



The substance was obtained in 23% yield as an orange powder that was thermally unstable and sensitive to both light and moisture. Decomposition in the presence of air yielded 2,4-cyclopentadienone and its dimer as well as a dark brown Fe(III)-containing sludge. The EI mass spectrum of the ferrocenophane exhibited the molecular ion as the base peak and an intense peak

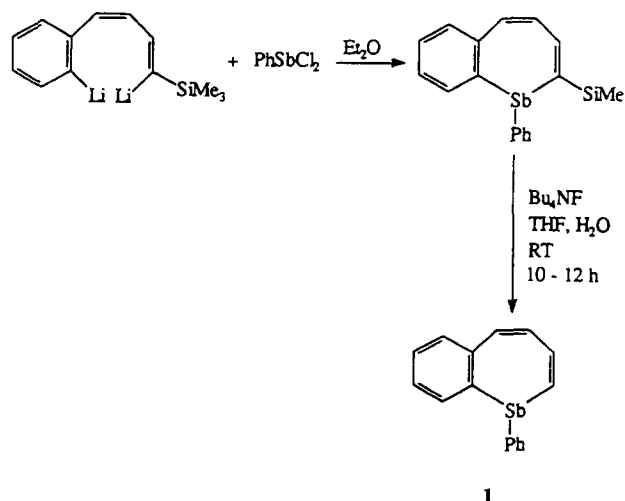
(80%) corresponding to the loss of the *tert*-butyl group. NMR (^1H and ^{13}C) spectra were also recorded. An $[[\text{AB}]_2]_2$ pattern was observed, which persisted even at low temperatures (-90°C) in CD_2Cl_2 solution.

1-Phenyl-2-(trimethylsilyl)-1-benzostibole, prepared by the interaction of phenyldichlorostibine and a dilithio reagent, has been converted into the corresponding *C*-unsubstituted benzostibole by detrimethylsilylation [20a]:

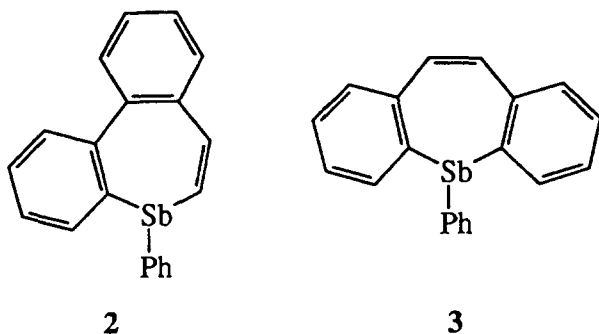


The same synthetic route was employed for the preparation of other Group 15 (P, As, and Bi) benzometallobes as well as analogous compounds of Group 14 (Si, Ge, Sn) and Group 16 (S, Se, Te). The stiboles and other new benzometallobes were investigated by ^1H NMR and mass spectroscopy. Further information about this study is given in the Annual Survey of Bismuth for 1993 [20b].

Seven-membered heterocyclic rings containing a Group 15 element have also been prepared from dilithio reagents [21]. Thus, the benzostibepine **1** has been obtained by the following sequence of reactions:

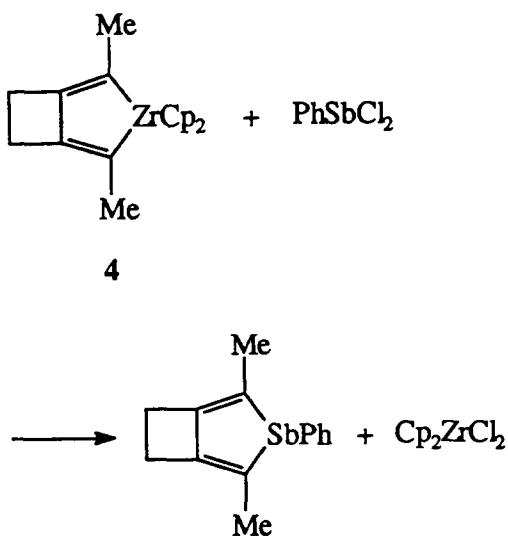


The dibenzostibepines **2** and **3** were synthesized in a similar manner.



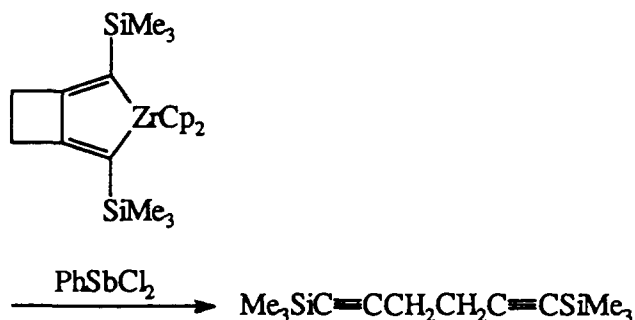
Analogous benzo and dibenzo derivatives of phosphorus, arsenic, and bismuth were also prepared and studied by ^1H NMR. The benzostibepine **1** was the most stable of the four C-unsubstituted heteroepines; it had a half life of 837 min in toluene at 60°C . The presence of the trimethylsilyl group in the 2-position was found to increase the stability of the heteroepines. Thus, the trimethylsilyl derivative of **1** could be kept for several weeks at room temperature even in solution. The dibenzoheteroepines were far more stable than the corresponding benzoheteroepines. Even the C-unsubstituted dibenzoheteroepines remained unchanged when heated at 60°C for 20 h in toluene. Further information about this study is also given in Ref. [20b].

A variety of main-group metallocycles have been prepared in recent years via transmetalation from zirconocene derivatives. Thus, it was not surprising when the expected phenylstibole was obtained by the reaction of the zirconocene **4** with phenyldichlorostibine [22]:

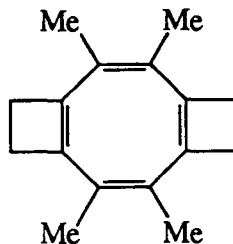


When the methyl groups in **4** were replaced by

trimethylsilyl groups, however, the zirconocene derivative was cleanly converted into a diyne:



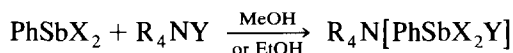
Furthermore, treatment of the zirconocene **4** with antimony trichloride, bismuth trichloride, or gallium trichloride did not result in transmetalation but gave the following cyclooctatetraene as the main organic product:



The tetraene was characterized by NMR (^1H and ^{13}C), mass spectroscopy, and X-ray diffraction. Further information about this study is given in Ref. [20b].

The stibinidene complex $[\{\eta^6\text{-C}_6\text{H}_5\text{CF}_3(\text{CO})_2\text{Cr}\}_2\text{-SbI}]$ has been obtained in 50% yield by the reaction of irradiated $[\eta^6\text{-C}_6\text{H}_5\text{CF}_3\text{Cr}(\text{CO})_3]$ in THF with phenyldichlorostibine (in the presence of zinc dust as a reducing agent) [23]. The fate of the phenyl group attached to the antimony atom was not elucidated. No products could be isolated, however, when *tert*-butyldichlorostibine was allowed to react with compounds of the types $[\text{arene Cr}(\text{CO})_3]$ or $[\text{arene}(\text{CO})_2\text{Cr}(\text{THF})]$.

Nine mixed phenyltrihaloantimonates(III) have been prepared by the following type of addition reaction [24]:

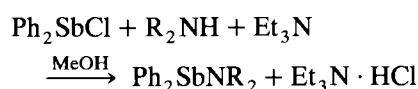
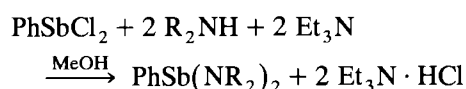


(where R was Me, Et, or Bu; X was Cl or Br; Y was Cl, Br, or I; and X was always different from Y).

The products precipitated from the reaction mixtures as microcrystalline powders, which were sensitive to moisture to varying extent. They were soluble in methanol, ethanol, acetonitrile, dichloromethane, and DMSO, but were insoluble in benzene, ether, tetrachloromethane, and carbon disulfide. The bro-

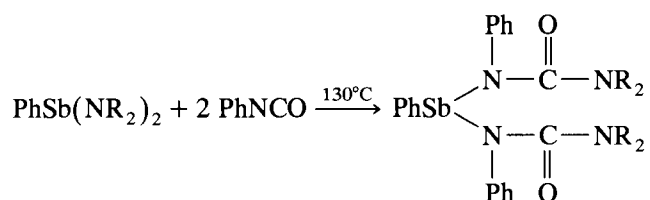
mochloroantimonates were colorless, the chloriodoantimonates were yellow, and the bromiodoantimonates were yellowish orange. Most of the compounds had sharp melting points. Molar conductance values in acetonitrile ($125\text{--}160\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) indicated that the compounds were 1:1 electrolytes in this solvent. Bands were observed in the far IR region ($500\text{--}30\text{ cm}^{-1}$) that could be assigned to Sb–C, Sb–X, and Sb–Y stretching vibrations. Four of the compounds were subjected to thermogravimetric analysis. They appeared to decompose in a single step in which the organic moieties and the halogens were lost simultaneously within the range $100\text{--}200^\circ\text{C}$. The ^1H NMR spectra of the three tetrabutylammonium phenyltrihaloantimonates confirmed the ratio of one phenyl group to four butyl groups in each compound. Peaks were assigned to the *ortho*, *meta*, and *para* protons of each phenyl group, and all of the signals were multiplets.

Eleven compounds containing the Sb–N bond have been prepared by the reaction of phenyldichlorostibine or diphenylchlorostibine with an isatin derivative in the presence of triethylamine [25]:

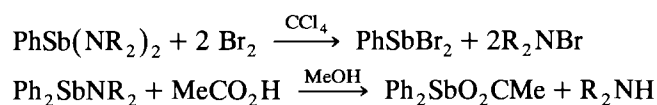


(where R_2NH was 6-chloro-5-methoxyisatin, 6-methoxy-5-bromoisatin, 7-chloroisatin, 5-methoxy-5-bromoisatin, 5-methoxyisatin, or 5-bromoisatin).

The aminostibines were obtained in moderate yields (58%–81%) as colored solids with sharp melting points. Cryoscopic measurements in nitrobenzene showed that the compounds were monomeric in this solvent, and the molar conductances in acetonitrile at 30°C ($12\text{--}22\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) suggested the absence of ionic species in solution. The compounds were hydrolytically unstable but were unaffected by ethanol or carbon disulfide. Phenyl isocyanate, however, was found to add across the Sb–N bond:



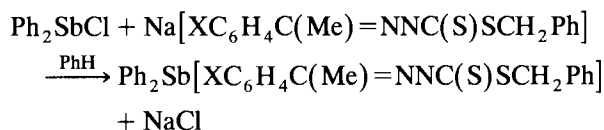
The Sb–N bond was readily cleaved by bromine or acetic acid:



Attempts to prepare phenyldiacetatostibine by cleavage of the Sb–N bond were, however, unsuccessful.

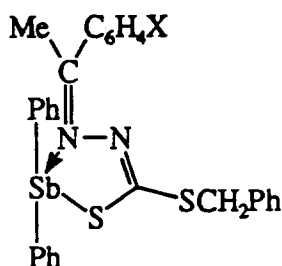
The cleavage of the Sb–N bond by tellurium tetrachloride was also mentioned, but no details of this type of reaction were given.

Six ketone derivatives of benzyl hydrazinecarbodiithioate have been converted to their sodium salts and then allowed to react with diphenylchlorostibine [26]:



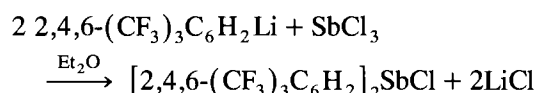
(where X was 4-F, 4-Cl, 4-Br, 2-OH, 4-OH, or 4-OMe).

The products were yellow viscous liquids and were soluble in common organic solvents. They were shown to be monomeric by means of osmometric molecular weight measurements in chloroform at 45°C . Their IR spectra indicated that the antimony was bonded to sulfur and to the β -nitrogen of the ligand. The following type of trigonal-bipyramidal structure was suggested:



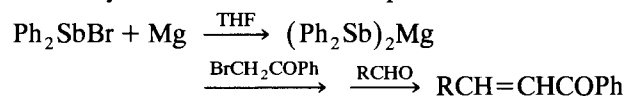
The results of NMR (^1H , ^{13}C , and ^{19}F) spectroscopy appeared to be consistent with the above type of structure.

The interaction of tris(trifluoromethyl)phenyllithium and antimony trichloride in a 2:1 or 3:1 molar ratio has been found to give a chlorostibine [27]:



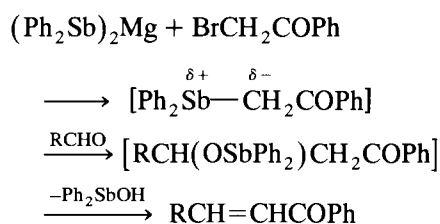
There was no evidence for the formation of the corresponding tertiary stibine. The chlorostibine was obtained in 35% yield as large, colorless crystals, mp 99°C . Its EI mass spectrum showed a low intensity (2%) molecular ion and a base peak corresponding to $(\text{CF}_3)_3\text{C}_6\text{H}_2\text{SbCl}^+$. The IR spectrum exhibited the absorption of the CF_3 groups as strong bands at 1200 and 1152 cm^{-1} .

Magnesium diphenylstibide (prepared from diphenylbromostibine) has been used to mediate the olefination of aldehydes with α -bromoacetophenone [28]:

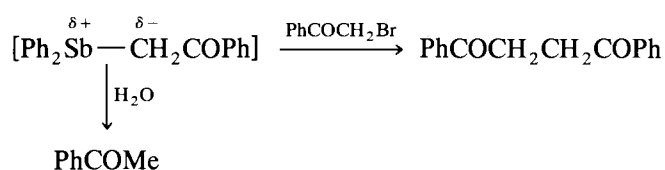


(where R was Ph, 4-MeC₆H₄, Bu, Me(CH₂)₈, or MeCH=CH).

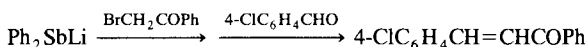
The yields of α,β -unsaturated ketones ranged from 73% to 88%. Cyclohexanone was olefinated in a similar manner to give a 24% yield of 2-cyclohexylidene-1-phenylethanone. The following mechanism was suggested for the olefination of the aldehydes:



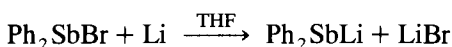
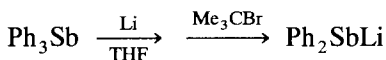
Small amounts of reductive and coupling products were also obtained and may have been formed from the intermediate tertiary stibine:



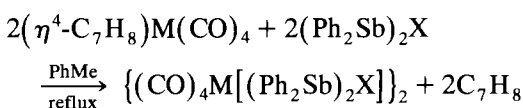
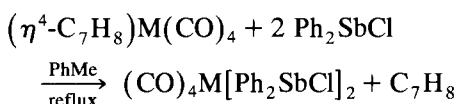
In at least one case, lithium diphenylstibide was used to mediate the olefination of an aldehyde:



The yield of the α,β -unsaturated ketone was 87%. Two methods were employed for the preparation of the lithium reagent:

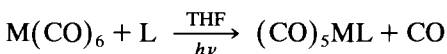


Tetracarbonyl complexes of chromium or molybdenum with diphenylchlorostibine, oxybis(diphenylstibine), or thioabis(diphenylstibine) have been obtained by the following types of substitution reactions [29]:



(where C_7H_8 was norbornadiene; M was Cr or Mo; and X was O or S).

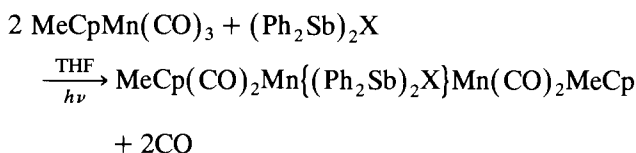
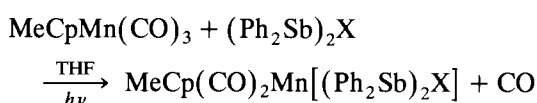
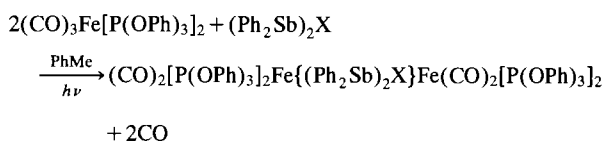
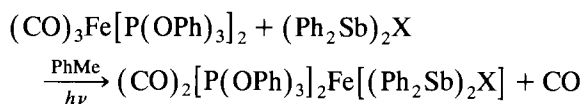
Photochemical reactions were used to prepare pentacarbonyl complexes of chromium, molybdenum, or tungsten with the same organoantimony ligands:



(where M was Cr, Mo, or W; and L was Ph_2SbCl , $\text{Ph}_2\text{SbOSbPh}_2$, or $\text{Ph}_2\text{SbSSbPh}_2$)

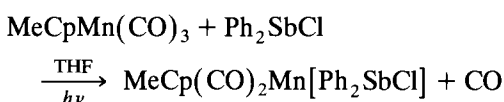
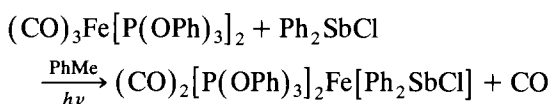
The complexes prepared in this investigation were studied by IR spectroscopy and, in some cases, by molecular weight determinations and X-ray diffraction.

Mononuclear and bridged binuclear complexes of iron or manganese with oxybis(diphenylstibine), thioabis(diphenylstibine), or methylenebis(diphenylstibine) have been prepared by the following types of photochemical reactions [30]:



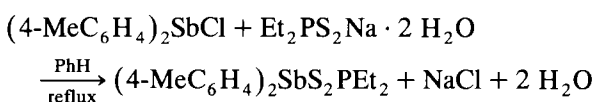
(where MeCp was η^5 -methylcyclopentadienyl; and X was O, S, or CH_2).

Photochemical reactions have also been employed for the preparation of mononuclear complexes of iron and manganese with diphenylchlorostibine:



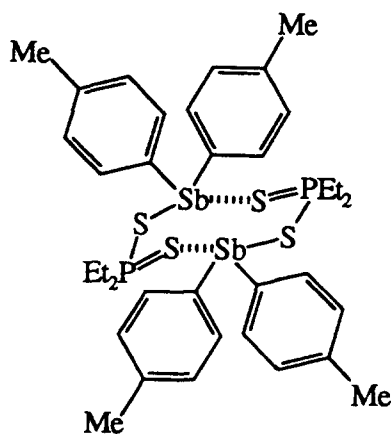
All of the complexes prepared in this investigation were studied by IR and NMR (^1H , ^{13}C , and, where applicable, ^{31}P) spectroscopy.

A diethyldithiophosphinate derivative of antimony (III) has been prepared in 88% yield by means of the following reaction [31]:



The compound was isolated from the reaction mixture as slightly yellowish prismatic crystals, which were quite soluble in organic solvents such as benzene, acetonitrile, and chloroform. The IR spectrum exhibited strong absorption bands at 591 and 479 cm^{-1} , which were assigned to asymmetric and symmetric PS_2 stretching vibrations, respectively. The ^1H NMR spec-

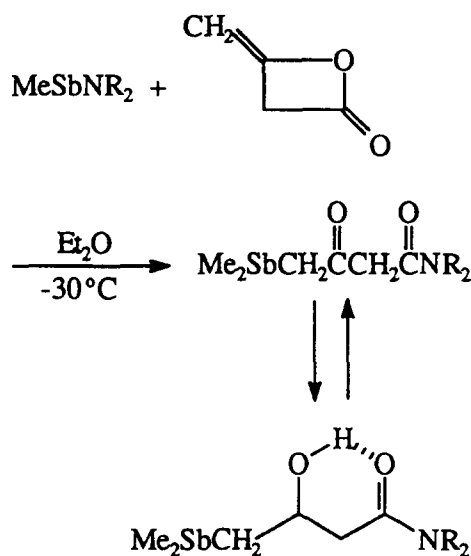
trum in C_6D_6 contained a doublet of doublets centered at 7.67 and 6.88 ppm for the protons *ortho* and *meta* to the antimony atom and a single resonance at 2.03 ppm for the methyl protons of the 4-tolyl groups. The proton resonances of the ethyl groups attached to phosphorus exhibited the pattern expected for phosphorus–proton and proton–proton couplings, i.e. a doublet of quartets ($\delta = 1.73$ ppm) for the methylene protons and a doublet of triplets ($\delta = 1.05$ ppm) for the methyl protons. The ^{31}P NMR spectrum in C_6D_6 , which showed a singlet at 76.2 ppm, was consistent with the presence of a single kind of phosphorus atom. The largest fragment observed in the mass spectrum of the compound was attributed to $[M-H]^+$; the base peak corresponded to Et_2PS^+ . The solid-state structure was shown by X-ray diffraction to be a cyclic dimer held together by weak (semibonding) antimony–sulfur interactions:



The eight-membered $P_2S_4Sb_2$ ring had a twist-chair conformation in which the sulfur and antimony atoms were almost in the same plane and the phosphorus atoms were above and below this plane. The normal covalent Sb–S distances were 2.485 and 2.509 Å, while the semibonding $Sb \cdots S$ distances were 3.556 and 3.318 Å. The average length of the P–S single bond was 2.077 Å, while each P=S double bond had a length of 1.965 Å. The lone pair of electrons of each antimony appeared to be stereochemically active. Thus, the coordination geometry around the metal could be described as pseudo trigonal–bipyramidal, with two carbon atoms of the aromatic groups and the lone pair in equatorial positions and sulfur atoms in axial positions (the $S-Sb \cdots S$ angle was about 174°).

The reaction of diketene with a (dialkylamino)dimethylstibine has been found to result in cleavage of the

Sb–N bond and the formation of a 4-dimethylstibino-3-oxobutanamide [32]:

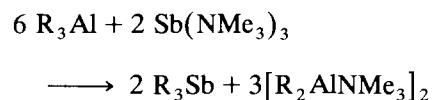


(where R was Me, Et, Pr, Me_2CH , Bu, or $MeEtCH$).

The adducts were characterized by NMR (1H and ^{13}C) and IR spectroscopy. It was concluded that they existed as keto enol mixtures, in which the keto isomers predominated both in solution and in the pure liquid state. Antimony chloride, antimony alkoxides, and antimony thiolates did not, however, react with diketene even when the mixtures were stirred for five days at room temperature.

Gas electron diffraction has been used to investigate the molecular structures and conformational preferences of two compounds of the type Me_2SbEMe , where E was S or Se [33]. In both cases, the predominant conformer was one in which the dihedral angle (defined by the E–C bond, the Sb–E bond and the presumed direction of the lone pair at the Sb atom) was found to be between -45° and $+45^\circ$. The Sb–S and Sb–Se bond distances (the first such distances to be determined in gaseous molecules) were 241.4 and 255.5 pm, respectively.

Tertiary stibines have been prepared by the interaction of trialkylaluminum reagents and tris(dimethylamino)stibine [34]:

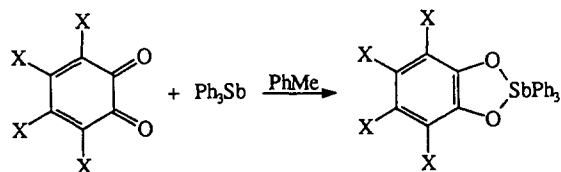


(where R was Me, Et, Pr, Bu, or Me_2CHCH_2).

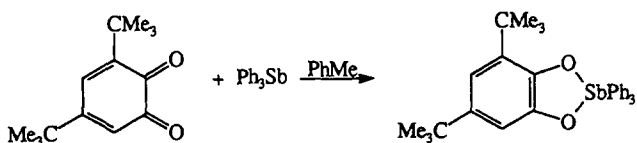
The reactants were mixed at $0^\circ C$, slowly warmed to room temperature, stirred for 4 h, and then heated for 12

h at 120°C. Fractional distillation gave good yields of the tertiary stibines. Complete ^{13}C and ^1H NMR spectral data of all of the products were reported.

The oxidation of triphenylstibine by substituted *ortho*-benzoquinones has been found to give essentially quantitative yields of substituted catechol derivatives [35]:



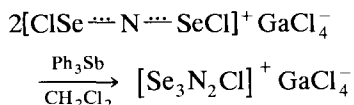
(where X was Cl or Br)



The reaction at room temperature were too rapid for study by ESR, but weak signals were detected when solutions of the individual reactants were mixed at 77 K and allowed to warm slowly. It was concluded that the oxidations were one-electron transfer processes that produced semiquinone intermediates.

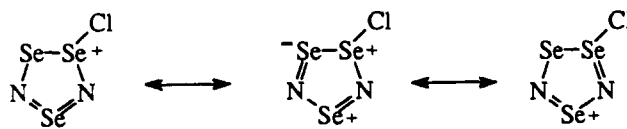
Triphenylstibine in the presence of UV radiation has been found to be converted by dioxygen to a species that exhibited an absorption band at 660 cm^{-1} attributed to $\nu(\text{SbO})$ [36]. Under similar conditions, the coordination compound $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ was oxidized to *trans*- $[\text{Ru}(\text{NO})\text{Cl}_3(\text{OSbPh}_3)_2]$. The IR spectrum of this substance had an absorbance at 555 cm^{-1} assignable to the $\nu(\text{SbO})$ of a coordinated triphenylstibine oxide ligand. The ^1H NMR spectrum and elemental analysis were also consistent with the proposed structure of the oxidized complex.

Dechlorination with triphenylstibine has been used for the synthesis of a five-membered ring system containing two nitrogen and three selenium atoms [37]:

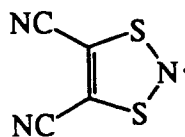


The yield of the red salt thus produced was 50%, but the exact stoichiometry of the reaction was not elucidated. By-products of the process included triphenylantimony dichloride, triphenylchloroantimony tetrachlorogallate, and triphenylantimony selenide. The structure of the cyclic cation was established by X-ray diffraction

and was found to be well represented by the following canonical structures:

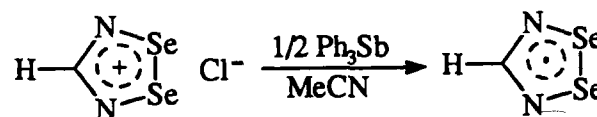


The following 4,5-dicyano-1,3,2-dithiazol-2-yl radical has been prepared by treatment of the corresponding hexachloroantimonate salt with tetraethylammonium chloride and subsequent reduction with triphenylstibine [38]:



The ESR spectrum of this radical in dichloromethane at 298 K was very simple, consisting of three sharp lines having intensity ratios of 1:1:1. A powder spectrum was also obtained, and spectral parameters were derived.

A diselenadiazolyl radical has been obtained by the reduction of 1,2,3,5-diselenadiazolium chloride with triphenylstibine [39]:

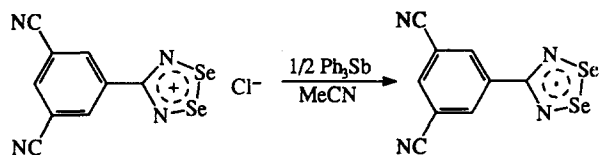


The ESR signal of the radical (in dichloromethane at 295 K) consisted of a featureless singlet with g equal to 2.041. The crystal structure of the dimer of the radical was determined by X-ray diffraction.

Further information about the above radical and its dimer has been given in a subsequent publication [40]. This paper also described the preparation of the 1,2,3,5-dithiadiazolyl radical by the reduction of 1,2,3,5-dithiadiazolium chloride with triphenylstibine in liquid sulfur dioxide. The ESR spectrum of this radical in toluene at room temperature consisted of a poorly resolved quintet at $g = 2.0102$. When the solution was cooled to 169 K, the resolution improved, and analysis of the second-derivative spectrum revealed a quintet of doublets. X-ray diffraction was employed to determine the crystal structure of the dimer of this radical.

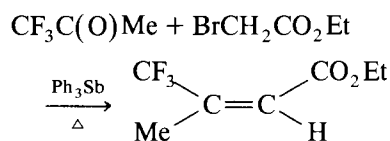
A 3,5-dicyanophenyl derivative of the 1,2,3,5-diselenadiazolyl radical has also been prepared by reduc-

tion of the corresponding chloride with triphenylstibine [41]:

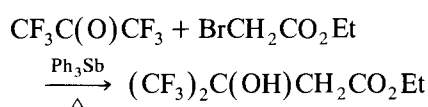


The green solid thus obtained was shown by X-ray diffraction to consist of stacked arrays of radical dimers. The structure of this substance was compared with the structures previously observed for the 3-cyanophenyl and 4-cyanophenyl derivatives [42].

Triphenylstibine has been used to mediate the olefination of 1,1,1-trifluoro-2-propanone with ethyl bromoacetate [43]:



A study of the product by mass and ^1H NMR spectroscopy indicated that the product possessed the *Z* configuration. Attempted extension of the above reaction to hexafluoroacetone, however, yielded an alcohol:



There have been numerous recent publications that described the use of tertiary stibines as antimony sources for the preparations of epitaxial layers of various antimonides. For example, the newly developed *tert*-butyldimethylstibine (in conjunction with trimethylgallium) has been employed for the OMVPE growth of GaSb layers at temperatures ranging from 500 to 650°C [44]. Good surface morphologies were obtained when the ratio of the stibine to organogallium compound was about unity. The growth efficiency of about $10^4 \mu\text{mol}^{-1}$ indicated that there were negligible parasitic reactions between the two precursors. It was concluded that *tert*-butyldimethylstibine was a good replacement for trimethylstibine over a wide range of growth temperatures.

Since *tert*-butyldimethylstibine has been shown to be 50% pyrolyzed at 470°C, the relatively high temperature ($\geq 500^\circ\text{C}$) required for the epitaxial growth of GaSb has been ascribed to the pyrolysis characteristics of trimethylgallium (only 50% decomposed at 560°C) [45]. Trimethylindium, however, has a slightly lower pyrolysis temperature than the stibine, and the use of these precursors has allowed the growth of InSb at 400°C. The pyrolysis kinetics of trimethylstibine, *tert*-butyldimethylstibine, trimethylgallium, and trimeth-

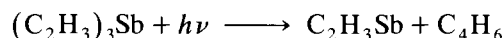
ylindium were determined under real growth conditions by means of in situ UV spectroscopy.

Other studies have investigated the use of *tert*-butyldimethylstibine or triisopropylstibine (in conjunction with trimethylindium or triethylindium) for the growth of InSb by MOCVD [46–48]. A temperature range of 350 to 475°C and pressures between 200 and 660 Torr were employed. In all cases the surface morphology of the InSb was very rough for growth temperatures $\leq 425^\circ\text{C}$. Surface morphology improved with higher temperature, pressure, and the ratio of trialkylstibine to trialkylindium.

Trimethylstibine has continued to be popular as the antimony source for the MOCVD growth of GaSb [49–52] and InSb [53,54]. It has also been employed for the growth of GaInSb [55], InPSb [56], and strained-layer InSb/GaSb quantum wells [57]. Both trimethylstibine and triethylstibine have been used in the production of InAsSb buffer layers by MOCVD [58], and triethylstibine has been employed for growing GaInSb by MOCVD [59] and GaAsSb by metalorganic molecular beam epitaxy (MOMBE) [60].

Triethylstibine has been included in a study of the explosive decomposition in the gas phase of volatile alkyl organometallic derivatives of elements of Groups 12–16 of the periodic table [61]. The explosive susceptibility was theoretically evaluated at the flame temperature from ΔG for the reaction $\text{MR}_n \rightarrow \text{M} + n/2\text{RR}$. Since $\Delta G < 0$ for all the reactions considered, it was concluded that explosive decomposition was expected in principle in every case. Explosive decomposition did not occur, however, for seven of the compounds studied (Me_2Zn , Me_3Al , Et_3Al , Me_3Ga , Et_4Sn , Et_3As , and Et_2Te). Explosibility was empirically correlated with the strength of the carbon–metal bond. Safety procedures for handling these compounds were also discussed.

Pulsed 193 nm excimer-laser radiation has been employed in an investigation of the UV photochemistry of trivinylstibine adsorbed on a cold quartz surface [62]. The UV absorption spectrum was measured in the pressure range of 0.135 to 5.185 Torr. At 193 nm the extinction coefficient was found to be $16687 \text{ L mol}^{-1} \text{ cm}^{-1}$. Photodissociation (PDIS) and photodesorption (PDES) components were determined with a quadrupole mass spectrometer. The PDIS species observed were $(\text{C}_2\text{H}_3)_2\text{Sb}$, $\text{C}_2\text{H}_3\text{Sb}$, Sb , C_2H_3 , and C_2H_2 . Ethene, 1,3-butadiene, and diantimony were also produced, probably via combination reactions at the surface. Some of the diene may have been formed by a direct elimination reaction:

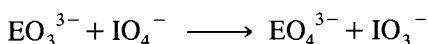


A mechanism was proposed for the photochemistry of adsorbed trivinylstibine.

Trimethylstibine and the radical cations Me_3Sb^+ and Me_6Sb_2^+ have been included in a PM3 SCF study of the molecular and electronic structures of organometallic radicals derived from methyl derivatives of elements of periodic Groups 13–16 [63]. The calculated values of the C–Sb distance and C–Sb–C angle for trimethylstibine were in satisfactory agreement with the corresponding experimentally determined values; experimental values for the radical cations have not been determined. In keeping with the expected stereochemical effect of the lone pair in trimethylstibine, the loss of one electron to form Me_3Sb^+ led to a significant increase in the calculated C–Sb–C angle of the latter species.

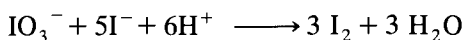
Capillary gas chromatography has been employed for the determination of traces of triethylstibine (and of other alkyl derivatives of elements of Groups 14–17) in high purity diethyltellurium [64]. The limit of detection of these impurities was 10^{-3} to 10^{-6} mol%.

Triphenylstibine has been included in a study of the iodometric microdetermination of arsenic or antimony in organic compounds [65]. The method involved decomposing the organic compound with a mixture of nitric and sulfuric acids, reducing the inorganic arsenic or antimony thus obtained, and then oxidizing the resulting arsenite or antimonite with periodate:



(where E was As or Sb).

The iodate and arsenate or antimonate formed by the above type of reaction were allowed to react with iodide:



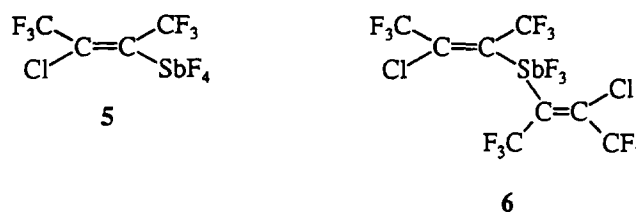
The average recovery for antimony was 99.5%, and the average standard deviation was 0.34%.

In addition to papers already discussed [30,36], there were a number of other reports published in 1993 that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included cobalt [66], gold [67], iron [68], molybdenum [69,70], osmium [71], palladium [72], platinum [72,73], rhodium [74], ruthenium [75], titanium [76], and tungsten [70].

A Japanese patent has described the use of organoantimony compounds in preparing electrophotographic developer toners [77]. The compounds included triarylstibines, triarylstibine oxides, and substances of the type $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{R}^5\text{Sb}$, where R^1 and R^2 were aryl, R^3 and R^4 were aryl, halo, hydroxy, cyano, or thiocyanato, and R^5 was halo, hydroxy, cyano, or thiocyanato. Other Japanese patents have mentioned trimethylstibine as an example of a starting material for the production of

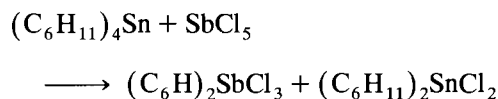
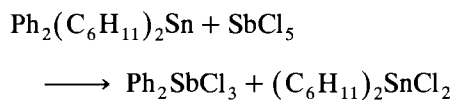
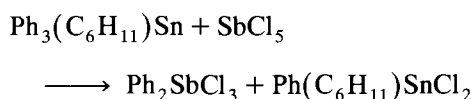
carbon-containing semiconducting compounds of Group 13 and Group 15 elements [78] and triphenylstibine as a promoter in the preparation of alicyclic diisocyanates by the thermal decomposition of alicyclic biscarbamate esters [79]. An American patent has listed triphenylstibine as a metal compound useful for the preparation of ceramic composites having high density, strength, and hardness [80].

Chepick and coworkers [81] have studied some electrophilic reactions of 2-chloroperfluoro-1,3-butadiene, $\text{CF}_2=\text{CCl}-\text{CF}=\text{CF}_2$. The butadiene did not react with anhydrous HF at temperatures 20–150°C, nor with trifluoromethane or fluorosulfonic acid, but did react with antimony pentafluoride in SO_2ClF at -10°C to give the following two compounds:



The ratio of **5** to **6** was 6:1. The products were not separated but were identified in the mixture by ^{19}F NMR and mass spectrometry. When the mixture was warmed in 70% H_2SO_4 , the Sb–C bonds were cleaved to give 2-chloro-3-hydrohexafluoro-2-butene.

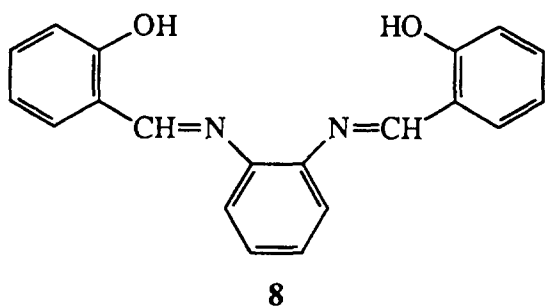
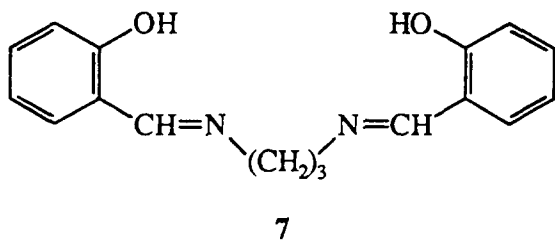
In a paper devoted to the cleavage of the Sn–C bond in several cyclohexyl tin compounds by various electrophilic reagents, organoantimony(V) compounds were formed when SbCl_5 was the electrophile [82]:



The reactions were carried out in toluene at RT. The Ph_2SbCl_3 was identified by mp and IR spectroscopy, while $(\text{C}_6\text{H}_{11})_2\text{SbCl}_3$ was characterized by elemental analysis as well as by IR spectroscopy.

Jha and coworkers have previously reported a series of organoantimony(V) complexes of the type R_3SbL , where R was an alkyl or aryl group and L was a polydentate Schiff base. A new paper from Jha's laboratory has described complexes of the type R_2SbXL ,

where X was Br or Cl and L was one of the following Schiff bases [83]:



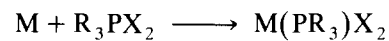
Schiff base **7** was condensed with the organoantimony compounds Ph_2SbBr_3 , $(4\text{-MeC}_6\text{H}_4)_2\text{SbBr}_3$, and Ph_2SbCl_3 ; Schiff base **8** was condensed with the same antimony compounds as well as with Me_2SbBr_3 . The reactions were carried out by adding the disodium salt of the ligand in benzene-methanol solution to the antimony compound in benzene. The products, after recrystallization, were yellow or orange solids, sensitive to moisture to varying extents. They were monomolecular in benzene and non-conducting in acetonitrile. The new compounds, as well as the uncoordinated Schiff bases, were characterized by elemental analysis and by ^1H NMR and IR spectroscopy. The two methyl groups of the complexes obtained from Me_2SbBr_3 and from $(4\text{-MeC}_6\text{H}_4)_2\text{SbBr}_3$ were in two different environments. On the basis of these results the authors concluded that the Schiff base ligands were tetradentate and that the antimony atom possessed a pentagonal-bipyramidal structure with the halogen atom and one R group in axial positions.

Raj, Saxena, and coworkers have published several papers on organoantimony(III) and organoantimony(V) compounds containing the pentafluorophenyl group. A new paper by Saxena and coworkers [84] has described the preparation and properties of nine new compounds of the type $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{O}_2\text{CR})_2$, where R was a phenyl or substituted phenyl or where R was a methyl or substituted methyl group. In addition to the pentafluorophenyl compounds, bis(phenoxyacetato)trimethylantimony was prepared. Two different methods were used for preparing the new compounds. By one method the

potassium (or sodium) salts of the acids $\text{HO}_2\text{CCH}_2\text{O}-\text{C}_6\text{H}_5$, $\text{HO}_2\text{CCH}_2\text{OC}_6\text{H}_4\text{Cl}$ -4, $\text{HO}_2\text{CCH}_2\text{OC}_6\text{H}_3\text{Cl}_2$ -2,4, and $\text{HO}_2\text{CCH}_2\text{OC}_6\text{H}_2\text{Cl}_3$ -2,4,5 were treated with tris(pentafluorophenyl)antimony dichloride in benzene solution in the presence of catalytic amounts of 18-crown-6 or 15-crown-5. This same method employing trimethylantimony dibromide and the sodium or potassium salt of phenoxyacetic acid was used to prepare bis(phenoxyacetato)trimethylantimony. By the second method the phenoxyacetic acid and tris(pentafluorophenyl)antimony dichloride were stirred and refluxed in benzene solution in the presence of triethylamine. This same method was used with trimethylantimony dibromide to give bis(phenoxyacetato)trimethylantimony. The second method gave slightly larger yields than the first method, and it was the only method used to prepare the acetato compounds $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{O}_2\text{CR})_2$ (where R was Me, CF_3 , CCl_3 , CHCl_2 , or CH_2Cl). The reaction between acetic acid (or α -halogenated acetic acid) and tris(pentafluorophenyl)antimony dichloride (first method) did not yield crystalline products. Finally, bis(acetato)tris(pentafluorophenyl)antimony was prepared by a third method. Tris(pentafluorophenyl)stibine in octane was stirred and refluxed with acetic anhydride and periodic acid. After concentration and cooling, a 95% yield of the desired compound was obtained.

All of the new compounds were crystalline solids with sharp mps and were fairly stable to air and moisture. They were non-electrolytes in methanol solution. They were characterized by elemental analysis, IR, UV and ^1H , ^{13}C , and ^{19}F NMR spectroscopy. On the basis of the NMR spectral results, it was concluded that the pentafluorophenyl (or methyl) groups were all in one plane. The IR and UV spectral results were in accord with the acetato groups behaving as monodentate ligands. These results suggested that the geometry of the antimony atom was that of a trigonal bipyramid with the acetato groups in axial positions.

Transition metal complexes containing tertiary phosphine ligands have been widely studied. Although these have usually been prepared from a metal salt and the tertiary phosphine, McAuliffe and coworkers have reported a method for their preparation from tertiary phosphine dihalides and a metal:

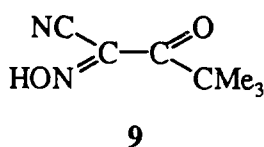


(where X was Br or I, and M was a metal).

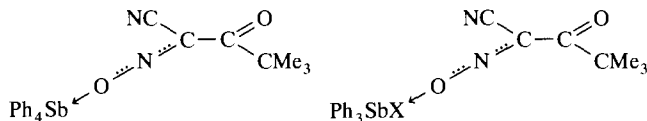
A new paper from McAuliffe's laboratory [66] described the preparation of a considerable number of cobalt complexes of the type $[\text{PR}_3\text{I}][\text{Co}(\text{PR}_3)\text{I}_3]$, where R was an aryl or alkyl group. The syntheses were carried out by the reaction between coarse-grain cobalt powder and two molar equivalents of the tertiary phosphine dihalide in diethyl ether for 15 days at RT or in a sealed tube for 5 days at 50°C . In addition to the phosphine complexes, the authors prepared the tertiary

stibine complex $[\text{Ph}_3\text{SbI}][\text{Co}(\text{Ph}_3\text{Sb})\text{I}_3]$ from triphenylantimony diiodide and cobalt metal in diethyl ether in a sealed tube at 60°C for 5 days. The antimony compound was characterized by elemental analysis, and by comparison of its Raman and electronic spectra with those of the corresponding phosphorus complexes. Two shoulders in the Raman spectrum at 118 and 164 cm^{-1} were assigned to $\nu(\text{Sb}-\text{I})$ and $\nu(\text{Co}-\text{I})$, respectively, while a peak at 221 cm^{-1} was tentatively assigned to $\nu(\text{Co}-\text{Sb})$.

Fedorenko and coworkers [85] have prepared the oxime **9** and studied complexes of the corresponding anion with a number of metals, as well as with the tin compound Me_2SnCl_2 and with the antimony compounds Ph_3SbCl_2 , Ph_3SbBr_2 , and Ph_4SbCl .



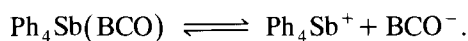
The antimony complexes were obtained by the reaction between one equivalent of Ph_4SbBr , Ph_3SbCl_2 , or Ph_3SbBr_2 and one equivalent of the silver salt of **9** in acetonitrile. Only one halogen was displaced from the two triphenylantimony compounds. The three products were characterized by elemental analysis (nitrogen only) and by IR spectroscopy. On the basis of their IR spectra, it was suggested that they possessed the following structures:



(where X was Cl or Br).

Gerasimchuk and coworkers [86] have prepared the oxime $\text{PhCOC}(\text{CN})\text{NOH}$ (HBCO) from which they prepared a number of metallic salts as well as two tin and two antimony derivatives (namely $\text{Ph}_3\text{Sb}(\text{Cl})(\text{BCO})$ and $\text{Ph}_4\text{Sb}(\text{BCO})$). All of the compounds were characterized by elemental analysis (results not reported) and by IR spectroscopy. An X-ray diffraction study of the antimony compound $\text{Ph}_4\text{Sb}(\text{BCO})$ was also carried out. The geometry of the antimony atom was that of slightly distorted trigonal bipyramid with one phenyl group and the oxygen atom of the NO in axial positions. The axial $\text{C}-\text{Sb}-\text{O}$ angle was 175.4° . The oxime was in the nitroso configuration. The benzoylcyanooxime ligand was monodentate, i.e. there was no coordination between the carbonyl oxygen and the antimony atom. The compound in the solid state and in benzene solution was colorless, but in DMSO and in hot DMF the solutions were yellow. The authors suggested that these results

were due to complex ionization in polar solutions:



The crystal and molecular structures of only a few triphenyldihalo derivatives of Group 15 elements are known. Chekhlov [87] has now determined the crystal and molecular structure of difluorotriphenylantimony by X-ray diffraction. The geometry of the antimony atom was classical trigonal-bipyramidal with axial fluorine atoms. The $\text{F}-\text{Sb}-\text{F}$ angle was 179.51° . Almost all of the bond angles at the antimony atom were close to the ideal values for the trigonal-bipyramidal structure. The conformation of the phenyl rings was a propeller arrangement with torsion angles ($\text{F}-\text{Sb}-\text{C}-\text{C}$) which varied from 3.5 – 21° . All of the $\text{H}\cdots\text{F}$ intramolecular bond distances involving the *ortho* hydrogen atoms were considerably shorter (0.25 – 0.40 \AA) than the sum of the van der Waals distances. The $\text{C}\cdots\text{F}$ distances to the carbons bearing the *ortho* hydrogen atoms were also shortened. These results suggested the formation of $\text{Sb}-\text{F}\cdots\text{H}$ hydrogen bonds involving the *ortho* hydrogens of the phenyl rings. The attractive energy of these hydrogen bonds apparently overcame the energetically unfavorable conformation of the phenyl rings (close to eclipsed with the fluorine atoms). All of the short intermolecular contacts of the difluorotriphenylantimony molecule were close to the sums of the corresponding van der Waals radii of the atoms.

Begley and Sowerby [88] have determined the crystal and molecular structures of dibromo- and dichlorotriphenylantimony by X-ray diffraction. The structure of the latter compound had been reported earlier [89]; the present redetermination was undertaken in order to obtain more accurate parameters. In both compounds the geometry of the antimony atom was classical trigonal-bipyramidal with the halogens in axial positions. The $\text{Br}-\text{Sb}-\text{Br}$ angle was 179.06° , while the $\text{Cl}-\text{Sb}-\text{Cl}$ angle was 176.07° . The structure of the two compounds differed principally in the orientation of the phenyl groups around the antimony atom. In the dichloro compound the orientation of the phenyl groups was that of a propeller-like arrangement with torsion angles (with respect to one of the $\text{Sb}-\text{Cl}$ bonds) of 48.3° , 58.6° and 28.2° . The small torsion angle of 28.2° allowed short intermolecular contacts between *ortho* hydrogen atoms and the chlorine atoms. In the dibromo compound the torsion angles of the phenyl groups (with respect to one of the $\text{Sb}-\text{Br}$ bonds) were 55.8° , 55.8° and -67.7° , respectively.

A number of papers by Dodonov, Grishin, and coworkers have appeared in 1993 in which organoantimony(V) peroxides have been used as initiators for the polymerization of monomeric alkenyl compounds. In addition to the antimony compounds, trialkylboron

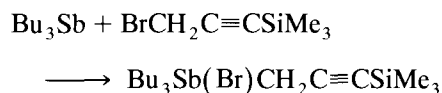
compounds were also employed in these polymerizations. Thus, the copolymerization of vinyl acetate with acrylonitrile, vinylidene chloride, vinyl chloride, or ethylene was carried out using triisobutylboron and either di-*tert*-butylperoxytriphenylantimony or *tert*-butylperoxytetraphenylantimony [90]. Peroxy compounds of germanium, tin, or silicon [91] were also used. At least with the copolymerization of C₂-C₆ olefins with vinyl monomers, the organoantimony compounds were the most effective [92]. Other papers dealing with the polymerization and copolymerization of various alkenyl compounds by these authors have also appeared [93–98].

Bis(2,4,6-tribromophenoxy)triphenylantimony has been prepared from Ph₃SbX₂ (where X was a halogen) by treatment with 2,4,6-tribromophenol [99]. The flame retardant properties of the compound were tested.

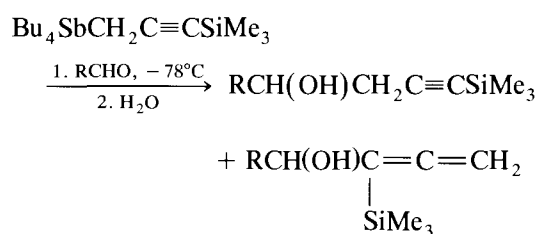
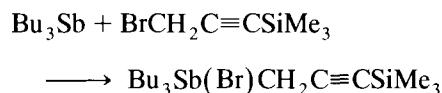
Arvanitis and coworkers [100] have prepared two new tetraphenylantimony compounds by the reaction between tetraphenylantimony bromide and 2-mercaptopyridine *N*-oxide (or the corresponding 2-seleno compound) in the presence of triethylamine. The reaction of the mercapto compound was carried out in refluxing ethanol, but the seleno compound was prepared in ethanol at 40°C. Both compounds were characterized by elemental analysis and by IR, ¹H and ¹³C NMR spectroscopy. The ¹H NMR signals of the *ortho* and *para* protons broadened on cooling to 223 K, but no limiting spectrum was obtained. The IR spectra of the two compounds suggested that the pyridine *N*-oxide ligands were bidentate. The crystal and molecular structure of the mercapto compound was determined by X-ray diffraction. The N–O distance was within the extremes of Sb–O bonds of Sb(V) compounds, and the Sb–C bond lengths were those expected for an octahedral compound. All such results showed that the geometry of the antimony atom was octahedral. The two compounds were tested for antimalarial activity and found to be about as active as chloroquine, a widely used antimalarial drug.

In a previous paper from Huang's laboratory [101], the reaction of allenyltetra-butylantimony or propargyltetra-butylantimony with aldehydes was reported. The reaction of tributylstibine with propargyl bromide gave the allyl compound Bu₃Sb(Br)CH=C=CH₂ which reacted further with butylmagnesium bromide to give Bu₄SbCH=C=CH₂. Reaction of this stiborane with aldehydes RCHO (where R was an alkyl or aryl group), followed by aqueous workups, gave homopropargylic alcohols, RCH(OH)CH₂C≡CH. By contrast, tetra-butyl-2-butynylantimony (obtained from tributylstibine and 1-bromo-2-butyne, followed by treatment of the bromo product with butylmagnesium bromide) reacted with aldehydes to give mixtures of homopropargylic and allylenic alcohols. In a new paper from Huang's laboratory [102] the reaction of trimethylsilylpropargyl bromide with tributylstibine was found to give the

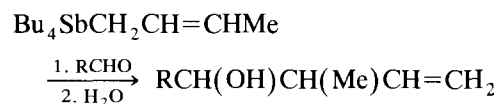
acetylenic compound according to the following equation:



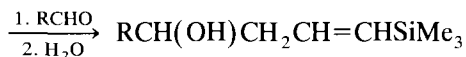
Treatment of this bromo compound with either butylmagnesium bromide or butyllithium gave the stiborane Bu₄SbCH₂C≡CSiMe₃. When this reacted with aldehydes, RCHO, and the reaction product was hydrolysed, a mixture of acetylenic and allylenic alcohols was produced:



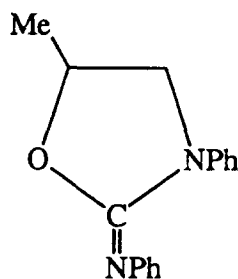
It was found, however, that the regioselectivity of the above reaction was largely determined by the reagent (BuMgBr or BuLi) used to form the stiborane. Thus, when the stiborane, prepared from butyllithium in THF/hexane (5:1), reacted with benzaldehyde, the ratio of acetylenic:allylenic alcohol was 94:6 (with a total yield of alcohol of 80%). By comparison, the ratio was 60:40 when butylmagnesium bromide in THF was used to prepare the stiborane. The total yield of alcohol in this case was 88%. However, when lithium bromide was added to the reaction using the Grignard reagent, the ratio of the two products was 90:10. This effect of lithium reagent vs. Grignard reagent was also found when the solvent used in the reactions was ethyl ether. When cyclohexane carboxaldehyde was used with the stiborane prepared from: (a) butyllithium, (b) butylmagnesium bromide, or (c) butylmagnesium bromide plus lithium bromide, the ratios of acetylenic to allylenic alcohol were 92:8; 65:35; and 92:8, respectively. Heptaldehyde with butylmagnesium bromide plus lithium bromide gave the acetylenic and allylenic alcohols in a ratio of 85:15. 4-Chlorobenzaldehyde and 4-methylbenzaldehyde with butyllithium in THF both gave the acetylenic alcohol vs. the allylenic alcohol in a ratio of 95:5. Finally, crotyltetra-butylantimony was prepared from crotyltributylantimony bromide using either butyllithium or butylmagnesium bromide. Reaction of this stiborane with aldehydes gave only one product:



The trimethylsilyl allylic compound also gave only a single product:



Tetraphenylantimony iodide has been used as a catalyst for the preparation of oxazolidine imines [103]. Thus, the reaction of propylene oxide and $\text{PhN}=\text{C}=\text{NPh}$, catalyzed by Ph_4SbI and ZnBr_2 in benzene, gave the following imine:



A similar patent from the same laboratory employed tetraphenylantimony derivatives as catalysts for the preparation of β -hydroxyethers [104]. Thus, cyclohexene oxide, ethanol, and tetraphenylantimony triflate at 80 °C gave a 70% yield of *trans*-2-ethoxy-1-cyclohexanol.

A Russian patent has described the use of paraform for the preparation of compounds of the type $\text{R}_2^1\text{SbR}_2^2(\text{OCH}_2\text{R}^1)$ from compounds of the type $\text{R}_3^1\text{SbR}_2^2$, where R^1 and R^2 were alkyl or phenyl groups [105].

Kitazawa and coworkers [106] have prepared $[\text{Ph}_4\text{Sb}]_2$ $[\text{Cd}(\text{CN})_4]$ from $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{K}_2[\text{Cd}(\text{CN})_4]$, and Ph_4SbOH . The crystal and molecular structure of the compound was obtained by X-ray diffraction. The anion contained an infinite chain of Cd coordination tetrahedra linked by cyanide groups. The Ph_4Sb^+ ions had a weak interaction to the nitrogen of the non-bridging cyano group. This resulted in distortion of tetrahedral symmetry of the cation.

Tetraphenylantimony sulfate has been used in the determination of palladium as the PAR complex [107]. The Pd-PAR complex plus the antimony compound was extracted with CHCl_3 from an acetate-buffered solution at pH 4.4, and the Pd was determined spectrophotometrically.

A Japanese patent described the use of tetraalkyl or tetraarylantimony derivatives (triflates, perchlorates, and nitrates) as cross linking catalysts for preparing epoxy resins for use as coatings, adhesives, and moldings [108].

In a paper devoted to the differences of interactions of solvent molecules with cations and anions, the solubility products and molar Gibbs energies of transfer (from acetonitrile to a wide variety of other solvents) of several electrolytes were measured [109]. Tetraphenylstibonium tetrafluoroborate was one of the reference electrolytes studied.

Although the crystal and molecular structures of pentaaryl derivatives of Group 15 elements are quite well known, very few molecular structures of pentaalkyl derivatives of Group 15 elements have been reported. Haaland and coworkers have now reported gas electron diffraction studies on pentamethylantimony [110]. The configuration of the antimony atom was trigonal-bipyramidal (D_{3h}) with equatorial Sb–C distances of 214.0 pm and axial Sb–C distances of 226.4 pm. The authors compared these bond distances with equatorial and axial Sb–C bond distances in other known organoantimony(V) compounds which possessed trigonal-bipyramidal configurations. The equatorial Sb–C bond distances in Me_5Sb , $\text{Ph}_5\text{Sb} \cdot 0.5\text{cyclohexane}$, and $\text{Me}_3\text{Sb}(\text{C}\equiv\text{CMe})_2$ were indistinguishable, and the axial bond distances varied only slightly from each other. The equatorial and axial Sb–C distances were somewhat shorter in $\text{Sb}(\text{C}\equiv\text{CMe})_5$ (205 and 215 pm (respectively), while the equatorial bond distances in Me_3SbCl_2 and Me_3SbF_2 were 210.7 and 209 pm respectively. From these data the authors concluded that axial Sb–C bond distances were more sensitive to the substitution in equatorial positions than vice versa. In addition to gas electron diffraction studies, the ^{13}C NMR spectrum of Me_5Sb was determined in CDCl_2 at 20 and -90°C . At each temperature only a single peak was found. This peak sharpened noticeably as the temperature decreased.

Finally, ab initio MO calculations were carried out on trigonal-bipyramidal and square-pyramidal models of Me_5Sb and on the unknown compound Me_5Bi . Both trigonal-bipyramidal and square pyramidal models were optimized at the SCF MO level. Calculations at this level suggested that the trigonal-bipyramidal configuration of Me_5Sb was more stable than the square-pyramidal configuration by 7.1 kJ mol $^{-1}$. Calculations on Me_5Bi suggested that the trigonal-bipyramidal configuration would also be more stable than the square-pyramidal configuration.

References

- [1] H.J. Breunig, *Main Group Met. Chem.*, 16 (1993) 143.
- [2] G.B. Stringfellow, *J. Cryst. Growth*, 128 (1993) 503.
- [3] E. Yablonoitch, G.B. Stringfellow and J.E. Greene, *J. Electron. Mater.*, 22 (1993) 49.
- [4] Y. Yamamoto and N. Asao, *Chem. Rev.*, 93 (1993) 2207.
- [5] M. Vahter and E. Marafante, *Met. Ions Biol. Syst.*, 29 (1993) 161.

- [6] G.A. Cutter, *Mar. Chem.*, 40 (1992) 65.
- [7] D.A. Armitage, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, 88 (1993) 49; 89 (1993) 53.
- [8] J.L. Wardell, *Organomet. Chem.*, 22 (1993) 138; *Chem. Abstr.*, 120 (1994) 54568f.
- [9] J.A. Chamizo, J. Morgado and P. Sosa, *Organometallics*, 12 (1993) 5005.
- [10] A.P. Sadimenko, A.D. Garnovskii and N. Retta, *Coord. Chem. Rev.*, 126 (1993) 237.
- [11] J.S. Thayer, *Met. Ions Biol. Syst.*, 29 (1993) 1.
- [12] D.G. Hendershot and A.D. Berry, *J. Organomet. Chem.*, 449 (1993) 119.
- [13] R.W. Gedridge, Jr., K.E. Lee and C. Lowe-Ma, *Chem. Mater.*, 5 (1993) 979.
- [14] R.W. Gedridge, Jr., K.E. Lee and C.K. Lowe-Ma, *Mater. Res. Soc. Symp. Proc.*, 282 (1993) 81; *Chem. Abstr.*, 120 (1993) 233163s.
- [15] J. Shin, K. Chiu, G.B. Stringfellow and R.W. Gedridge, Jr., *J. Cryst. Growth*, 132 (1993) 371.
- [16] C. Hill, J. Shin and G.B. Stringfellow, *Proc.—Electrochem. Soc.*, 93–27 (1993) 26; *Chem. Abstr.*, 120 (1994) 233831h.
- [17] R.S. Dickson, K.D. Heazle, G.N. Pain, G.B. Deacon, B.O. West, G.D. Fallon, R.S. Rowe, P.W. Leech and M. Faith, *J. Organomet. Chem.*, 449 (1993) 131.
- [18] M. Herberhold, C. Dörnhofer, A. Scholz and G.-X. Jin, *Phosphorus, Sulfur Silicon Relat. Elem.*, 64 (1992) 161.
- [19] M. Herberhold and H.-D. Brendel, *J. Organomet. Chem.* 458 (1993) 205.
- [20] (a) J. Kurita, M. Ishii, S. Yasuie and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, (1993) 1309; (b) G.O. Doak and L.D. Freedman, *J. Organomet. Chem.*, in press.
- [21] S. Yasuie, H. Ohta, S. Shiratori, J. Kurita and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, (1993) 1817.
- [22] R.E.v.H. Spence, S.L. Buchwald and J.F. Richardson, *Acta Chem. Scand.*, 47 (1993) 326.
- [23] F. Bringewski, G. Huttner, W. Imhof and L. Zsolnai, *J. Organomet. Chem.*, 439 (1992) 33.
- [24] N.K. Jha, J.R. Ugal and P. Sharma, *Indian J. Chem., Sect. A: Inorg., Bio-Inorg., Phys., Theor. Anal. Chem.*, 32A (1993) 71.
- [25] K. Singhal, *Synth. React. Inorg. Met.-Org. Chem.*, 23 (1993) 1363.
- [26] R. Karra, Y.P. Singh and A.K. Rai, *Indian J. Chem., Sect. A: Inorg., Bio-Inorg., Phys., Theor. Anal. Chem.*, 32A (1993) 78.
- [27] J.-K. Buijink, M. Noltemeyer and F.T. Edelman, *J. Fluorine Chem.*, 61 (1993) 51.
- [28] L.-J. Zhang and Y.-Z. Huang, *J. Organomet. Chem.*, 454 (1993) 101.
- [29] M. Wieber and N. Graf, *Z. Anorg. Allg. Chem.*, 619 (1993) 1991.
- [30] N. Graf and M. Wieber, *Z. Anorg. Allg. Chem.*, 619 (1993) 2061.
- [31] C. Silvestru, I. Haiduc, R. Kaller, K.H. Ebert and H.J. Breunig, *Polyhedron*, 12 (1993) 2611.
- [32] F. Ando, R. Mio and J. Koketsu, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1998.
- [33] A. Haaland, H.P. Verne, H.V. Volden, H.J. Breunig and S. Gülec, *Z. Naturforsch., B: Chem. Sci.*, 48 (1993) 1065.
- [34] C.J. Thomas, L.K. Krannich and C.L. Watkins, *Polyhedron*, 12 (1993) 89.
- [35] Z. Tian and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, (1993) 1381.
- [36] J.E. Fergusson and R.K. Coll, *Inorg. Chim. Acta*, 207 (1993) 191.
- [37] R. Wollert, B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 616 (1992) 191.
- [38] Y.-L. Chung, S.A. Fairhurst, D.G. Gillies, G. Kraft, A.M. L. Krebber, K.F. Preston, L.H. Sutcliffe and G. Wolmershäuser, *Magn. Reson. Chem.*, 30 (1992) 774.
- [39] A.W. Cordes, S.H. Glarum, R.C. Haddon, R. Hallford, R.G. Hicks, D.K. Kennepohl, R.T. Oakley, T.T. M. Palstra and S.R. Scott, *J. Chem. Soc., Chem. Commun.*, (1992) 1265.
- [40] A.W. Cordes, C.D. Bryan, W.M. Davis, R.H. de Laat, S.H. Glarum, J.D. Goddard, R.C. Haddon, R.G. Hicks, D.K. Kennepohl, R.T. Oakley, S.R. Scott and N.P. C. Westwood, *J. Am. Chem. Soc.*, 115 (1993) 7232.
- [41] W.M. Davis, R.G. Hicks, R.T. Oakley, B. Zhao and N.J. Taylor, *Can. J. Chem.*, 71 (1993) 180.
- [42] A.W. Cordes, R.C. Haddon, R.G. Hicks, R.T. Oakley and T.T. M. Palstra, *Inorg. Chem.*, 31 (1992) 1802.
- [43] H. Abele, A. Haas, M. Lieb and J. Zwingenberger, *J. Fluorine Chem.*, 62 (1993) 25.
- [44] C.H. Chen, C.T. Chiu, L.C. Su, K.T. Huang, J. Shin and G.B. Stringfellow, *J. Electron. Mater.*, 22 (1993) 87.
- [45] R.M. Graham, A.C. Jones, N.J. Mason, S. Rushworth, A. Sables, T.-Y. Seong, G. Booker, L. Smith and P.J. Walker, *Semicond. Sci. Technol.*, 8 (1993) 1797.
- [46] R.M. Biefeld, *Mater. Res. Soc. Symp. Proc.*, 282 (1993) 11.
- [47] R.M. Biefeld, *J. Cryst. Growth*, 128 (1993) 511.
- [48] R.M. Biefeld and K.C. Baucom, *Mater. Res. Soc. Symp. Proc.*, 312 (1993) 179.
- [49] B. Zhang, T. Zhou, H. Jiang, Y. Jin, C. Hong, J. Yuan and G. Miao, *Rare Met. (Beijing)*, 11 (1992) 86; *Chem. Abstr.*, 120 (1994) 258612a.
- [50] Y.K. Su, H. Kuan and P.H. Chang, *J. Appl. Phys.*, 73 (1993) 56.
- [51] Y.K. Su, H. Kuan and P.H. Chang, *Solid-State Electron.*, 36 (1993) 1773.
- [52] Y.K. Su and S.M. Chen, *J. Appl. Phys.*, 73 (1993) 8349.
- [53] C. Besikci, Y.H. Choi, R. Sudharsanan and M. Razeghi, *J. Appl. Phys. Part 1*, 73 (1993) 5509.
- [54] S.N. Song, J.B. Ketterson, Y.H. Choi, R. Sudharsanan and M. Razeghi, *Appl. Phys. Lett.*, 63 (1993) 964.
- [55] A. Giani, F. Pascal-Delannoy, G. Bougnot, G.G. Allogho and J. Bougnot, *J. Electrochem. Soc.*, 140 (1993) 2406.
- [56] R.M. Biefeld, K.C. Baucom, S.R. Kurtz and D.M. Follstaedt, *J. Cryst. Growth*, 133 (1993) 38.
- [57] L.Q. Qian and B.W. Wessels, *Appl. Phys. Lett.*, 63 (1993) 628.
- [58] R.M. Biefeld and T.J. Drummond, *Mater. Res. Soc. Symp. Proc.*, 240 (1992) 39.
- [59] M. Totoki, T. Mizumoto, T. Fujisawa and Y. Naito, *Jpn. J. Appl. Phys., Part 1*, 32 (1993) 5637.
- [60] Y. Itani, H. Asahi, T. Kaneko, Y. Okuno and S. Gonda, *J. Appl. Phys.*, 73 (1993) 1161.
- [61] A.S. Nikishin, A.N. Moiseev and V.N. Votintsev, *Vysokochist. Veshchestva*, (1992) 133; *Chem. Abstr.*, 119 (1993) 139400z.
- [62] J.A. Tarr, S.-P. Lee and M.C. Lin, *Mater. Chem. Phys.*, 33 (1993) 93.
- [63] C. Glidewell, *J. Organomet. Chem.*, 461 (1993) 15.
- [64] V.A. Krylov, S.G. Krasotskii, A.V. Sarkisov and O. Yu. Chernova, *Vysokochist. Veshchestva*, (1993) 133; *Chem. Abstr.*, 118 (1993) 246592q.
- [65] A.B. Farag, M.S. El-Shahawi and E.M. El-Nemma, *Fresenius J. Anal. Chem.*, 346 (1993) 455.
- [66] S.M. Godfrey, H.P. Lane, C.A. McAuliffe and R.G. Pritchard, *J. Chem. Soc., Dalton Trans.*, (1993) 1599.
- [67] C.J. Aguirre, M.C. Gimeno, A. Laguna, M. Laguna, J.M. López de Luzuriaga and F. Puente, *Inorg. Chim. Acta*, 208 (1993) 31.
- [68] D.A. Brown, N.J. Fitzpatrick, W.K. Glass, H.A. Ahmed, D. Cunningham and P. McArdle, *J. Organomet. Chem.*, 455 (1993) 157.

- [69] P.K. Baker, K.R. Flower, H.M. Naylor and K. Voigt, *Polyhedron*, **12** (1993) 357.
- [70] P.K. Baker and M. van Kampen, *Inorg. Chim. Acta*, **204** (1993) 247.
- [71] H.G. Ang, C.H. Koh, L.L. Koh and W.L. Kwik, *J. Organomet. Chem.*, **452** (1993) 181.
- [72] E.C. Alyea and G. Malito, *Gazz. Chim. Ital.*, **123** (1993) 709.
- [73] R. Usón, J. Forniés, M. Tomas, B. Menjón, C. Fortuno, A.J. Welch and D.E. Smith, *J. Chem. Soc., Dalton Trans.*, (1993) 275.
- [74] P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **32** (1993) 1480.
- [75] N.R. Champness, W. Levason and M. Webster, *Inorg. Chim. Acta*, **208** (1993) 189.
- [76] I. Suzuki and Y. Yamamoto, *J. Org. Chem.*, **58** (1993) 4783.
- [77] M. Orihara, S. Kuramoto and T. Hagiwara, *Jpn. Kokai Tokkyo Koho JP 04 291, 267* [92 291, 267]; *Chem. Abstr.*, **118** (1993) 222839z.
- [78] H. Koda and K. Wada, *Jpn. Kokai Tokkyo Koho JP 05 90, 166* [93 90, 166]; *Chem. Abstr.*, **119** (1993) 107336s.
- [79] T. Ookawa, Y. Sato, H. Igarashi and S. Suzuki, *Jpn. Kokai Tokkyo Koho JP 05 148, 216* [93 148, 216]; *Chem. Abstr.*, **119** (1993) 180453g.
- [80] K.E. Howard and D.J. Magley, *US Pat. US 5, 227, 345*; *Chem. Abstr.*, **119** (1993) 232357a.
- [81] S.D. Chepick, G.G. Belen'kii, V.A. Petrov and L.S. German, *J. Fluor. Chem.*, **65** (1993) 223.
- [82] K. Singhal, *Indian J. Chem., Sect. A: Inorg., Bio-inorg. Phys., Theor. Anal. Chem.*, **32A** (1993) 542.
- [83] N.K. Jha, P. Sharma and J.R. Ugal, *Indian J. Chem., Sect. A: Inorg., Bio-inorg. Phys., Theor. Anal. Chem.*, **32A** (1993) 74.
- [84] A.K. Saxena, A. Ranjan and P.S. Venkataramani, *J. Fluor. Chem.*, **64** (1993) 107.
- [85] D.A. Fedorenko, N.N. Gerasimchuk and K.V. Domasevich, *Zh. Neorg. Khim.*, **38** (1993) 1535.
- [86] N.N. Gerasimchuk, V.V. Skopenko, V.V. Ponomareva and K.V. Domasevich, *Zh. Neorg. Khim.*, **38** (1993) 1042.
- [87] A.N. Chekhlov, *Dokl. Akad. Nauk SSSR*, **328** (1993) 205.
- [88] M.J. Begley and D.B. Sowerby, *Acta Cryst., Sect. C: Cryst. Struct. Commun.*, **C49** (1993) 1044.
- [89] T.N. Polynova and M.A. Porai-Koshits, *Zh. Strukt. Khim.*, **7** (1966) 742.
- [90] D.F. Grishin and V.A. Dodonov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **35** (1992) 107; *Chem. Abstr.*, **118** (1993) 81506z.
- [91] D.F. Grishin and O. Yu. Chinyaeva, *Vysokomol. Soedin., Ser. B.*, **35** (1993) 156; *Chem. Abstr.*, **119** (1993) 96262m.
- [92] D.F. Grishin and V.B. Zhislina, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **35** (1992) 47; *Chem. Abstr.*, **118** (1993) 39471j.
- [93] D.F. Grishin and T.V. Zakharova, *Vysokomol. Soedin., Ser. B.*, **34** (1992) 18; *Chem. Abstr.*, **118** (1993) 39502v.
- [94] D.F. Grishin, V.K. Cherkasov and P.S. Razmaev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **35** (1992) 63; *Chem. Abstr.*, **118** (1993) 81522b.
- [95] V.A. Dodonov and D.F. Grishin, *Vysokomol. Soedin., Ser. B.*, **35** (1993) 47; *Chem. Abstr.*, **119** (1993) 28678b.
- [96] V.A. Dodonov and D.F. Grishin, *Vysokomol. Soedin., Ser. B.*, **35** (1993) 137; *Chem. Abstr.*, **119** (1993) 96261k.
- [97] V.A. Dodonov, I.N. Aksenova and S.N. Ziburdaeva, *Vysokomol. Soedin., Ser. B.*, **34** (1992) 34; *Chem. Abstr.*, **119** (1993) 117896p.
- [98] V.A. Dodonov, L.L. Semenycheva, Yu. V. Ovchinnikov and V.A. Titova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **36** (1993) 90; *Chem. Abstr.*, **119** (1993) 181349q.
- [99] W. Shu, D. Liu, K. Huang, K. Wang and Y. Li, *Trans. Nonferrous Met. Soc. China*, **2** (1992) 32; *Chem. Abstr.*, **118** (1993) 192808u.
- [100] G.M. Arvanitis, M.E. Berardini, T.B. Acton and P.E. Dumas, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **82** (1993) 127.
- [101] L.-J. Zhang, Y.-Z. Huang and Z.-H. Huang, *Tetrahedron Lett.*, **32** (1991) 6579.
- [102] L.-J. Zhang, X.-S. Mo, J.-L. Huang and Y.-Z. Huang, *Tetrahedron Lett.*, **34** (1993) 1621.
- [103] K. Iwamoto, H. Matsuda and A. Baba, *Jpn. Kokai Tokkyo Koho JP 04 261, 164* [92 261, 164]; *Chem. Abstr.* **118** (1993) 80925y.
- [104] H. Matsuda, A. Baba and K. Iwamoto, *Jpn. Kokai Tokkyo Koho JP 04 282, 335* [92 282, 335]; *Chem. Abstr.* **118** (1993) 191178b.
- [105] V.V. Sharutin, V.V. Zhidkov, V.T. Bychkov and O.K. Sharutina, *USSR SU 1, 796, 629*; *Chem. Abstr.*, **120** (1994) 8748a.
- [106] T. Kitazawa, M. Akiyama, M. Takahashi and M. Takeda, *J. Chem. Soc., Chem. Commun.*, (1993) 1112.
- [107] A. Yin and H. Xiang, *Lihua Jiannan, Huaxue Fence*, **28** (1992) 83; *Chem. Abstr.*, **118** (1993) 115779h.
- [108] N. Tomita, H. Yoneda, H. Aoki and K. Iwamoto, *Jpn. Kokai Tokkyo Koho JP 04 320, 418* [92 320, 418]; *Chem. Abstr.*, **119** (1993) 10525q.
- [109] M. Pirklbauer and G. Gritzner, *J. Solution Chem.*, **22** (1993) 585.
- [110] A. Haaland, A. Hammel, K. Rypdal, O. Swang, J. Brunvoll, O. Gropen, M. Greune and J. Weidlein, *Acta Chem. Scand.*, **47** (1993) 368.